The Pennsylvania State University

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THE DEVELOPMENT OF HIGH STRENGTH CORROSION RESISTANT PRECIPITATION HARDENING CAST STEELS

A Dissertation in Industrial Engineering by Rachel A. Abrahams © 2010 Rachel A. Abrahams Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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ABSTRACT

Precipitation Hardened Cast Stainless Steels (PHCSS) are a corrosion resistant class of materials which derive their properties from secondary aging after a normalizing heat treatment step. While PHCSS materials are available in austenitic and semi-austenitic forms, the martensitic PHCSS are most widely used due to a combination of high strength, good toughness, and corrosion resistance. If higher strength levels can be achieved in these alloys, these materials can be used as a lower-cost alternative to titanium for high specific strength applications where corrosion resistance is a factor. Although wrought precipitation hardened materials have been in use and specified for more than half a century, the specification and use of PHCSS has only been recent. The effects of composition and processing on performance have received little attention in the cast steel literature.

The work presented in these investigations is concerned with the experimental study and modeling of microstructural development in cast martensitic precipitation hardened steels at high strength levels. Particular attention is focused on improving the performance of the high strength CB7Cu alloy by control of detrimental secondary phases, notably delta ferrite and retained austenite, which is detrimental to strength, but potentially beneficial in terms of fracture and impact toughness. The relationship between age processing and mechanical properties is also investigated, and a new age hardening model based on simultaneous precipitation hardening and tempering has been modified for use with these steels. Because the CB7Cu system has limited strength even with improved processing, a higher strength prototype Fe-Ni-Cr-Mo-Ti system has been designed and adapted for use in casting. This prototype is expected to develop high strengths matching or exceed that of cast Ti-6Al-4V alloys.

Traditional multicomponent constitution phase diagrams widely used for phase estimation in conventional stainless steels, give poor estimates of secondary phases in PHCSS. No measureable retained austenite was observed in any of the CB7Cu-1 steels studied, in spite of the fact that austenite is predicted by the constitution diagrams. A designed experiment using computationally derived phase equilibrium diagrams and

actual experimental tests on CB7Cu of different compositions suggests that the ferrite phase is less stable than the constitution diagrams for austenitic stainless steels suggest.

Delta ferrite was also more stable in slower-cooled sand cast material as compared to thin, fast-cooled investment cast material. High temperature solutionizing treatments were effective in dissolving delta ferrite at temperatures above 1900°F (~1040°C). Delta ferrite dissolution was found to proceed at high rates during initial dissolution, and then was found to slow after 1 hour. Diffusion during the later stages is well-predicted by classical diffusion models. Repeated solution treatments were found to modestly increase both ductility and strength, likely due to subgrain refinement through austenite regrowth. Multistaged aging provided superior strength and toughness increases over similarly peak-aged and near peak-aged material aged at a single temperature. Peak-aged material fractography suggested that low energy quasi-cleavage fracture was likely due to age precipitate embrittlement along with some nucleation of MnS particulates at prior austenite grain boundaries.

Yield strengths approaching 190 ksi (1310MPa) can be achieved in CB7Cu-1 if appropriate best-practices "+" processing techniques are used. This includes hot isostatic processing to reduce solidification segregation and heal microporosity, high temperature homogenization for effective age hardening and ferrite reduction, double-cycle solutionizing for structure refinement, and multistaged age strengthening for finer precipitate control.

The experimental prototype 11-11PH (Fe-Ni-Cr-Ti-Mo) casting alloys was cast and was found to be delta-ferrite free in the as-cast condition. In this material, proper quench processing to eliminate excessive retained austenite was found to be most influential in terms of high strengths. It was also found that cooling below 0°C provided the best combination of strength and toughness, with the specific strength of the material exceeding that of cast Ti-6Al-4V material. Fractography studies suggest that titanium carbon-nitride-sulfide inclusions limit the toughness of cast materials due to long exposures to ideal growth conditions during initial cooling. OIM studies also suggest that the retained austenite in properly processed 11-11PH alloy takes on an interlath structure, which likely contributes to toughness of the alloy, even at high-

strength, peak aged conditions. Yield strengths approaching 235 ksi (1620 MPa) were achieved during initial heat treatment trials. It is expected that further improvements in properties can be achieved with continued improvement of processing for this new cast alloy system.

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-ПЕТРОУ А

Chapter 1 -An Introduction to PH Hardened Steels

Steels are one of the most common engineering materials in use, due to the wide availability of iron and carbon and their diversity in terms of engineering properties. The many variations in properties attainable in steels are due to the variety of microstructures that can be made by adjusting alloying elements and processing. Cast steels in particular represent a family of steels which are poured into mold cavities to produce net or near net shape geometries. Because cast steels solidify into their near-finished shape, thermomechanical treatments, which are applied to wrought materials, cannot be used to optimize cast microstructures. Therefore, chemical and processing treatments differ between cast and wrought materials.

Stainless steels represent the corrosion resistant family of steel materials. Stainless steels generally contain at least 11% Chromium. Molybdenum is often added in small amounts to many stainless steels to enhance pitting corrosion resistance. At these contents, Cr forms a tenuous, passive, oxide film which self-heals after damage, resulting in excellent corrosion protection in a wide variety of environments. A variety of corrosion resistant formulations of stainless steels have been developed for a variety of mechanical and corrosion property requirements. Cast stainless steels are further divided into two families - corrosion resistant (C) and heat-resistant (H) families. Heat resistant castings generally have lower strength levels than the corrosion-resistant castings, but have better corrosion resistance at higher temperatures. Standard corrosion resistant alloys generally contain at least 60% Fe, and have martensitic, austenitic, ferritic, or duplex/triplex (mixed) microstructures. The precipitation hardened stainless steels are a special subclass of high strength stainless steels. While they may contain austenitic, martensitic, or mixed martensite/austenite duplex microstructures, their strength is derived from precipitate hardening reactions. These materials are versatile as precipitation size and distribution can be influenced by heat treatment time and temperature, allowing for one composition of material to have a range of desirable properties.

Recently, there has been a need to develop strong, cast corrosion-resistant materials with good toughness to serve as alternatives for titanium. Because the cost of both the raw material and complex processing are very high when producing cast titanium parts, stainless steels provide an attractive alternative to the use of titanium in cast materials. At this time, many of the current corrosion resistant grades of stainless steels are not strong enough to approach the strength-to-weight ratio required to replace titanium (particularly Ti-6Al-4V) in most applications. Of the possible stainless steel choices, the martensitic PH stainless steels offer the greatest opportunity to provide the required strength and toughness for use to compete with cast titanium in high strength applications.

Extensive development of wrought alloy compositions and specifications has occurred since the 1960's. However, in terms of cast materials, specifications exist for only two commonly used high strength grades of precipitation hardening steels. These steels are CB7Cu-1 and Cb7Cu-2, which are the copper-precipitation analogues of wrought alloys 17-4PH and 15-5PH, respectively. The two steels are very close in chemistry and share similar ASTM specifications and base heat treatment guidelines. In many cases, the cast Cb7Cu alloy grades are more commonly referred to by the similar wrought alloy designations, though they differ in chemistry and processing. These alloys both depend on a copper-rich precipitate as the secondary hardening particulate.

While a small body of literature exists in terms of the 17-4PH/15-5PH wrought processed systems, there has been little in the way of scientific examination and research that has focused on the existing cast precipitation stainless steels. This is particularly important as castings are subject to different solidification processing conditions than their counterpart wrought material analogs. In particular, these cast alloys are influenced through solidification to contain different microstructures than wrought material. As opposed to castings, wrought products are subjected to forms of thermomechanical treatment, which refine the microstructure developed during solidification and promote the formation of martensite from austenite. On the other hand, cast 17-4PH often contains more silicon to promote fluidity and lower contents of austenite stabilizing elements to enhance resistance to solidification cracking. With higher amounts of ferrite-

stabilizing elements, CB7Cu solidifies in a nearly fully ferrite mode and is suggested to reduce hot tearing susceptibility during solidification. Because delta ferrite "stringers" can lead to defects and stress tears during thermomechanical processing, wrought producers prefer a delta-ferrite free material upon cooling to the processing temperature.

Recently, new higher-strength precipitation hardening wrought stainless steel alloys have been developed. These precipitation systems are of higher strength than the current precipitation systems used with castings and can match the high strength-to-weight ratio of cast Ti-6Al-4V alloys. These advanced precipitation systems have the potential of reaching higher strengths than copper based precipitation systems while maintaining the same levels of ductility and fracture toughness. However, these systems have not yet been adapted for use as cast materials. While these systems present a challenge to cast because of higher contents of oxide-forming elements, newer techniques in melting and processing provide possibilities in adapting these systems for air-melt or inert-cover casting processes.

Chemical composition and heat treatment guidelines for cast PHSS have been developed based upon a combination of results from both computer simulation and direct experimentation. Direct experimentation has been performed on heats of material provided by investment and sand cast foundries. Chemistry guidelines have been developed based on optimizing the combination of austenite-forming and ferritepromoting elements without interfering with the strength of the martensitic matrix developed through heat treatment. Heat treatment variables include aging times and temperatures, homogenization times and temperatures, solution annealing temperatures, quenching temperatures, the addition of HIP processing, and the addition of cryotreatment. Materials were evaluated by tensile properties, impact toughness, X-ray diffraction studies, microstructural phase characterization, and fracture surface examination.

1.1 A Brief History of Precipitation Hardened Steel Development

Table 1 summarizes the development of wrought PHSS from the initial materials to current specifications. The earliest martensitic precipitation hardening stainless steel in commercial use, Stainless W, (Fe-Cr-Ni-Al-Ti) was developed in 1945 by U.S Steel. [1] This was followed by the first of the high strength copper precipitate systems (Fe-Cr-Ni-Cu), including the highly successful Armco 17-4PH / 15-5PH alloys. [2] Because of their Cr-equivalent, Ni-equivalent composition balance, these two grades of alloys form relatively large amounts of delta ferrite upon solidification, which affect both the overall strength and toughness. 15-5PH, which is similar to the parent 17-4PH alloy, was developed with higher nickel content and lower chromium content to avoid excessive ferrite contents for thick-sectioned products. Both of these wrought alloys are still widely used because of their relatively low cost, good mechanical properties, acceptable corrosion resistance, and ease of processing. Following the development of the early Cu-based PH steels, there was a realized need for steels with better toughness at high strength levels, particularly for aerospace applications. Armco developed PH13-8Mo (Fe-Cr-Ni-Mo-Al) to reach those goals, along with improved stress corrosion cracking resistance. [3] Unlike the previous systems, PH13-8Mo utilized vacuum processing to limit residuals and to avoid reactivity of aluminum with free oxygen and nitrogen in the atmosphere. The βNiAl precipitate exploited in PH13-8Mo provides superior strength at similar toughness levels as compared to the Fe-Cr-Ni-Cu based alloys.

During this same time frame, the high strength maraging steels, which used Ni₃(Ti, Mo) as a strengthening precipitate were developed. For the most part, the use of maraging steel systems was impractical due to the effects of residuals and carbon on the highly reactive titanium, molybdenum and aluminum additions required for precipitation. Because the melting and refinement practice had improved since the introduction of early precipitation hardening systems, the production of materials with low detrimental residuals (carbon, oxygen, etc) was now possible on the industrial scale. Despite the high strength from the maraging precipitate system, early maraging systems were not corrosion resistant. At the same time, many proprietary variations on the early Cr-Ni-Cu

and Cr-Ni-Mo PHSS alloys were developed by a myriad of steel companies. However, the use of most of these other early alloys has waned as compared to the wide use of the 17-4/15-5PH alloys.

Ultrahigh strength maraging steel alloys were also under intense development. Although most of these maraging steels were not corrosion resistant, the ultrahigh strength, good toughness, and simple heat treatment made these materials attractive to aerospace developers. Due to the high cost of these cobalt-containing alloys, along with some processing difficulties, high cobalt grades of maraging steels rapidly fell out of favor. Cobalt-free Ni-Cr-Ti-Mo maraging alloys were first developed in the 1970's (IN7xx grades of material). [4], [5]These alloys have blurred the distinction between traditional PH stainless steels, which generally develop strength from Cu or NiAl precipitates, and maraging steels, which are usually dependent on Ni_3X precipitation systems. With the assistance of computer-aided thermodynamic models, carefully balanced patented commercial "stainless maraging" alloys have been recently developed. [6] These recent systems take advantage of ultra-low residual processing, subzero post quench treatments, and carefully balanced Cr-Ni systems to promote adequate precipitation and achieve strengths >250 ksi (1700MPa). The latest chemistries of ultrahigh strength PH steels incorporate intermediate amounts of cobalt (<15%) to further enhance precipitation hardening in a Ni₃Ti precipitation based system, adding to the strength and toughness achievable in these alloys.[7]

Period	Developments	Representative Alloys
1945-1960	Early PH Steels (Fe-Cr-Ni-Cu)	Stainless W (1945)
		17-4PH (1949)
		15-5PH
1970-1980	Early Alternative Precipitate	PH 13-8Mo (1971),
	Development βNiAl + Mo (Fe-	17-4Mo
	Cr-Ni-Mo-Al)	
	Cobalt-free Maraging Steels (Fe-	IN 733,736
	Ni-(Ti,Al))	
	Improved Cu + Mo systems (Fe-	Carpenter Custom 450
	Cr-Ni-Mo-Cu)	Carpenter Custom 455
Mid 1980's - 2000	Early Cobalt-Free Stainless	Marval X12 (1988)
	Maraging Development	
	(Fe-Ni-Cr-Mo-Ti)	

Table 1 - Wrought PH Steel Development

	Cobalt-Free Stainless Maraging Systems (Fe-Ni-Cr-Mo-Ti)	Sandvik IRK91 (1996) Custom 465 (1997)
2000+	Advanced Stainless Maraging Systems (Fe-Ni-Cr-Co-Mo-Ti)	Custom 475 (2003)

1.2 - Adaptation of Wrought Precipitation Hardened Steels for Casting

Cast grades of precipitation hardened stainless steels are summarized in Table 2. The history of many high-alloy cast steel grades has long been tied to the adaptation of As early as the 1960's, Armco was licensing select foundries to wrought grades. produce cast versions of the 17-4PH and 15-5PH alloys. [2], [8]

Table 2- Cast Grades of Precipitation Hardened Stainless Steels

Period	Developments	Alloy Representatives
1960-1970	Early PH Steels Licensed by	17-4PH
	ARMCO to foundries for casting	15-5PH
1072 1074		CD7C 102
19/3-19/4	ASTM A/4/ – Casting PH	CB/Cu-1&2
	Specification	
	(Fe-Cr-Ni-Cu)	
1990	PH13-8 Vacuum Investment	PH13-8Mo (preliminary development
	Castings	only)
	(Fe-Cr-Ni-Mo-Al)	- 57

In general, chemistry adjustments were required to adapt the wrought compositions for casting. The resultant cast alloys could be readily air-melted and heat treated in standard heat treatment furnaces. Manganese was reduced to prevent excessive interdendritic segregation and nickel and copper levels were more tightly controlled to ensure proper precipitation control. In 1974, 17-4PH and 15-5PH cast alloys had their chemistries officially adjusted for casting and were given a separate designation in ASTM A747 as the casting grades CB7Cu-1 and Cb7Cu-2, respectively.[9]These materials display high strength levels at their peak aging temperatures. Unfortunately, at the peak aged temperatures, they also suffer from reduced ductility and general toughness, and have a higher susceptibility to stress corrosion cracking. [10-15]Since the 1970's, there has been little work reported on improving the performance of the Cb7Cu alloys.



Figure 1 - History of Development of Cast Stainless Steel Grades [16]

CB7Cu is not unique in terms of general cast steel development history. Many of the specifications for cast stainless steels were developed directly from the wrought alloys, usually lagging about ten years or more behind that of the wrought material specifications. (Figure 1) Unlike the AISI wrought grade specifications, the American Casting Institute (ACI) designates cast stainless steels by service temperature and purpose. The first letter of the specification represents whether the casting alloy is designated for heat-resistance (H) or for general corrosion resistance (C) service. Corrosion resistant castings are for operating environments less than 650°C, while heat-resistant castings are suitable for high temperature corrosion conditions at temperatures greater than 650°C. Castings are then further classified by their chromium and nickel content, representing the second letter of the casting alloy designation. Materials with the W, X, Y designations as the second letter are generally nickel superalloys, containing a majority nickel content as opposed to iron. (Figure 2)



Figure 2- Chromium and nickel contents in ACI standard grades of heat- and corrosion-resistant steel castings.
[17]

Inevitably, the nickel and chromium content of the alloys influence the final intended microstructure of the castings. The final casting can have ferritic, martensitic, austenitic, or mixed microstructures. The most common mixed microstructure steels are the ferriticaustenitic (duplex) steels, where the mixed microstructure provides a synergistic combination of strength and corrosion resistance that is difficult to replicate in wrought parts. [18] The precipitation hardened grades are designated CB7Cu-1 (17-4PH), and CBCu-2 (15-5PH), and are the only precipitation hardened systems that have been adapted for cast use. These alloys have similar chemistry (Table 3) and heat treatment specifications to their wrought counterparts, 17-4PH and 15-5PH. These systems are well-adapted as a casting alloy due to their martensitic-ferritic as-cast structure, high allowable content of silicon for fluidity, and ability to be melted and heat treated in standard atmospheres. While development and study on other cast grades was started in the early to mid 20th century, the specifications for precipitation-hardened grades of cast steel were developed only thirty years ago. The current casting alloy specification contains nearly duplicate information from the wrought specification of 17-4 and 15-5PH (ASTM A747).

Little research has been conducted on the adapted cast PHSS alloys; therefore most of our understanding of these alloys has been developed from research performed on copper precipitation wrought systems. In several cases, this work gives at least a partial basis for the science involved in developing improved processing in the cast PHSS alloys.

Chemistries for popular wrought and cast precipitation hardened grades are detailed in Table 3. Although higher strength PHSS wrought alloys have been developed over time with improved performance compared to the 17-4PH and 15-5PH Fe-Cr-Ni-Cu alloys, there are barriers preventing these systems from being fully exploited by casting processes. This is best illustrated by considering cast alloys based on PH13-8Mo compositions for investment castings. Investment cast PH13-8Mo performance characteristics and processing guidelines were developed in the 90's, but the material is rarely cast due in part to melt and pouring practice challenges for this aluminum-containing steel. [19-21]. Similarly, potential precipitation and maraging precipitation systems using titanium for strengthening (Ni₃Ti, Mo, etc) have not been developed for casting applications because of premium melting and pouring practice challenges for these titanium alloyed steels.

	17-4PH Type 630 WROUGHT	CB7Cu-1 CAST	15-5PH (XM-12) WROUGHT	Cb7Cu-2 CAST	PH13-8Mo WROUGHT	Carpenter 465 WROUGHT
Chromium	15.00-17.50	15.50- 17.70	14.0-15.5	14.0-15.5	12.25- 13.25	11.00-12.5
Nickel	3.00-5.00	3.60-4.60	3.50-5.50	4.50-5.50	7.50-8.50	10.75- 11.25
Manganese	1.00	0.7	1.00	0.7	0.2	0.25
Carbon	0.07	0.07	0.07	0.07	0.05	0.02
Silicon	1.00	1.00	1.00	1.00	0.1	0.25
Molybdenum					2.00-2.50	0.75-1.25
Phosphorous	0.040	0.035	0.040	0.035	0.010	0.015
Sulfur	0.030	0.030	0.030	0.030	0.008	0.010
Aluminum					0.9-1.35	
Titanium						1.50-1.80
Copper	3.00-5.00	2.50-3.20	2.5-4.5	2.50-3.20		
Niobium + Tantalum*	0.15-0.45	0.15-0.35	0.15-0.45	0.15-0.35		
Nitrogen		0.05		0.05		
Fe	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

Table 3 - Compositions of widely used PH Stainless Steels

Currently, the MMPDS-4 (Metallic Materials Properties Development and Standardization) property database used by design engineers for aerospace applications includes a number of wrought high strength stainless steel materials. (Table 4-Table 5) However, currently only 17-4PH and 15-5PH alloys are listed for stainless steel

investment casting applications. [22] Of the other potential high strength stainless steel casting alloys, only PH13-8Mo has been included in AMS specifications – a preliminary step toward inclusion in MMPDS databases. Overall, there is little selection in terms of designated high strength corrosion resistant materials for casting (3) as compared to those available for wrought selection (12) as per the MMPDS-4. In addition, none of these material specifications attain strength levels of 160 ksi (1100MPa), as compared to the several materials available in wrought form. Increasing the selection of high strength PH stainless steels would lead to broader, lower-cost, options for designers and suppliers compared to what currently exists.

	UTS		YS (0.2%)		Elong
	(ksi)		(ksi)		(%)
Basis	А	В	А	В	S
PH 13-8Mo H950	217	221	198	205	10
PH 13-8Mo H1000	201	208	190	200	10
Custom 465 AMS5936 (H950)	240	251	220	226	10

Table 4 – MMPDS-4 Design Properties, Wrought Strip, Sheet and Plate [22]

Table 5 - Investment Cast PH Materials, MMPDS-4 [22]

	UTS (ksi)	YS (%0.2) (ksi)	Elong (%)
Basis	S		
17-4PH IC AMS5344 (H900)	180	160	4
15-5PH IC AMS5400 (H935)	170	155	6

The specific strengths of the corrosion resistant cast materials are only about 70% of that of titanium in the highest strength states. While some of the wrought corrosion resistant steels are capable of achieving and exceeding cast titanium specific strengths, they have not been studied in terms of casting. Therefore, there is a need to understand methods to

develop higher strength in existing alloying systems, as well as adapt stronger precipitation hardening systems for casting processes.

Despite the fact that the current PH designated materials have been specified for over 30 years, little research exists on the effects of processing and composition variables and heat treatment of Cb7Cu/17-4PH. Past literature on the wrought 17-4PH systems has generally focused on the study the precipitation reactions [23-27] as compared to critically examining processing effects on the microstructure. There have been no comprehensive studies on the cast precipitation systems. Other high strength cast stainless steel alloys have only received cursory attention in the literature. Work on the stainless maraging systems is, for the most part absent in cast literature, though there has been some limited processing and composition studies on investment cast PH13-8Mo. [19-21]

1.4 Problem Statement/Thesis Outline

While the science of modeling precipitation hardened *aluminum* alloys has continued to advance, there has been little study of PHSS counterparts. Even less work has been performed on cast PHSS alloys. Formation and dissolution of problematic phases, such as delta ferrite have not been well explored. There is a need to understand these processes in the context of cast processing so that proper relationships between heat treatment parameters, compositions, and mechanical properties can be developed. This is problematic as there has not been much in terms of characterization of these materials, particularly at high strength levels. This research is directed toward improving cast precipitation hardened steels by characterizing the existing cast precipitation systems in terms of microstructure, processing, and strength, and then developing improved heat treatment and chemistry guidelines to promote high strength while preserving good ductility.

This dissertation is divided into several parts. The first part provides a general introduction and background to stainless steels, along with this brief discussion of the organization of the thesis. This part gives a description of the stainless steel technology as it consists today. Chapter 2 includes a discussion of the science and literature that is

relevant to a) composition and b) microstructure of CB7Cu-1 and other cast PH steels. Effects of particular elements and the basic theory of age-hardening are covered in detail, along with some existing models for related metallic materials. Because much of the literature only centers on the wrought alloys, a basis for the research has been drawn from studies on 17-4PH, 15-5PH and PH13-8Mo; while their processing is different, basic structure and kinetic mechanisms are related as the steels share similar composition limits. Chapter 3 describes in detail the research goals and methodologies used in this dissertation in order to familiarize readers with terminology and techniques used.

The bulk of the results and discussion are described in Chapter 4-7. The first two chapters focus on the improvement of CB7Cu materials in terms of phase control. Phase control is accomplished by both composition and processing, and a chapter is devoted to each aspect in terms of CB7Cu. Chapter 4 presents studies performed in order to understand the effects of composition on major and minor phases. This includes the use of experimental work and CALPHAD modeling with design of experiments to quantify effects of elements on phase stability. Chapter 5 presents experimentation and modeling work that show the effects of processing on the phases and age-hardening processes in CB7Cu alloys. A modified age-hardening model for precipitation hardening steels is presented and also verified against data. Chapter 6 presents initial studies into a new, nickel-based precipitation alloy and the insight of experiments into development of initial processing guidelines.

The final chapter of the dissertation summarizes major conclusions from the investigations in this thesis and describes future directions and possible present applications of the current work. The appendices in the work provide auxiliary information. Appendix A presents outputs from the CALPHAD modeling study and Appendix B presents outputs from the age-hardening model. Appendix C contains mechanical testing data from the experiments in this investigation.

Chapter 2 -A Literature Review of Precipitation Hardening Stainless Steels

Martensitic precipitation hardened steels rely on martensite as the major matrix constituent phase, with delta-ferrite and austenite as minor residual or reverted phases. Other minor phases include precipitates and the small amount of intermetallics formed from residual levels of carbon and nitrogen. The control of these phase contents and resultant mechanical properties are results of both processing and composition. While little investigation has been performed on the cast precipitation hardened steels, there has been some investigation on the wrought copper precipitation systems as well as work on wrought martensitic stainless steels. The literature is separated into two distinct sections because both composition and processing effect the phase microstructure and resultant properties. Literature involving effects from composition is discussed first, followed by information from studies on the processing effects. Finally, the current state of understanding regarding precipitation reaction control in the related high-strength copper and nickel based systems is discussed in detail, along with the current status of precipitation modeling.

2.1 Microstructures of Precipitation Hardened Steels

Both wrought 17-4PH and analog cast CB7Cu-1 alloys are often air melted in large furnaces. Upon solidification, high temperature, body centered cubic delta ferrite (δ -ferrite) initially forms. As solidification continues, delta ferrite transforms into the more stable face centered cubic austenite. Depending upon subsequent cooling after solidification, a number of intermetallic carbon and nitrogen-rich phases can precipitate in the austenitic field. At a critical temperature (dependent upon composition), austenite undergoes a transformation to martensite upon cooling. Cooling rates between the critical martensite start temperature (M_s) and martensite finish temperature (M_f) influence the ratios of retained austenite and martensite in the quenched product.

2.1.1 Martensite in CB7Cu-1

Martensite is the primary matrix phase in CB7Cu-1 as well as the other martensitic stainless steels. The formation of this phase proceeds upon cooling below a temperature, referred to as the martensite start temperature (denoted as M_s). Martensite itself is an intermediate, metastable structure that occurs between the γ to α crystal transformation. Austenite, the parent structure of martensite, has a close-packed face-centered cubic structure. (Figure 3) Upon transformation, martensite crystal has a *bct* (body centered tetragonal) structure, with one axis elongated. The interstitial content has a large role in determining the length of the strained member of the crystal structure; carbon increases the c/a ratio of the alloy. Because CB7Cu contains extremely low amounts of carbon and other interstitials, the c/a ratio of the crystal is nearly 1, rendering it similar to ferrite in a nearly cubic structure (bcc). The martensite retains some characteristics of the parent austenite; a 45° angle rotation to austenite along the face results in a similar structure. This intermediate behavior is known as the Bain correspondence of martensite. [28] The structure of low carbon martensite (α) more closely resembles an intermediate of ferrite and austenite, without the severe lattice strain common to higher carbon martensites. In general, the martensite of precipitation-hardened stainless steel is low carbon in nature to prevent the formation of excessive amounts of M23C6 chromium carbide upon cooling and brittle alloy-rich carbides upon tempering, which can both embrittle the material and contribute to reduced corrosion performance. The crystallographic orientation between the parent austenite and the resultant low carbon martensite is described as the Kurdjumov-Sachs relationship, where:

$$\{1 \ 1 \ 1\}_{\gamma} || \{0 \ 1 \ 1\}_{\alpha}$$
$$< 1 \ 0 \ \overline{1} >_{\alpha} || < 1 \ 1 \ \overline{1} >_{\gamma}$$

This relationship has been well-observed in 17-4PH steel studies, and is suggested to be same in CB7Cu-1. [10], [23]Some evidence of martensitic twinning, which is generally

seen in medium carbon and higher nickel alloys, has been seen in some studies of 17-4PH [23], but other studies report an absence of twinning. [10] Essentially, the low-carbon martensite matrix provides a good, high strength for the alloy compared to ferritic copper precipitating alloys, which can be age-hardened in a similar fashion. However, in the solution annealed condition, the ultimate tensile strength of the material is only typically about 100-140 ksi. The untempered martensite is also highly strained and embrittled. It is important to note that simultaneous tempering (softening) reactions that take place during age-hardening can lead to material with better combinations of strength and toughness than material in the solution annealed condition. [29]



Figure 3 - Illustration of transformation from austenite to martensite. O indicates positions of Fe atoms, X indicates positions available for C atom. [28]

2.1.2 Untransformed Austenite in CB7Cu-1

Austenite in CB7Cu alloys generally exists in two forms in martensitic stainless steel:

- Retained austenite which refers to untransformed austenite that remains stable after martensitic transformation. Because the martensitic transformation has an asymptotic nature, there is always some measure of retained austenite that remains in the alloy. Retained austenite generally forms between martensitic laths in PH-type alloys.
- Reverted austenite refers to austenite that forms after reheating of the alloy from room temperature. Unlike retained austenite, which is randomly distributed, reverted austenite is often formed in localized areas around austenite stable areas,

such as redissolved precipitates. Reverted austenite tends to be more blocky in shape and nature.

For the most part, retained austenite is considered detrimental to the age strengthening reaction in precipitation hardened martensitic stainless steels. Retained austenite lacks the strength of tempered martensite, and also retains copper and other precipitation hardened phases in solution, limiting the process of age hardening. However, small amounts of retained austenite have been found to increase the impact toughness of otherwise brittle peak-aged materials. [30] Evidence from multiple investigations suggest that the increase in strength is derived from the transformation of thermally stable austenite to martensite under the extreme pressures induced during fracture.[31-33]The additional energy absorbed by the phase transformation is reflected through improved impact and fracture toughness measurements. Some of the earlier investigations performed on steels have proposed different mechanisms for austenite-mediated toughness increasing, including ductile austenite blunting and possible trapping of detrimental constituents within lath formations. [11], [34]

Retained austenite is influenced by both composition and processing in CB7Cu-1. Nishiyama [28] describes three modes of austenite stabilization:

- 1. Chemical Stabilization (Chemical Composition)
- 2. Thermal Stabilization (Thermal Treatment)
- 3. Mechanical Stabilization (Plastic Deformation)

Only thermal and mechanical stabilization will be discussed in this section. Chemical stabilization will be discussed in later composition control sections of this document.

2.1.3 Thermal Stabilization of Austenite

The martensite start temperature (M_s) is an accepted way to measure austenite stability in steel alloys. Control of the martensite start temperature is of great importance in several stainless steel alloys, because of the fact that many of these temperatures hover close to room temperature. Lower martensite start temperatures can cause difficulty in quench-

processing the material to ensure a near complete martensite structure. If the related martensite finish temperatures of an alloy is lower than room temperature, special techniques must be used to ensure that the material is fully martensitic. Even small amounts of retained austenite, resulting intentionally or from insufficient quenching, have been known to have a significant effect on yield strength. [35], [36]There are several composition and processing factors that have an effect on the given M_s and M_f temperature of a particular material.



Figure 4 - Generalized Martensite Transformation Curve (Totten)

The relationship between martensite and temperature is generally in the shape of a sigmoidal curve, with an asymptotic nature at both the martensite start and finish temperature. Lowering the M_s temperature of an alloy will generally shift the entire curve, also lowering the M_f temperature. Delaying the quench between the M_s and M_f will often stabilize austenite by allowing the relaxation of strain energy responsible for transformative processes in the martensitic matrix. Holding for extended times at temperatures closer to the M_s temperature exaggerates the amount of untransformed austenite as compared to holding closer to the M_f temperature. This has strong implications in terms of both the age-hardening potential of PHSS as well as the matrix base strength in terms of adequate cooling after heat treatment.

The temperature at which 95% of the martensite is transformed is referred to as the martensite finish temperature. Several models, both empirical and theoretical, have been

developed to relate fraction transformed to the M_s and final cooling temperature. [37], [38] A simple model by Koistinen-Marburger relates the martensitic content (1-fraction of retained austenite) to the quench temperature conditions and the M_s temperature, which is dictated by the compositions. The equation is as thus follows:

$$1 - V_{\alpha'} = \exp\{\beta(M_s - T_q)\}$$
 where $\beta \cong -0.011$

Where $V_{\alpha'}$ = fraction of martensite; and

 T_q = temperature which the sample is cooled (must be below M_s)

It is important to note that the M_s must be below that that of the equilibrium ferriteaustenite phase. At the temperature where total free energy of γ (austenite) = α (ferrite), the transformation will not proceed; excess free energy must be included to overcome both surface energy and transformation strain energy. The martensite volume fraction appears to be independent of time, and dependent on the difference of the temperatures only during quench treatment. This is due to the velocity of the reaction of transformation of austenite to martensite. Martensite transformation has been observed to proceed at rates greater than $1100 \text{m} \cdot \text{s}^{-1}$, which is inconsistent with traditional diffusion processes. The fact that the transformation from austenite to martensite is diffusionless causes the composition of the material phases to remain relatively stable; the martensite formed will generally carry the same composition as parent austenite. [28]

In certain Fe-Ni alloys, multiple thermal cycling of $\gamma \rightarrow \alpha'$ transformations is has been found to both increase the amount of retained γ as well as increase the strength of the resultant martensite phase. In Fe binary alloys containing at least 28% Ni, this increase in strength is appears to be significant. [28] Other studies have found that only primary 'retained' austenite in certain alloys strengthen the material. [36] While repeated cycling may be useful in some Fe-Ni alloys to control the amount and distribution of interlath retained austenite, multiple cycling from high to low temperatures is a rather impractical technique for industrial processing because of the extensive time and energy required for multiple cycles.

2.1.4 Mechanical Stabilization of Phases

Extremely high levels of hydrostatic pressure have been known to affect the martensite start temperature. Large amounts of hydrostatic pressure shrink atomic distances and cause a decrease in the effective transformation temperature. While hot-isostatic pressure treatment is a process discussed within the realm of these studies, the pressures obtained through hot isostatic processing appear to be too low to induce a significant effect on martensitic transformation. [28] Stress induced transformation is one of the major strengthening mechanisms of semi-austenitic stainless steel alloys, even if their composition at equilibrium suggests that they should be completely austenitic. Tensile stress on material tends to raise the M_s temperature of iron alloys. Several semi-austenitic grades of steels use stress-induced transformations to ensure at least some form of martensitic formation. Early "controlled" transformation steels developed by Pickering and Irvine also utilized this mechanism [39], [40]. During stress induced transformations, vacancies become more numerous and nucleation sites for austenite to martensite transformation are increased, which stabilizes martensite. The opposite is true under high isostatic pressures, in which the martensite start temperatures are decreased. The isostatic pressures used in HIP do not approach those used in experimentation, and are therefore thought to have a negligible effect.

2.1.5 Studies on Characteristics of Retained Austenite

For the martensitic and austenitic stainless steels, there is a positive correlation between content retained austenite and impact toughness. The positive correlation between impact strength and retained austenite in precipitation hardened steel was observed in a study concerning 15.9Cr-7.3Ni-1.2Mo steel. [35] In this study, a linear reduction in strength characteristics in relationship to retained austenite content was observed. Interestingly, the reduction in yield strength tends to be more rapid with increasing amounts of retained austenite for both the 15-7PH system as well as cast 17-4PH (CB7Cu-1) as compared to the reduction in the ultimate tensile strength.[41]
Retained austenite is not the only type of austenite seen in precipitation hardened steels. Aging at temperatures close to or above the AC1 temperature can result in the formation of reverted austenite. At lower aging temperatures used to maximize strength in CB7Cu, austenite reversion is not likely seen. Sources report no observed reversion after aging material at 510°C (1050°F) for 2 hours, [10] but there are several reports of reverted austenite in the overaged condition (1100-1150°F/593-620°C). [23], [10], [42], [43] Overaged maraging steels have also been seen to develop reverted austenite at higher aging temperatures and longer aging times. [28], [44]It is important to note that in the observed studies, the temperature at which austenite reversion occurs is much higher than that of the M_s temperature. The reversion to austenite is also thought to be diffusionless and proceeds in the same 'military' form of transformation as the original transformation from M to γ . Because CB7Cu-1 precipitates are rich in copper, the regions local to the precipitates are suggested to be higher in copper, and therefore more prone to reversion than precipitate-free areas. Viswanathan proposes this mechanism in 17-4PH to explain why the austenite reversion temperature observed in 17-4PH appears to be higher than that of the M_s temperature. [10] In addition, there are observations that have found that reverted austenite in Cr-Ni-Co-Mo cast steels does not appreciably affect the fracture toughness, while the primary retained austenite was found to do so. [36]One point common to these discussions is that controlling the amount of retained austenite by stabilization through heat treatment is difficult, especially in castings where properties may not be uniform. The difficulty of this stems from the widely different M_s temperatures that are possible within the specifications of many of these alloys. In the case of Nikol'skaya's investigation, a magnetic measurement technique was used to adjust and measure retained austenite by a 'brute-force' method of determine optimal chemistry. Even with the specialized equipment, a full 2% of heats failed to reach minimum required guidelines for mechanical properties.

2.1.6 Studies on the Characteristics of Delta Ferrite

In wrought materials, formation of delta ferrite on solidification is considered detrimental due to susceptibility of cracking during thermomechanical treatments. Wrought alloys are usually adjusted to be nearly delta ferrite free after initial solidification. In the case of

castings, delta ferrite is considered beneficial to avoid hot-tearing during solidification. In any case, delta ferrite is well known to be detrimental to both strength and impact toughness in finished castings, therefore elimination in the finished casting is important. Considerably less literature appears to focus on the prediction of delta ferrite in terms of precipitation hardened steels and/or in terms of stainless steel castings, as compared to contents in austenitic and duplex stainless steel welds. It is known that small amounts of delta ferrite are beneficial in austenitic cast stainless steels, due to the increased resistance to stress corrosion cracking. [18] This is opposed to wrought materials, which are strictly single phase materials due to ferrite-stringer cracking during deformation processing. [45] While cast dual phase austenite-ferritic materials (duplex) materials exploit the fact that castings often solidify with duplex microstructure, martensitic materials often do not exhibit the same behaviors in combination with ferrite. There have been some attempts to try to quantify predicted delta ferrite in welds using neural networks and previous data [46], [47]. However, this technique depends on copious data connected with ferritscope measurements and so far has been only developed for a small composition range of austenitic and ferritic steels. Whether or not these computation models extend to martensitic steels of PH concentration is somewhat questionable, as data on ferrite content and compositions is not available for PH/martensitic stainless steels.

Sigma Phase, a brittle intermetallic phase seen in many Fe-Cr-Ni steels, is not generally observed to be a problem with the current chemistries of martensitic precipitation stainless steels. Sigma phase generally forms in steels that contain at least 4% by weight molybdenum and must be held at temperatures from 500-900°C for extended periods of time. Most martensitic stainless steels do not contain enough molybdenum and are not aged at the appropriate temperatures to facilitate sigma precipitation.

2.1.7 Other Detrimental Structures and Intermetallics in Fe-Cr systems

One of the obstacles of heat-treating chromium stainless steels is that the range for agehardening generally overlaps the classical range for 475°C (885°F) embrittlement. Ferrous materials that contain about 13-35% Cr are particularly susceptible to this form of embrittlement due to the fact that the composition places the material in spinodal decomposition region for binary Fe-Cr alloys. Decomposition of this type has been observed in duplex cast alloys which contain higher levels of chromium than that of the PH steels. [48], [49] Alloys that are exposed for long periods of time between 750°F and 950°F are particularly susceptible. Embrittlement generally accelerates with increasing amounts of chromium to about 40Cr and aging at temperatures close to the 475°C region. [45] Chromium rich precipitates initially form at the grain boundaries, though in most cases, the partitioning is thought to be local and fine. Nickel in Fe-Cr alloys has been demonstrated to exacerbate the effect. [50] In addition, spinodal decomposition also has been observed in Fe-Ni-Cu alloys; however, the Cu contents in these steels were much higher. [51] In effect, this partitioning is a form of precipitation hardening, which leads to higher measures of strength at the expense of ductility and impact toughness. The segregation of chromium also leads to fields of chromium depleted material, adversely affecting corrosion resistance. [52] However, even at 30% atomic weight chromium, it takes more than 50 hours for the first decomposition material to be detectable. [53] Therefore, in 17-4PH and 15-5PH there is little possibility for spinodal decomposition to happen during normal aging processes. However, there is some implication of embrittlement in long term use under high operating temperatures. There have been some cases of spinodal decomposition observed in 17-4PH material, [54], [43], [27] but the material in these studies was exposed to intermediate temperatures (300-400°C) for several magnitudes of time greater than what is seen during processing. Material that has suffered from this partitioning displays limited impact toughness and elongation at higher levels of strength, and is often a cause of failures in nuclear installations and other situations where the operating temperature may approach or exceed the limits for prescribed service temperatures. [54]

Though CB7Cu alloys are low in carbon, there is generally some residual carbon, usually resulting from the industrial ferrochrome additions and scrap material. Residual carbon is allowed to 0.07% by weight in the CB7Cu alloys. While some of the carbon in these alloys remains in the matrix, a fraction of the carbon will form intermetallic carbides at temperatures ranging from 900°C to 500°C, generally at the grain boundaries. The carbides that form are of the structure $M_{23}C_6$, and deplete the matrix of chromium and molybdenum. This can also cause susceptibility to corrosion due to insufficient

chromium to allow for continuous formation of the protective Cr_XO_Y films in some areas of the material. Depending upon the cooling rate, these carbides can be difficult to remove by heat treatment and can cause problems in terms of coalescence between grain structures. Because of their large size and differential hardness from the matrix, they are often sites for initiation of cracks and limit the toughness. In wrought systems, carbon residual levels are usually below 0.03% in precipitation hardened systems and subject to tighter controls than that of cast precipitation systems.

2.2 Composition Control and Alloying Effects in CB7Cu-1

Stainless steel chemistry is defined by mixtures of iron, chromium, carbon, and other alloying elements. Elements are added to alloys in specific combinations to affect size, shape, and formation of different phase fields. These relationships are used to influence both the initial microstructure upon cooling and finished microstructure of a given product. While certain elements behave similarly in terms of stabilization of particular phases, the magnitude of stability across different elements differs greatly. (Figure 6)

In general, sufficient amounts of chromium are required in CB7Cu-1to obtain adequate corrosion resistance; however, high levels of chromium (and other ferrite forming elements such as silicon and molybdenum) result in increased prevalence of delta ferrite stringers. These tendencies must be balanced with appropriate nickel (and to a certain extent manganese and silicon additions). Carbon and nitrogen levels must also be controlled as both of these elements are very potent austenite stabilizers. In addition, the effects of each of these, and other alloying elements, on heat treatment response must also be considered. Early work with binary Fe-X alloys demonstrated the effect of particular elements on the M_stemperature. Table 6 summarizes the influence of various alloying elements on ferrite formation and austenite stability (M_stemperature) from the classic work of Pickering and Irvine [39], [55], [56]. Alloy additions which can be used to eliminate ferrite stringers during solidification, tend to overstabilize the austenite, making it difficult to successfully quench from the solutionizing temperature without leaving undesirable stabilized austenite in the quenched structure.

Element	Change in ä-Ferrite	Change in M _s temperature
	[%ferrite/wt% addition]	[^o F/wt% addition]
Ν	-200	-450
С	-180	-450
Ni	-10	-20
Co	-6	+10
Cu	-3	-35
Mn	-1	-30
W	+8	-36
Si	+8	-50
Мо	+11	-45
Cr	+15	-20
V	+19	-46
Al	+38	-53

 Table 6 - Effect of alloying elements on the constitution and M_stemperature of 17% Cr-7% Ni stainless steels

 [10-12]

Carbon and nitrogen play an important role not only during solidification but also during heat treatment. Successful heat treatment of 17-4PH depends on careful control of carbonitride precipitation and can be influenced by the presence of microalloying elements (particularly niobium). During solutionizing, some of the carbon and nitrogen are re-dissolved back into the solution. This in turn, influences the resultant austenite stability upon quenching. However at conventional solutionizing temperatures, complex carbonitrides that contribute significantly to final alloy strength levels remain in the austenite matrix. High nitrogen levels in particular may lead to increased strength from nitrides formed during solutionizing. However, this can also lead to increased brittleness, decreased weldability, and poor fracture properties if nitrogen levels are not balanced with the addition of nitride and carbonitride forming elements, such as niobium and tantalum. [57] A further description of specific alloying elements was given in the following sections.



Figure 5 - Effect on M(s), Fe-X Binary Systems [28]



Figure 6 - Effect of Alloying Elements on the Fe-X Phases (Tisza)

2.3 Compositional/Alloying Effects by Element

2.3.1 Carbon

The most widely used alloying element in steels is carbon. Steels can contain up to 2.11% carbon, at which point, the system is considered a lean cast iron. Carbon is generally responsible for the hardenability of steels by forming carbides with iron or other alloying elements, such as in HSLA steels, to precipitate fine M_3C / MX carbides for strength. However, to promote corrosion resistance, stainless steels generally contain well over 10% Cr. With increasing amounts of chromium, even small amounts of carbon can combine with chromium to form coarse M₂₃C₆ chromium carbides, which are known preferentially nucleate at grain boundaries and cause reduced toughness. (Figure 7) In addition, chromium carbides are well known to deplete the surrounding matrix of chromium, leading to loss of corrosion resistance. In 17-4PH and many of the other alloys, carbon is generally kept to extremely low levels (>0.07 % wt. max) to suppress the formation of $Cr_{23}C_6$ carbides, and prevent the stabilization of retained austenite in the material. In order to suppress the formation of chromium carbide, elements with greater carbide stability are introduced into the system. In CB7Cu-1, Niobium and Tantalum are often used to to form dispersive carbides, preferentially in contrast to the coarse M23C6 carbides. Vanadium is used as well, but both are potent ferrite stabilizers, so the uses are limited in martensitic steels. Titanium, which is essential for precipitation hardening in cobalt free nickel-PH systems, also forms carbides at high-temperatures, often high enough to form in the liquid + solid temperature region of the alloy. In wrought highstrength low alloy steels, the formation of TiC is seen as advantageous to pin grain boundaries in the alloy and prevent excessive grain growth. [58], [59]In castings, this may be less advantageous due to the relatively long solidification times and opportunity for growth in the liquid + solid range. However, because many casting alloys contain some residual carbon and are exposed to free nitrogen during atmospheric contact, the potential for the formation of small amounts of TiC and TiN must be considered.



Figure 7 - Fe-Cr-C Phase Diagrams, with (a) 0.05C and (b) 0.40C [60]

2.3.2 Niobium/Tantalum

Niobium and/or tantalum are Group V transition metals which are commonly added to steels in small amounts. In terms of metallurgical effects, Niobium and tantalum are essentially identical in behavior, and often one is substituted in place of the other by supply and cost basis. Both are used as an addition to suppress formation of $Cr_{23}C_6$ in martensitic stainless steels. Niobium and tantalum MC carbides are more stable than those of $Cr_{23}C_6$ carbides at higher temperatures, hence they tend to form preferentially as compared to chromium carbides, promoting retention of corrosion resistance and decreasing hardness losses at higher aging temperatures. Niobium is often intentionally added to precipitation hardening steels to stabilize desirable MC, which provides tempering resistance during aging. Niobium levels must be strictly controlled and balance with residual C and N levels; excessive niobium carbon and nitrogen from solution. [61] There is also evidence that NbC interacts with trace phosphorous to enhance

phosphorous embrittlement at the grain boundaries. General practice suggests materials added at ratios of 4:1 to 8:1 by weight with carbon/nitrogen for casting alloys.

2.3.3 Silicon

Silicon is generally added at lower levels in wrought 17-4PH; however, it is intentionally often kept at higher levels in casting facilities. In cast alloys, higher silicon is used primarily to increase fluidity. Because silicon is a strong ferrite stabilizer, the chromium-equivalent and nickel-equivalent must be re-balanced for alloys with high silicon levels to avoid ferrite stringers that decrease hardness and strength. [62] Excessive silicon can lead to excessive ferrite, which lowers the strength of the material. This is perhaps one of the many reasons that 17-4PH was adapted to the cast condition so quickly. Other higher strength PH system alloys have drastically less silicon allowed than the cast 17-4PH alloy.

2.3.4 Phosphorous + Sulfur

Phosphorus and sulfur are generally seen as impurities in CB7Cu castings, and concentrations of these alloys are kept to a minimum. Phosphorous tends to segregate towards grain boundaries, where it lowers the surface energy and reduces grain cohesion. 17-4PH is observed to have higher diffusivity of phosphorous than other studied martensitic stainless steels, and behaves very similarly to α -iron in terms of diffusion. [63] In addition, both trace elements have been suggested to promote dendritic segregation and possibly enhance phosphorous diffusion to grain boundary sites. Sulfur and phosphorous are controlled at much lower levels in ultrahigh strength wrought stainless steels. Rare-earth additions and/or titanium additions are used to control the size and distribution of inclusions by forming smaller metal-rich sulfides as opposed to the manganese sulfides found in conventional wrought steels and castings.

2.3.5 Nitrogen

Nitrogen is a viable substitute to carbon in many austenitic stainless steels as it has fewer propensities to cause intergranular corrosion while still stabilizing the austenitic phase. There has been some work in terms of developing nickel-free 17%Cr steels, using various composition levels of nitrogen and manganese as substitutions for nickel, but most of the work has focused on compositions for replacement of austenitic materials. [64], [65]These systems depend on the preferential strengthening of fine nitrides such as Cr₂N and Fe₂N as well as formation of fine carbonitrides with vanadium. The elimination of delta ferrite in these systems appears to be an aim in terms of research rather than the formation of martensite, and these materials do not provide the strength that is attained by current grades of precipitation hardened steels.

Nitrogen-modified precipitation steels may benefit in terms of toughness due to the favorable formation of finer Cr_2N precipitates as compared to $Cr_{23}C_6$ carbides at grain boundaries. Nitrogen additions to martensitic stainless steels have been considered in research as a way to improve impact properties. However, nitrogen behaves much like carbon and also acts as a potent austenite stabilizer. There has been some research in developing high-strength nitrogen steels, [64], [65] though most work was performed with Cr contents of 9-12% Cr. Early studies focused on C+N steels and the formation of (FeCrV)(CN) and (NbV)(CN) at aging temperatures below 500°C. Combinations of high nitrogen and manganese have been proposed as a replacement for the more expensive nickel as an austenite stabilizer for austenitic grades. [64]

2.3.6 Copper

Copper in terms of precipitation hardening has been discussed in the previous section. Due to the high copper levels contained in Cb7Cu alloys, significant copper segregation can be expected during solidification. However the influence of solidification cooling rate on copper segregation has not been firmly established for these alloys. Excessive copper, above 5%, has been reported to form dendritic segregations and lead to some embrittlement and poor weldability of the material. [8] Copper is a moderate austenite stabilizer, but the amounts contained in 17-4PH contribute little compared to the nickel that is contained within the alloy.



Figure 8 - Effect of copper & cobalt on relative stability of alpha and gamma phases in Fe-rich alloys [66]

2.3.7 Cobalt

Cobalt is one of the major alloying elements seen in the maraging steels, a class of ultrahigh strength steels which use Ni₃Ti or Ni₃Mo precipitates for age strengthening. Multiple investigations indicate that cobalt itself is only a minor constituent in terms of order strengthening, but instead displaces molybdenum from austenite, which is particularly important in strengthening of maraging systems. Systems with molybdenum alone do not experience as dramatic of a hardening peak as those with the addition of cobalt. [5], [44], [67], [68] Cobalt is also thought to lower the stacking fault energy and prevents cross slippage in alloys, increasing the sites for precipitation nucleation.[67] While there is evidence that cobalt acts as a weak austenite stabilizer, there is also evidence that this austenite stabilization is temperature dependent (Figure 8) and may occur only at high temperatures, which may be beneficial to casting alloys with large amounts of ferrite stabilizers. [66]

2.3.8 Nickel and Manganese

Nickel is used as a toughening agent in CB7Cu alloys, as well as an austenite stabilizer. The addition of nickel increases the fracture toughness and decreases the ductile to brittle transition temperature in steels. The additions of nickel also behave as an austenite stabilizer. Manganese is used as a deoxidizing agent in steels and is also added to steels to promote the formation of smaller MnS sulfides over the more detrimental FeS intermetallic inclusions. Manganese, being less costly than steels, is often added to steel as a substitute austenite stabilizer in place of nickel; however, it lacks the similar toughening properties that are common with nickel additions.

2.4 Predictive Phase/Constitution Diagrams

Predictive Phase diagrams have been developed for stainless steels for the purpose of microstructure volume prediction upon welding. The best known of these is the Schaeffler diagram [69], which predicts phases based on austenite stabilizing elements and ferrite promoting elements at room temperature. The original diagram was developed for a limited number of compositions [70]; further studies have focused on refining chromium and nickel equivalent models for various alloys. A number of chromium and nickel equivalents are given in Table 7.

Cr Eq	Ni Eq	Source
Cr + Mo + 1.5Si + 0.5Nb	Ni + 30C + 0.5Mn	Schaeffler (1949)
Cr + 2Si + 5V + 5.5Al + 1.75Nb +	Ni + Co + 0.5Mn + 0.3Cu	Pickering (1984)
1.5 Ti + 0.75 W	+ 25N + 30C	
Cr + Mo + 1.5Si + 0.5Nb	Ni + 0.5Mn + 30C + 30N	Delong (1960)
Cr + Mo + 0.7Nb	Ni + 35C + 20N +0.25Cu	WRC-1992 Koteki et al. (1992)
Cr + 1.21Mo + 0.48Si + 0.14Nb +	Ni +(0.11Mn - 0.0086Mn ²)	Hull (1974)
2.27V + 0.72W + 2.20Ti +	+24.5C + 14.2N + 0.41Co	
0.21Ta + 2.48Al	+ 0.44Cu	
Cr + 2Mo 10[Al + Ti]	Ni + 35C + 20N	Balmforth & Lippold (2000)

Table 7 - Various Nickel and Chromium Equivalents

Many of these equivalents were developed for specialized cases of different steel compositions. The most comprehensive of these equivalents is described in work by Pickering and is given as:

$$Cr(EQ) = (Cr) + 2(Si) + 1.5(Mo) + 5(V) + 5.5(Al) + 1.75(Nb) + 1.5(Ti) + 0.75(W)$$

Ni(EQ) = Ni + Co + 0.5(Mn) + 0.3(Cu) + 25(N) + 30(C)[56]

Constitution diagrams define phase contents on linear functions of the Cr(EQ) and Ni(EQ) numbers. In particular, martensite, austenite, and ferrite contents are measured, but not carbides and other minor phases. In terms of industrial use, metalcasting workers use these constitution diagrams as a general guide to determine phase content given a particular chemistry. There are a few caveats to using these diagrams for the cast corrosion resistant system:

- In many cases, the intended ranges for these diagrams are almost always for nonmartensitic alloys. The original Schaeffler diagram was designed for 304 stainless steels, which consists primarily of austenite at room temperature. Because of this, most phase prediction diagrams are only well detailed in terms of phase contents in the austenite-ferritic regions. Bounds for the austenite/martensite, and ferrite/martensite, particularly at the 0-100% levels are non-quantitative and were never meant to be used as a measurement tool for alloys in this region. (Figure 9)
- The experiments for many of these alloys consisted of cooling of welded sections and then mechanical testing and/or ferritescope measurements. Mechanical 4point bend testing was performed to only determine whether martensite was present or not. There was no microstructural evaluation to quantify the amount of martensite phase content in samples. Ferritescope measurements depend on the ferromagnetic nature of ferrite and can be used to distinguish austenite and ferrite and give reasonable estimates of percent magnetic phase in irons and steels. Because martensite is also magnetic, ferritescope measurements cannot properly assess martensite/ferrite combinations and often give poor indications of martensite/austenite combinations.

- The Schaeffler and other constitution diagrams do not take into account differentiation of cooling rates, and or aging treatments applied to precipitation hardened steels. Weldments likely cool quicker than most castings and far from thermodynamic equilibrium. Kinetics and cooling rates play a large part in phase stability by relaxing or creating lattice strain.
- Intermetallic phases can form when slower cooling rates apply, such as those in an insulative cast material. Once intermetallics precipitate, they are removed from the matrix, and no longer act as a stabilizing force within the lattice. Because Schaeffler assumes fast cooling rates from liquid (form of weld) to room temperature due to the size of the weld, it is highly unlikely that Schaeffler is taking into account the possibility of secondary phase precipitation.
- Schaeffler diagrams are intended to represent an "as-welded" microstructure. This is different from castings, which usually go through some form of mandatory high temperature treatment in order to homogenize and desegregate contents. In the case of precipitation-hardening steels, solution treatment and the subsequent age-hardening heat treatment are essential to develop useful mechanical properties. Note that the subsequent age-hardening treatments cause the precipitation of copper from the matrix and may influence austenite stability, particularly in the overaged condition, where some of the copper begins to redissolve into the matrix structure, creating a zone of relative austenite stability.



Figure 9–Original Schaeffler Diagram [70]

It is also important to realize that the effects of the microstructure by particular elements are not exclusive; elements that are austenite stabilizers may also promote delta ferrite to some extent. In addition, elements which stabilize austenite may or may not have a marked effect on the M_S temperature. In terms of the precipitation hardening stainless steels, many of the steels occupy a portion of the graph around the convergence point between the M + F and A + M + F boundary lines when using the expanded chromium and nickel equivalents. (Figure 10)



Figure 10 - High Strength Precipitation Hardened Steels on Modified Schaeffler Diagram

A diagram of the specification ranges of the high strength precipitation steels is shown in Figure 10. The inclusion or exclusion of elements within a predictive phase diagram has a drastic effect on the predicted phases. (Figure 11) The early Schaeffler diagram was only designed to quantify the effects of a relatively small amount of elements. Changes between the calculations can be drastic. For example, on the original Schaeffler diagram, PH13-8Mo is expected to solidify in the M + A field, with little ferrite. The later calculated equivalents expect that the alloy should solidify A + M. Neither is particularly correct, as PH13-8Mo generally solidifies at room temperature with a martensitic matrix with small amounts of delta ferrite. In most cases, later constitution diagrams shift the original diagrams to the right and upward. Later studies added elements to the chart, culminating with the WRC-1992, which is commonly used with welding studies today.



Figure 11 - Field differences between Original Schaeffler predictions and Modified Schaeffler Predictions

Other diagrams which are predictive include the Delong Diagram[71] as well as the WRC-1992[72]. Unfortunately, the usefulness of these alloys in predicting ferrite and austenite contents in a primary martensitic matrix are somewhat rendered short as potent alloying elements are often either a) out of range for the given diagram, or b) are not included at all in the particular equation. In addition, the boundary estimations for the upper martensite formation from austenite still remain in question. Some work has been done to develop better estimates of initial martensite formation [73], [74], but the current predictive diagrams provide little guidance on relative amounts of austenite + martensite

present in a particular alloy. Rather, they only state rough boundaries of where martensite may begin to form or where a material may become fully martensitic. Others completely exclude austenite formation and focus only on martensite + ferrite boundaries, but the focus so far has extended only to the boundary and not to predicting particular amounts of ferrite vs. martensite. [75]

2.5 Predictive Martensite Start Equations

Predictive martensite start equations are used for different purposes than the constitution diagrams. Unlike constitution diagrams, these equations are used for all types of steels and even for non-ferrous martensites. Martensite start temperature calculations are mostly empirical in nature and were developed through experimental dilatometry measurements. Eichelman and Hull [76] developed a well-known empirical relationship based on research with various 18Cr-8Ni steels:

$$M_s (C^{\circ}) = 1302 - 42(\% Cr) - 61(\% Ni) - 33(\% Mn) - 28(\% Si) - 1667(\% [C+N])$$

Pickering gives the following martensite start equation:

 $M_{s}(C^{\circ}) = 502 - 810(\%C) - 1230(\%N) - 13(\%Mn) - 30(\%Ni) - 12(\%Cr) - 54(\%Cu) - 6(\%Mo)$ [56]

Estimation of the martensite start temperature gives a good relative idea of the austenite stability. Alloys with martensite start temperatures near room temperature or below room temperature will be difficult to transform using standard quenchants, and will likely require specialized treatments to form significant amounts of austenite. Note that the martensite start temperature does not necessarily give an estimate of the martensite finish temperature, as cooling rate and processing can affect the fraction of martensite attainable. Both equations have been used to provide estimates for martensite start in 17-4PH, with mixed results as best. Eichelman and Hull's equation gives a martensite start temperature of approximately 230°C for 17-4PH. While empirical models remain widely in use, development and refinement of computational databases for predicting M_stemperatures in alloy steels remains a popular topic in computational thermodynamics. [60], [77], [78] There has been some work with using neural networks and past data to

predict M_s temperatures based on past data. Note that there still exist limitations and uncertainties with each form of modeling, including the difficulties of incorporating precipitation systems as well as out-of-range alloys.

2.6 Literature on the Heat Treating/Processing of Cast Precipitation Hardened Steels

Most steel castings are subject to some form of heat treatment in order to provide for uniformity of properties, stress relief, and/or to promote development of desired microstructure. In cast precipitation hardened steels, specific heat treatment is also required to develop the full strength of the product due to secondary hardening. The typical treatment for cast precipitation hardening contains a homogenization step to desegregate chemical imbalances followed by a slow cooling, a solution anneal to austenize the material, a fast quench step to form martensite, and finally the aging step to cause copper precipitate to form. (Figure 12)



Figure 12 - Typical Precipitation Heat Treatment Diagram, Precipitation Hardening System

The major advantage of casting is that it produces a part that is near net-shape, which greatly reduces cost and time to market through the elimination of intermediate machining steps. On the other hand, wrought materials generally go through thermomechanical treatments, which lead to smaller grain sizes and closing of pores due to temperature/pressure-assisted yielding. In addition, compositions of analogous materials tend to have higher amounts of silicon for fluidity, and in the case of air-meltable alloys, are generally less reliant on systems that may react with oxygen at high

temperatures. The as-cast structure of high-alloy steels generally suffer from some form of microsegregation due to chemical partitioning of elements in solids and liquids during solidification and the subsequent formation of dendritic structures. Because of the ensuing segregation, homogenization is generally thought as beneficial as it reduces the local differences in segregation due to solidification. CB7Cu-1 and 2 provide examples of these issues with cast materials; while they serve as analogues to 17-4PH/15-5PH, copper ranges are narrower, and silicon contents, although not specified, are usually higher. Delta ferrite, which cannot be tolerated in wrought materials, is often preferred in small amounts in castings. On the other hand, fully austenitic structures are generally not preferred in castings due to the propensity of hot-tearing.[79]

2.6.1 High Temperature Treatments - Homogenization and Solution Treatment

Castings generally solidify through dendritic growth. Because of this, concentrations of alloying elements will become distributed unevenly through microsegregration. Homogenization is used to promote back-diffusion of elements which can be described through Fick's Second Law:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right)$$

Fredriksson and Akerlind[80] give the following model for the expression of concentration of an alloying element at a given position and time during heat treatment:

$$x = x_0 + \frac{x_0^M - x_0^m}{2} \sin\left(\frac{2\pi y}{\lambda_{den}}\right) \exp\left(-\frac{4\pi^2 D}{\lambda_{den}^2}t\right)$$

By manipulation, the equation can be changed to solve for homogenization time based on diffusion constant and dendrite arm distance:

$$x = x_0 + \frac{x_0^M - x_0^m}{2} \sin\left(\frac{2\pi y}{\lambda_{den}}\right) \exp\left(-\frac{4\pi^2 D}{\lambda_{den}^2}t\right)$$

There has been limited modeling on Cr segregation in cast 17-4PH. [41] It is predicted that there should be at least some Cr segregation upon solidification (Figure 13), and possibly some Cu segregation as well. Homogenization results in literature on 17-4PH material have been mixed at best. Hildebrand found no improvement in tensile/yield strength (2-3% reduction on average) in wrought 17-4 material aged at both H900 (aged at 900°F, 1.5 hr) and H1075 (aged at 1000°F, 4 hr) conditions. However, Hildebrand did observe an increase in terms of ductility and a decrease in variance of ductility when material was homogenized at 2150°F for 2 hours vs. solution annealed material. Amounts of delta ferrite in the wrought material were not discussed in the paper; therefore it is impossible to determine the nature of the homogenized vs. the as-cast material. [81]



Figure 13 - Modeled Cr segregation in Cast 17-4PH [41]

Only a single paper addresses the effect of homogenization times on cast 17-4PH. [82] Results from the paper imply that the change in delta ferrite reduction seems to diminish with increasing homogenization time. The investigation also shows a peak in both impact energy and strength, but the reverse in terms of hardness. Impact energy also appears to decrease after peaking at 1 hour. The decrease in impact toughness may be resultant of the grain growth/Hall-Petch effect, due to the fact that the delta ferrite phase has been implicated in impeding austenite grain size.

Also note that the delta ferrite phase that remains in the casting may not necessarily take on the same dendritic nature. Delta-ferrite is a remnant product, which remains on the periphery of child austenite-grain structures rather than in the typical modeled sinusoidal form. Nevertheless, modeling of delta ferrite dissolution has not been performed for the 17-4PH wrought or CB7Cu cast materials.

2.6.2 Hot Isostatic Processing

Hot isostatic pressing (abbreviated HIP) is a process where material in a solid state is held under high temperatures and pressures to improve mechanical properties of the part. [83], [84] While hot isostatic pressing is an integral step in terms of powdered metal processes, it is less studied in terms of casting densification. Material is first exposed to high temperatures (greater than $0.7T_m$) to promote plastic flow of material under high pressure heal porosity. Much study has been afforded to HIP processing in terms of modeling for powdered metals, but the validity of applying PM models to castings has been questioned. [85] Only internal defects are healed with hot-isostatic pressing; pores with openings to the surface are not healed. Some alloys do not respond well to HIP processing, especially those that form oxide films along the surface of the pores. It is theorized that while the pores collapse, bifilms interfere with the cohesion between welded surfaces. It is well agreed that in most alloys, HIP improves the mechanical properties of castings is affected. [79], [86]

2.6.3 Quench Control

There have been very little in the way of studies in terms of cooling rates after annealing for the 17-4/15-5PH system. ASTM A747 specifies that the alloy must reach 90°F within one hour. Parts with thicker sections may be cooled using water or oil quenching techniques. Literature remains scarce on the specific effects of cooling rates on 17-4PH and other precipitation hardening systems. No CCT curve data is readily available for determining the effects of cooling rates on these materials. Generally, the cooling rate above the M_s is agreed to have no effect on martensite formation or M_s . [28]Nishiyama deduces that is suspect to state that cooling rate has no effect on Ms in terms of carbon steels. However, it is well-agreed that the cooling rate between Ms and Mf are known to have an effect on the final martensite and retained austenite percentages. (Figure 14)



Figure 14 - Retained Austenite after Quenching on Fe-C Steels [28]

2.7 Precipitation in CB7Cu alloys

In precipitation hardened steel, a great deal of the strengthening comes from the post quench age step. The age hardening step serves two purposes: a) to temper the low-carbon martensite, promoting toughness and b) to promote the formation of the copper rich precipitates. 17Cr-4Ni-2Cu, whether wrought or cast, is aged at temperatures between 900-1150°F for various amounts of times. The minimum properties expected between the cast and wrought materials differ greatly; in the near peak-aged condition, wrought 17-4PH minimums are much higher than that of 17-4PH cast materials.

Table 8 - Aging Guidelines and Minimum Properties, 17-4PH Cast and Wrought [9], [87]

Condition	Age Temp (F°)	Age Time (h)	Cooling	YS/TS min CAST (ksi)	YS/TS min WROUGHT (ksi)	Elongation [CAST]/ [WROUGHT]
SA	Not PH hardened					<u> </u>
H900	900	1.5	Air Cool	145/170	170/190	5/10
H925	925	1.5	Air Cool	150/175	170/155	5/10
H1025	1025	4	Air Cool	140/150	155/145	9/12

H1075 1075 4 Air Cool 115/145 145/125 9/13 H1100 1100 4 Air Cool 110/135 140/115 9/14	
H1100 1100 4 Air Cool 110/135 140/115 9/14	
H1150 1150 4 Air Cool 95/125 135/105 10/16	
H1150M 1400 2 Air Cool	
1150 4	
H1150DBL 1150 4 Air Cool	
1150 4	

There has been some work on relating yield strength to aging conditions in aluminum alloys. The general methodology is to realize that the yield strength can be described as a function of time in an age-hardening alloy. There are many factors which can influence strength in an age hardening alloy. These include the decrease in solute concentration in the matrix and the subsequent growth of precipitates during early stages of precipitates, the coarsening of precipitation by Ostwald ripening, and the strengthening contribution ratio by the various modes of dispersion hardening and precipitation hardening.[88] While the preliminary work was performed on Al wrought alloys, [89] there has been an extension of the model to casting alloys. [90]

There is at least one complexity not faced in modeling aluminum alloys as compared to steel alloys; the intrinsic strength of the material in the case of the aluminum investigations is for the most part assumed to be constant. In PH steels, there are additional factors: the tempering of the martensite at lower transformation temperatures and the additional effect of the reversion of austenite (and reabsorption of copper precipitate into the matrix) at the higher aging temperatures. The solid solution strengthening term does not apply in this case as it is related to the strengthening due to the copper precipitate in solution.

2.7.1 Precipitation Systems in Current Precipitation Hardening Stainless Steels

Much of the early work with precipitation hardening materials was empirical in nature. The first experiments by Wilm with the Al-Cu-Mg-Mn alloy (Duralumin) provided the first discussion of precipitation hardening at the technical level. However, the workings of the precipitation hardening mechanism remained poorly understood for nearly half a decade. [91-94] Duralumin remained the only practical alloy in use until Merica postulated that precipitation occurred from supersaturated solid solutions; though at this time, precipitates responsible for age hardening could not be directly observed. [95] Direct observation and confirmation of Merica's early postulation did not occur until Guinier and Preston independently discovered submicron sized CuAl₂ particles in underaged specimens of Al-4Cu materials. Several books and literature reviews exist on the topic of precipitation hardening/particle strengthening in general [93], [96], [97], but for the purpose of this discussion, the focus is on precipitated hardened stainless steels. A brief overview of precipitation hardening mechanisms was given in the following section.

Early precipitation systems discussed in steels included the iron-tungsten and ironmolybdenum systems. Harrington developed early precipitation hardening of a multitude of materials and later developed an iron-cobalt steel patent. [98], [99] Sykes correlated hardness increases to both increases in concentration of W and Mo and the corresponding aging temperature. [100]The mechanism and precipitate was not known at the time; though it can be postulated that there was development of Fe₂W and Fe₂Mo Laves Phase, judging by the compositions and hardness developed. The first mention of precipitation hardening Fe-Cu steel comes from a description for a "new die steel with an alloy addition of copper" age hardened at 1000°F at the same 1939 conference. [94] The steels developed during these early investigations utilized the basic precipitation hardening principles, but were not corrosion resistant. This would change starting with the development of Stainless W. Stainless W, developed by US Steel in 1946 was the first commercial PH-SS grade. Stainless W (AISI 635) appears to utilize Ni₃Ti and Ni₃Al in terms of hardening, though in small and unbalanced amounts. The specification is quite wide in terms of both titanium and nickel contents. Later wrought alloys would mimic this system, except with lower allowable contaminants and a more balanced Ti and Al Steels such as 17-4PH, 17-7PH, PH13-8Mo, Custom 450, and other chemistry. recognizable common grades were developed over the next twenty-year period from 1940 to 1960. Of all the alloy systems, 17-4PH (15-5PH) is by far the most popular system in use today for precipitation hardening alloys, both wrought and cast. [45]

Precipitation in the 17-4PH steels appears to occur in a classical fashion, not unlike other precipitation hardening systems such as those seen in the Al-Cu and the Al-Zn-Mg systems. In order for the samples to properly age, the material temperature is increased and quenched at temperatures low enough to induce near complete martensitic transformation. [45], [18], [17] Copper-rich precipitates are responsible for increases in strength and hardness perceived during the secondary-hardening step. Copper is generally soluble up to about 5.5 (at %) in pure Fe austenite (γ). Amounts of copper greater than the solubility limits do not have practical purposes in precipitation hardening alloys as it forms a mixed field of fcc ε -copper and austenite, though it does find use in low carbon ferritic and austenitic alloys. [101-103] Therefore, copper is limited to about 5 wt. percentage in Cu-precipitation hardened alloys. To exploit the precipitation hardening ability of the material, CB7Cu-1 is heated to a temperature sufficiently above the upper critical boundary (AC3) to guarantee a fully austenitic structure. After heating, the material is subjected to either a quench in liquid or oil media to promote fast cooling rates. In the case of thin sections, air cooling to below 90°F within an hour is sufficient to ensure near complete transformation to martensite. This leads to a microstructure predominated by low carbon lath-martensite, with minor amounts of δ -ferrite and possible retained austenite, depending on both processing and composition. [45], [18], [17], [9], [52], [104] Because of the diffusionless nature of the martensitic transformation, the copper concentration between that of the martensite and austenite is essentially equivalent. Autotempering phenomena (interdiffusion of interstitial carbon and nitrogen) common to intentionally carbon-alloyed steels is absent in Cu-PH steels as substitutional element diffusion is extremely low at the predicted M_s temperatures.

Generally, CB7Cu-1 is aged for times ranging from 1.5-4 hrs between the temperatures of 900°F and copper-rich precipitate, which is similar to what is seen in Fe-Cu steels. [102], [105-107], [23]slightly overaged precipitates have been found in most investigations to be very fine fcc-precipitates. (Table 9) Current research strongly suggests that the peak-age strengthening observed is a product of modulus hardening, which is caused by a mismatch between elastic moduli between precipitate and matrix. [92], [10] Aging at temperatures above 1150°F do not result in appreciable hardening due to extreme coarsening of the overaged fcc-copper precipitate. While true peak aging

occurs at 850°F, ASTM guidelines allow for aging at 900°F for 1.5 hours, possibly due to the fact that while peak hardness is seen at 850°F, the material also becomes heavily embrittled. [8], [9] Currently, the form and content of the strengthening precipitate particle at early stages of precipitation are still in question. In general, precipitation is thought to proceed from spherical particles to 9R strain-relaxed transitional structures, and then finally to fcc particulates. While peak aging for 17-4PH occurs at 850°F, Murayama et. al. were unable to detect a secondary phase via selected area diffraction pattern analysis (SADP) in material aged for 4 hours at 580°C (1076°F). However, very fine, homogenous copper rich precipitates 150Å in size were observed after 2 hours of aging at 510°C (950°F). Wu and Lin [42] observed short ellipsoid-like precipitates after aging at 600°C. (Figure 15) While many studies have failed to detect the precipitate at peak-aging conditions [10], [42], [11], [23], a distinct increase in strength was seen in the material at the given peak-aging time and temperature combination. Precipitates were observed to coarsen with increased temperatures and longer times, to the point that rodshaped precipitates were observed in the H1100 condition material. In most cases, precipitates have been very difficult to observe, even with TEM, due to the combination of the small size of the precipitates and the high dislocation density of the lath structure of the low carbon martensite.



Figure 15 - Coarsening of Cu-rich Precipitates at 600C (a) 0.25 hr, (b) 32 hr [42]

Study	Heat Treatment Conditions	Precipitate	Composition	Detection Method
Rack and Kalish (1974)	510°C / 2hr	Cu-rich precipitate (fcc)?	17-4PH	TEM
	600°C / 2 hr	å-Cu (fcc) precipitate		TEM + SAD
Murayama (1999)	510°C / 2hr	Incoherent 50% at weight Cu precipitate (bcc)	17-4PH	FIM- Atom Probe + TEM
	400°C / 5000h	Large å-Cu (fcc) precipitate + ultrafine Cu-rich precipiate		
Hsiao et. al (2001)	480°C / 1 hr	15nm x 25nm Possible fcc precipitate, not well identified	17-4	FEG-TEM
Wu and Lin (2003)	600°C / 0.25-32hr	Incoherent å-Cu fcc precipitate	17-4PH	TEM
Goodman (1973)	500°C / 1 hr 500°C / 3 hr 500°C / 100hr	15 Å ~50% Cu (bcc) 15 Å ~50% Cu (bcc) 50 Å ~100% Cu (fcc)	Fe-1.4% at. Cu	FIM-Atom Probe
Viswanathan (1988)	510°C/ 2 hr	150 Å (fcc) precipitate	17-4PH	TEM + SAD

Table 9 - Precipitate found in Studies of Cu-bearing steels and 17-4 PH stainless steels

2.7.2 Theory of Precipitation Hardening in Stainless Steels

It is theorized that copper precipitate strengthens the matrix through modulus difference hardening, as the differences in shear moduli is directly related to the force required to shear a particle. [92], [97] Modulus strengthening modeling is somewhat difficult to perform because of the difficulty in acquiring measurements of the precipitated shear particle; however, there have been multiple models developed [96], [108] to determine critical resolved shear strength from particle characteristics. The strengthening relationship in the early aging of alloys can be summarized by the following simplified Friedel equation for spherical particles:

$$\tau_p = A\Delta^{\frac{3}{2}} \left(\frac{rf}{2S}\right)^{\frac{1}{2}}$$

Where:

- $\tau_{\rm p}$ = Shearing stress on the particle
- A = Constant
- f = Volume fraction,
- S = Dislocation line tension,
- $\mathbf{r} = \mathbf{Particle \ radius \ size, \ and}$
- Δ = Interaction Term between particle and matrix.

High strengths are possible in this portion of the hardening, as demonstrated by peakaged material. However, as heat is added, precipitates grow as larger particles are more thermodynamically stable. Eventually, a precipitate grows to a point where it becomes too difficult for dislocation lines to shear as the shearing force is directly proportional to particle radius. At this point, additional hardening results from Orowan process hardening as opposed to modulus hardening, as material now bypasses the growing particles, rather than shearing across the particulates. The following equation gives a general relationship between particle characteristics and CRSS for spherical particles:

$$\tau_c = \mu \frac{b}{\lambda}$$

Where:

 τ_c = CRSS (critical resolved shear stress)

 μ = shear modulus of matrix

 λ = interparticle spacing

If the particles are assumed to be spherical and we let the interparticle spacing λ be equal to (1 / number of particles contained per unit of surface area), the equation can be expressed as:

$$\tau_c = \left(\frac{3}{2\pi}\right)^{1/2} \left(\frac{\mu b}{r}\right) f^{1/2}$$

Where:

- τ_c = CRSS (critical resolved shear stress)
- μ , = shear modulus of matrix
- b = length of the Burgers vector of the dislocation
- f = Volume fraction, and
- r = Particle radius size

From the previous equation, it is clear that as the particle radius increases, the increment of CRSS gained continues to decrease. Because larger particles are more stable, smaller particles are removed from the matrix at the expense of the coarsening particles. Note that the particulate spacing is directly proportional to the radius of the particle. As both tend to increase with time, there is less probability that a dislocation will encounter a barrier at any point. The process, better known as Ostwald ripening, eventually leads to an overall drop in strength of the material as shear moduli hardening particles are drawn from the matrix. This mechanism is particularly evident in the overaged (H1000-H1150) conditions of the material, where strength is relatively low. In these conditions, the lattice planes of the precipitate are no longer continuous across the precipitate boundary, and dislocations in the matrix are forced to pass around the particle as per dispersive hardening particles as opposed to the modulus hardening mechanism in the case of the coherent particle. (Figure 16)



Figure 16 -An Illustration of (a) Coherent and (b) Incoherent Aging Particulates (Nembach)

PH steels aged at peak aged temperatures may also be susceptible to hydrogen embrittlement, but most of the concern seems to be with welding processes. The prevailing theory is that the small precipitates interfere with diffusion of gases that may become entrapped within the matrix. 17-4PH is no exception to this, peak-aged state as hydrogren diffusion paths are blocked by the fine nano-precipitates formed during coherent precipitation.[109]

2.7.3 Multistage aging

Multistage step-aging, remains a possibility in increasing strength and or ductility in terms of precipitation hardened steels. In aluminum alloys, two-step aging is generally used to reduce aging times by treating at higher temperatures to increase rates of precipitation. This is important as these alloys generally require days to weeks to reach required hardness. [110], [111] On the other hand, CB7Cu-1 and 2 are usually aged for a maximum of 4 hours, so practical concerns do not center around reductions in time as per the aluminum precipitation systems. However, two-step aging in CB7Cu-1 and other precipitation hardened alloys remains a possibility; in terms of strengthening, it is well known that the submicron sized Cu particles are responsible for the strengthening mechanism. The natures of the exact composition of these particulates are still in

question, but it is known that the precipitate-Cu particle growth is mainly influenced by temperature. There is evidence that heat treating Cb7Cu above a critical temperature for times greater than an hour (~950-1000°F) causes the precipitate to become incoherent and the material to soften. Hehemann suggests that by aging at temperatures slightly lower than the critical temperature, kinetics are more favorable to coherent copper zones as compared to that of the incoherent form. [110] Only a small body of research exists in terms of double-aging precipitation cast steels. Kimura examined two step aging of 17-4PH steel; however, the examination was focused on the development of an equivalent tempering parameter. The experiments focused little on low temperature to high temperature step-aging. It is important to note that the research did point out that double aging heat treatments at low temperatures lead to about 10% increased ductility as compared to the ASTM guideline peak-aged specimens.[112] Multistage aging from high to low temperature has been proposed in high strength, low alloy steels in order to stabilize existing reverted austenite. Aeromet 100 showed increased impact resistance with no loss of strength as compared to an overaged specimen, but this material has higher carbon contents and depends on M_2C carbide + γ -ordering for strengthening. [113]

2.7.4 Shercliff-Ashby Age Hardening Model [88]

Ashby and Shercliff (1990) developed an age-hardening model for Al-Mn-Si-Mg alloys based on the concepts of age-hardening previously stated by Friedel. By examining the relationship between time, temperature, and hardness change, as well as knowing some of the intrinsic properties of the material, a relationship between the precipitation kinetics and material properties could be established for precipitate aging behavior in general. The original model contained terms that related the following characteristics to age hardening:

- Growth in volume fraction of precipitate and decrease in solute concentration with time in the initial stages of precipitation
- Dependence on equilibrium volume fraction of precipitate on ageing temperature

- Precipitate coarsening by competitive growth between shear and bypassed precipitate
- Contribution of solid solution to the strength
- Contribution of shearable precipitate to strength
- Contribution of bypass precipitate to the strength

The Shercliff-Ashby model treats aging strength as a function of temperature adjusted time. (Figure 17) The net strength is a combination of the intrinsic strength of the matrix, solid solution strength, and the precipitation strength due to shearing and bypassing of particles. Solid solution strengthening is significant in aluminum based alloys. As the precipitate is removed from solution, a measure of solid solution strengthening is lost until the entire fraction of precipitate is removed, where the solid solution strength due to the shearing of small precipitates and the strength due to the bypass mechanism. Maximum strength is reached when the greatest fraction of particles is precipitated and the particles are all bypassed through shear. As aging progresses, the particles grow and increase interparticle spacing distance. These particles grow competitively with sheared, smaller precipitate, and eventually redissolve or absorb existing neighborhood precipitate in favor of growth.



Figure 17 - Shercliff Ashby Precipitation Diagram detailing the relationship between time, hardening mechanisms and strength [88]

Shercliff-Ashby Model Components

To determine the effect of aging behavior on peak-hardness, peak hardness is related to an extent of aging term. The extent of aging is described as the following temperaturecorrected time, P:

$$P = \frac{t}{T} \exp\left(-\frac{Q_A}{RT}\right)$$

Where t is the aging time (expressed in seconds), T is the temperature in Kelvin, R is the ideal gas constant, and Q_A is the activation energy. The temperature corrected time can also be related to the general coarsening of the material, assuming that the precipitate is spherical and follows the cubic coarsening rule. If the initial precipitate radius, $r_{ppt, 0} <<< r_{ppt}$, the following relationship between P and the coarsening of a precipitate holds true:

$$r(t) = C_1 P^{1/3}$$

Where C_1 represents a constant related to the concentration of the solute in the matrix. Not only must the coarsening of the precipitate must be taken into account, but also the effects of precipitate bypassing and precipitate shearing. As the parameter P increases, more precipitates are bypassed rather than sheared.

Relating Precipitate Coherency to Strength

For precipitate shearing, we turn to the simple relationship known as the Freidel effect. Friedel's research suggested that the contribution of sheared precipitates to the yield stress was related to the volume fraction f and particles of radius r through the following function:

$$\Delta \sigma_{\rm A} = c_3 f^m r^n$$

 c_3 , m, and n are constants. In multiple investigations most dislocation/particle interactions have values where m = n = 0.5.

Precipitate bypass occurs when the precipitates coarsen to a critical size where it is no longer energetically favorable for dislocations to shear across the precipitate. At this point, dislocations bow around the precipitate instead. Friedel's bowing stress is described as the following equation:

$$\Delta \sigma_{\rm B} = \frac{c' G \boldsymbol{b}}{l}$$

Where G is the shear modulus, and b is the Burgers vector. l is the particle spacing in the slip plane of the arbitrary dislocation. The particle spacing is directly related to the radius r of the precipitate, but also inversely related to the square of the precipitate fraction:

$$l = \mathsf{c}'' \frac{r_{ppt}}{f^{1/2}}$$

Combining these two equations, a relationship between bypass strength and precipitate fraction and radius can be made:

$$\Delta \sigma_{\rm B} = c_4 \frac{f^{1/2}}{r}$$

 c_4 contains all the constants in the previous two equations. Precipitate shearing and bypassing are complementary, but competing reactions. Because each reaction is occurring at competing rates, the harmonic mean is appropriate for relating the strength of the material:

$$\Delta \sigma_{\text{ppt}} = \left[\frac{1}{\Delta \sigma_A} + \frac{1}{\Delta \sigma_B}\right]^{-1}$$

If a precipitation hardening material follows the predictive Friedel equations, then the peak strength should be somewhere close to where both contributions are equal, e.g. where $\sigma_A = \sigma_B$. If we define the temperature corrected time P at the peak value as P_p, the following relationship holds true:

$$C_3 f_0^{1/2} f P_p^{1/6} = C_4 \frac{f_0^{1/2}}{P_p^{1/3}}$$

We now relate the temperature corrected precipitation time to a peak precipitation strength S_0 , which is defined by the previous relationships:

$$S_o = \frac{C_3}{2} f_o^{1/2} P_p^{1/6}$$

With the relationship between strength and time now established, precipitation strength from bypass mechanisms and precipitation from shear mechanisms can now be related according to strength and time.

$$\Delta \sigma_{ppt} = \frac{2S_o \left(\frac{P}{P_p}\right)^{\frac{1}{6}}}{1 + \left(\frac{P}{P_p}\right)^{\frac{1}{2}}}$$

In addition, the total volume fraction precipitated is dependent on the aging temperature as the metastable equilibrium and solubility are influenced by the temperature. Because of this, a temperature-precipitation relation equation is added to shape the precipitation curve:

$$S_o^2(T) = S_{o,max}^2 \left[1 - exp\left(-\frac{Q_s}{R}\left(\frac{1}{T} - \frac{1}{T_s}\right)\right) \right]$$

Hardness or strength can now be described as a function of both time and temperature:

$$S_{o}^{2}(t,T) = S_{o,max}^{2} \left[1 - exp(-\frac{Q_{s}}{R} \left(\frac{1}{T} - \frac{1}{T_{s}}\right) \right] \times \left[1 - exp(-t/\tau_{1}) \right]$$

 $S_{o, max}$ is the estimated maximum precipitation strength attainable. Q_s is the estimated heat of enthalpy, and T_s is the metastable solvus of the precipitate in the matrix. These terms can either be estimated from research data, or calibrated on known curve data. \hat{o}_1 , a scalable time constant, is related to t_p , the time to reach peak precipitation is defined by the following:

$$\tau_1 = K_1 t_p$$

 K_1 is a fitted constant, found through adjustment with expected coherent strength decay in terms of data.

While this is useful in terms of Al-Cu model, it does not translate directly to steelprecipitation because the microstructures of Al-Cu alloys are inherently different than those of Fe-Cr-Ni-Cu systems. For example, aluminum does not undergo tempering while the matrix microstructure of martensite is metastable. Aluminum alloys also derive a significant portion of their strength from the solution strengthening effects of dissolved elements in the matrix, and during heat treatment, those elements are incorporated into the age-hardening particles. Fe-Cu alloys do not undergo the same degree of solution strengthening, particularly through the metastable copper elements contained within the alloy. Therefore, the model as it stands has to go through significant changes to reflect proper age-hardening behavior in the alloy.
2.8 Precipitation in Next Generation Wrought Precipitation Hardening Systems (Fe-Cr-Ni-Mo-Ti,Al)

Typical properties of wrought 17-4PH steels have been noted to reach maximum ultimate tensile strengths of 200ksi at the peak-aged condition. There is likely an upper limit to strength that copper precipitation can provide, which is below that of the specific strength of titanium. Adding more copper does increase strength to about 5%, but above that, copper freely begins to precipitate from austenite in an fcc-FeCu phase, which is softer than the austenite matrix. Secondly, copper that is limited in CB7Cu alloys becomes of weld-repair issues. Because amounts of copper are limited in Cb7Cu as compared to the wrought 17-4PH alloy due to segregation during weld repair, there is less copper in the cast specification than allowed in the wrought alloy specification.

PH13-8Mo represents another precipitation hardening alloy which would be attractive to adapt to castings. Like 17-4PH, there have been difficulties in identifying the precipitate without overaging the material, but atom probe studies have confirmed the presence of a nickel and aluminum rich precipitate (β NiAl) at 510°C. [24] Wrought PH13-8Mo has a higher UTS and YS than 17-4PH at similar ductility levels. In addition, PH13-8Mo has the greatest resistance to stress corrosion cracking of the standard PH grades. A few attempts to cast PH13-8Mo using vacuum investment casting have been reported, but there has been no work reported of an air or inert melting system. [24], [19-21]Multiple difficulties exist to be overcome in adapting this system for air-melting. Most notably, the composition contains a high level of aluminum, which readily forms oxides at high temperatures. [79]

Fe-Ni-Cr systems with Ni₃Ti/Ni₃Mo systems, which are generally seen in maraging systems, present another attractive target as they provide the highest strengths with good ductility, impact strength, and corrosion resistance. The strengths of these systems are on the order of 30-50 ksi greater than the PH17-4 system with similar ductility, corrosion resistance and impact properties. [7], [5] Nickel-rich precipitates (Ni₃Al, Ni₃Ti, Ni₃Mo) are responsible for the strengthening seen in these alternative systems. Maraging steels, which are formulated without Cr, can develop strengths from 250-500ksi. [114]These

precipitates are by nature stronger than those of the PH Cu and-system, but also suffer from increased reactivity to both carbon, nitrogen, and oxygen. (Figure 18) While limited Ti(N,C) formations have been reported to prevent excessive grain growth, they also prevent the age-hardening of the material. Most of these precipitates usually depend on a matrix rich in cobalt as well as nickel, though development of many cobalt free grades has been successful. [115-120] In these materials, the hexagonal Ni₃M phase forms at peak-aging, while longer overaging times causes the precipitates to form into the more stable and brittle intermetallic Laves Fe₂M phase. Hexagonal Ni₃X phase is thought to harden the material by coherency strengthening. [114], [121] Austenite reversion has been observed to proceed quite quickly after overaging precipitates in some alloys. [5], [44]Whether or not this same behavior is apparent in the 11-11PH alloy is still unknown. It is important to note that the attempts at formulating stainless maraging steels are more limited, due to the fact that chromium additions stabilize ferrite, limit the strength of the matrix, and cause excessive loss of impact toughness as compared to the chromium-free maraging steels.



Figure 18 – Relative Carbide and Nitride Stability expressed as enthalpy of formation at standard temperature and pressure. TiC/TiN particulates are highly stable, and difficult to dissolve. [60]

2.9 Technique Description

This section presents a brief description of experimental techniques to acquaint the reader with the techniques used for the studies conducted in these investigations.

X-Ray Diffraction (XRD)

To examine both retained austenite contents and the effect of final temperature on martensite/austenite ratios, X-ray diffraction analysis was used to detect the amount of retained austenite in each of the heat treated samples. This technique utilized patterns made from a collection of the scattered electrons diffracting from the surface of a lattice plane. Particular crystal planes will diffract with different intensities due to differing orientations in the planes. While single phase materials are quite simple to identify based on diffractive peaks, multiple phase materials consist of diffractive patterns which may superimpose upon each other. Because martensite and austenite are allotropic (fcc vs. bcc) in nature, the two phases lend themselves to being analyzed using XRD analysis. When separating martensite from retained austenite, relative intensities of particular peaks are well known, and the percent of austenite can be estimated by noise removal and area for amounts of austenite as low as 2-5%. The general form for estimating volume fraction of retained austenite (γ) is:

$$V_{\gamma} = \frac{\frac{1}{q} \sum_{j=1}^{q} \frac{I_{\gamma j}}{R_{\gamma j}}}{\frac{1}{p} \sum_{i=1}^{p} \frac{I_{\alpha i}}{R_{\alpha i}} + \frac{1}{q} \sum_{j=1}^{q} \frac{I_{\gamma j}}{R_{\gamma j}}}$$

Where:

 V_{γ} = Volume fraction retained austenite, I_{γ} = Intensity of austenite in peak j, I_{α} = Intensity of martensite/ferrite in peak i, and $R_{\alpha,\gamma}$ = Material R-factor, based on material properties/detect.

Software can be used to fit curves and find areas under diffraction peaks. Peaks for fractions under 5% are generally detectable, but are not generally quantifiable. Peaks for fractions under 2% are usually undetectable using XRD. Samples in this study were studied with a PANalytical X'Pert PRO diffractometer with a Cu-source diffracted beam monochrometer. Samples were quantified in accordance with procedures contained within the ASTM E975 standard. In general, the <200> reflection from the austenite was compared to the <200> reflection from the austenite to measure retained austenite.

Optical Microscopy /Determining Volume Fraction by Systematic Point Count

In the investigation of metallographical phases, optical microscopy is essential to identify and differentiate bulk phases along with minor phase intermetallic inclusions. Along with identification, quantitative metallography can be performed to estimate phase contents by overlaying a grid upon a specimen and counting/weighting edge intersections along with complete intersections. As the expected phase volume fraction decreases, the number of grid points must be increased to improve accuracy. The number of fields and grid sizes were selected to provide at least a 20% relative accuracy as expressed by the following equation:

$$n = \left(\frac{4}{E^2 \times P_t}\right) \times \left(\frac{100 - V_v}{V_v}\right)$$

Where n is equal to the number of fields and P_T is the number of points on a grid. V_v represents the amount of volume fraction estimated. The number of points where a given phase are detected were counted. Points which fell on the boundaries of phases were given a value of 0.5. The average percentage from points P(hat)_p is calculated with the following equation:

$$\hat{P}_p = \frac{1}{n} \sum_{i=1}^n P_p(i) = \frac{1}{n} \sum_{i=1}^n P_p/P_t$$

The standard deviation estimate was calculated as:

$$s = \left(\frac{1}{n-1}\sum_{i=1}^{n} (P_p(i) - \hat{P}_p)^2\right)^{0.5}$$

OIM/EBSD

Electron backscattered diffraction (EBSD) or orientation image microscopy (OIM) can be used to examine crystallographic orientation, texture and/or phase content of materials. EBSD is performed using collected diffracted electrons, which produce a pattern of intersecting bands referred to as Kikuchi patterns or electron backscattered patterns (EBSP). This technique is performed using a scanning electron microscope equipped with a special phosphor screen electron collector. In order for the electron capture to be sufficient, the sample is often tilted in the chamber to allow for reflected electrons to be easily collected. The patterns of the collected electrons can be related to crystallographic features of the specimen. The bands themselves provide information about lattice structure, orientation, and spacings of atoms in crystal planes. Bands are transformed using Fourier patterns into Hough Patterns, where they correspond to peaks that give information about orientation and structure. These patterns are then computationally 'fit' to possible user-identified candidate structures and expressed in terms of statistical confidence.



Figure 19 - Kikuchi Pattern from Single Crystal of Silicon (EBSD)

EBSD only gives information about the crystalline structure and lattice spacings of a given crystal. The patterns often suffer from degradation due to surface texture and/or sample preparation. In many cases, two different phases are identified with equal confidence because of similar structures. An example of this is FCC-austenite and $M_{23}C_6$ carbides; the crystalline structures of both are the same, and the characteristics of the spacings and Hough patterns are often similar. To properly identify phases, the addition of EDAX/EDS chemistry analysis is often helpful and can be overlaid to give better confidence in phase detection and quantification.

SEM/EDAX (Scanning Electron Microscopy/EDAX)

Scanning electron microscopy with energy dispersive X-ray spectroscopy is a technique which allows for chemical analysis combined with the ability to observe fine features down to the nanometer scale. In general, features as small as 100nm are observable with a good instrument and proper analysis techniques. Images of the surface are produced through high-energy scattering of electrons. Signals from these scattered electrons are then detected, amplified, and converted to a rasterized image which can then be collected. Along with the SEM, there are a number of detectors which can provide further information on the sample other than surface features, including field emission detectors

and backscatter detectors. Energy dispersive X-ray spectroscopy allows for semiquantitative chemical analysis of a material surface. EDAX (or EDX) uses the collection of characteristic X-rays which are emitted as energy is added to surface materials.

Differential Thermal Analysis

Differential thermal analysis is generally performed by heating and cooling an inert reference material (often a non-reactive metal or ceramic) under the same conditions as a sample of interest. Both temperature and heating rate can be adjusted for experimental purposes, along with the atmosphere, to quantify possible atmospheric reactions. Because the reference sample is non-reactive and the sample material may exhibit phase reactions, differences in terms of heat release and/or absorption are measured. Both sample and standard are placed on an inert crucible, which fits over a specialized thermocouple. The assembly is surrounded by an insulating block to assure even heat distribution within the sample chamber. In many cases, the thermocouples are often in the form of flat discs to ensure good contact with parts. This also improves low temperature heat transfer so that accurate temperature measurement can proceed at even rates. In steels, reactions such as phase dissolution/reversion, martensite reaction start and finish temperatures, and age-hardening start/finish reactions, can be detected with DTA.

Mechanical Testing

Early mechanical property results from in-house machining and testing showed large amounts of variance in reported properties. This was generally due to difficulty oftest specimen machining and test machine limitations; these later investigations used heattreated blanks that were outsourced for mechanical testing and machining. Tensile and V-notched impact samples were sent to Westmoreland Mechanical Testing and Research for final machining and testing. All samples were machined and tested according to specifications in ASTM E8 & ASTM E23. The tensile specimens used in the testing were sub-sized specimens with a nominal gage diameter of 0.250" due to the high strength levels of these materials. Tensile specimens were machined and tensile tested at low strain rates in accordance with ASTM E8 order to avoid strain rate effects. (<0.01 in/in/min.)



Figure 20 – Sub-sized tensile specimen used in Figure 21 – Charpy specimen dimensions (ASTM E23) testing (ASTM E8)

In-house specimens were machined to the same ASTM E8 & ASTM E23 guidelines. Charpy test specimens were machined using electro-discharge machining (EDM). Tensile specimens were tested using an INSTRON 4206 machine with a 100kN rated load cell. Specimen results were discarded if samples did not break within the accepted gage length of the bar. All specimens were tested at room temperature.

CALPHAD Modeling

Phase diagrams present visual representations of phase content and stability at equilibria as a function of state variables such as composition, pressure, temperature, etc. However, constructing phase diagrams for complex alloys is extremely time-consuming as well as expensive. There are many references available in terms of deep discussion of CALPHAD modeling; an overview was provided here, adopted from discussions in reference literature [122-125].

Multi-component phase-equilibria can be modeled using the CALPHAD (CALculation of PHAse Diagrams) methodology, which operates on finding states with minimized free energy. The Gibbs free energy expresses the thermodynamic/chemical potential to perform work. At any given equilibrium state, Gibbs free energy is at a minimized state in a closed system, and can be represented as a general equation for chemical phases:

$$G_{\text{system}} = min \sum_{p} G_{p} n_{p}$$

The contributions to the Gibbs energy of a phase ϕ can be written as the following:

$$G^{\phi} = G^{\phi}_{\mathrm{T}}(T, x) + G^{\phi}_{P}(\mathbf{p}, \mathbf{T}, x) + \mathrm{G}^{\phi}_{\mathrm{m}}(\mathrm{T}_{\mathrm{c}}, \beta_{0}, \mathbf{T}, x)$$

Where $G_T(T,x)$ is the partial input to energy by the temperature, T, and the composition, x, $G_p(p,T,x)$ is the contribution of the pressure, p and $G_m(T_{C_1}, \beta_{o_1}, T, x)$ is the magnetic contribution of the Curie temperature, and the average magnetic moment per atom. Temperature dependence of the Gibbs free energy is commonly expressed as a power series of T:

$$G = a + bT + cT(\ln T) + \sum d_n * T^n$$

Where a, b, c and d_n are coefficients and n is an integer. If solution phases are considered, the following equation describes Gibbs energy of formation in a binary model. This model can be extended to ternary and higher order solutions:

$$G^{\phi} = x_A G_A^0 + x_B G_B^0 + RT\{x_A \ln x_A + x_B \ln x_B\} + x_A x_B \sum_{i=0}^n G_i (x_A - x_B)^i$$

Where xA and xB represent mole fractions of each solution constituent and GA0 and GB0 are the states at standard temperature and pressure (reference state) of element A and B. The third term is the energy contribution from mixing. The final term consists of excess Gibbs energy. The sum of the terms $(x_A - x_B)^I$ refers to the Redlich-Kister polynomial used in regular solutions. As the term *i* changes, the shape of the Gibbs energy contribution from fourth polynomial also changes.

Each of these phases have lattices and many sublattice structures which influence the elemental content of unique phases. For example, face centered cubic-iron (austenite) has 14 sites (8 sites at corners and 6 sites on each face) where substitutional atoms (Ni, Si, Cu, Mn, etc.) can replace Fe. In addition, between each of the substitutional sites, a sublattice exists where atoms with a smaller atomic radius (such as C and N) can reside. An atom may or may not reside at site *vacancies*, affecting the stability of the given lattice. Therefore, when calculating the Gibbs free energy in a sublattice model, it must

be considered that multiple configurations exist at each site. (e.g. Fe(1)C(1) or Fe(1) Va(1)) If a simple binary sublattice model is considered, assuming ideal entropy of mixing on the interstitial sublattice such as that seen in Fe-C binary systems, the Gibbs energy of a mole of fcc-austenite becomes:

$$G^{\text{fcc}} = x_{Fe}^{0} x_{Va}^{1} * G_{Fe;Va}^{0-\text{fcc}} + x_{Fe}^{0} x_{C}^{1} * G_{Fe;C}^{0-\text{fcc}} + RT\{x_{C}^{1} \ln x_{C}^{1} + x_{B}^{1} \ln x_{B}^{1}\} + e^{xcess} G^{fcc}$$

To extend values into higher component systems, free energy models are often simply added together to form higher order systems. Higher component systems can become much more complex; in many cases, binary component systems are assessed and data is extrapolated and extended to ternary and higher-order equations. Experiments are then done on higher order systems to correct discrepancies seen due to the extrapolation.

FACTSage 5.5 software was used to model systems at different equilibrium conditions and Scheil solidification to compare to both experimental data and give guidelines in terms of expected, stable phases. In most cases, the custom steel database included with FACTSage was used to provide estimates of phase contents at equilibrium.

Chapter 3 -Experimental Methodology/Goals

3.1 Introduction

The goal of this research was to develop compositions and heat treatments of corrosion resistant casting alloys with high strengths and acceptable toughness. The knowledge acquired from these studies will have broad applicability for all high-strength cast steels. As demonstrated in the literature review in the previous section, very little work has been performed on the widely used CB7Cu-1 and Cb7Cu-2 casting alloys as opposed to their wrought analogues. The composition between wrought and corresponding cast systems is different, because of castability requirements for castings. Furthermore, unlike the wrought precipitation hardened stainless steels, cast steels do not have the benefits of thermomechanical processing for microstructure refinement. Because of these differences, corresponding microstructures of similarly alloyed precipitation hardened cast steels are likely to differ in from their wrought counterparts. Since the mechanical properties are directly related to the microstructural condition, both processing and composition play influential roles in terms of determining final properties. Figure 23 maps goals and microstructural design requirements that are essential to improving strength in precipitation hardening cast alloys. In many cases, there have been no published results solidly linking effects from processing parameters to mechanical properties and microstructure.

The goal in terms of properties is a strong, tough, and corrosion resistant material. The goal is to meet the specific strength of titanium, which would require ultimate strength levels to exceed 220 ksi while maintaining elongation levels of at least 5%. Two different alloys have been used in this investigation - CB7Cu, which is well-specified and heavily used in industrial practice, and an Fe-Ni-Cr-Mo-Ti (11-11PH) material, with a system widely used in wrought practice, but not specified for use in sand or investment castings. The bulk of the effort and investigation has generally been performed on the

CB7Cu alloy, and a smaller effort has been provided in terms of the 11-11PH alloy. (Figure 22)



Figure 22 - Expenditure of research efforts for corrosion resistant cast materials used in this work.

While this problem has never been addressed in cast steels in particular, it is understood that the bulk microstructure is going to be key to addressing properties regardless of geometry. From the literature study, it is suggested that there are multiple mechanisms which may or may not independently affect the mechanical properties of castings in particular. Evidence presented in the previous chapter suggests that for these three goals, the microstructure should consist of mainly martensite. Delta ferrite and austenite, which are secondary bulk phases should be controlled. Large intergranular inclusions should be avoided. Finally, in particular with castings, microsegregation and grain growth may need to be controlled through processing (heat treatment, quench treatment, and age hardening) and composition.

While there are studies on similar wrought alloys, there is no fundamental understanding of how composition variables (% alloying elements) and processing relate to the microstructure. For example, there is an understanding that high-temperature holds favor the stability of austenite over delta ferrite. However, there is no quantitative or predictive model relating temperature and time to reduction in delta ferrite content.



Figure 23 - A Guideline to achieving high strength in precipitation hardening alloys

A large portion of the work in the current investigation is experimental in nature, as relationships in the cast material have not been established or studied previously. Though influence of time, temperature (energy input) on microstructure should be definable using general physical relationships, multicomponent solutions are very complex. Therefore, initial relationships in terms of processing variables (time/temperature, energy input/outputs) have been established, and fit to the best of current levels of physical understanding in similar systems.

Heat treatments for castings are often different than that in wrought materials in duration, time, and purpose. There are three stages of heat treatment that are used to control microstructure, independent of composition. The studies attempt to examine the role of each of these treatments, while remaining aware of the possibility of dependence between each of the treatments (e.g. the possibility of high temperature treatment having an effect

on the age-hardening behavior.) Many of the experiments were explicitly designed to separate effects and determine the role of each of the treatments on microstructure.

Computational tools were also used to look at general energy balances and stability of phases at equilibrium across alloy compositions. However, computational tools are often limited in terms of predicting microstructure in materials subjected to repeated heating and cooling cycles at conditions far from equilibrium conditions. Therefore, computational tools were used as 'predictive' tools and combined with experimental work to determine relationships between phase content and composition.

In terms of practical knowledge, these studies better characterize the behavior of the cast precipitation hardened stainless steels using current processing and composition guidelines, as they are often included as a baseline measurement scenario. Once relationships are established, further development of improved heat treatment and composition is used to promote the best combination of mechanical properties and castability. As stated previously, current CB7Cu-1 and 2 materials as specified may be incapable of reaching high strength at a level of acceptable ductility. However, using the copper based strengthening system, together with other systems, may be a viable choice for providing the highest strength levels in tough, corrosion resistant cast alloys.

In any case, there is a limit to the strength achievable by CB7Cu based alloys dictated by both theoretical limits as well as practical means. Therefore, a portion of the effort in this work is dedicated to examining the behavior of adapted high strength wrought systems in castings. In the past, these advanced alloy systems have remained virtually unused by the metalcasting industry because of perceived difficulties in processing. However, with the availability of specialized melt and thermal processing techniques, alloys with these precipitation systems may provide an opportunity to develop lower-cost high-strength corrosion resistant materials. These candidate high strength alloy systems must also have adequate castability and toughness.

Information from the CB7Cu system is essential in producing high strength alternative PH-system cast steel. While CB7Cu systems are chemically distinct from these high strength nickel-based precipitation systems, they are microstructurally similar, and

therefore principles from the study on CB7Cu can be applied in many cases to the nickelbased precipitation systems. Therefore, the knowledge in terms of heat treatment, composition, and processing will be used as a predictive basis to limit the experimental space in such that the best material (high strength, good toughness) will be produced. Again, computational tools are used in a predictive manner to provide basic composition guidelines.

3.2 Organization of Experiments, Modeling, and Discussion

Two different cast alloy systems were examined in this investigation; these include the CB7Cu alloy (Cu precipitation system) followed by 11-11PH (Ni₃Ti precipitation system). In terms of the CB7Cu alloy, chapter 4 primarily details <u>composition</u> studies, and Chapter 5 details <u>processing</u> control studies. Chapter 6 details work performed on the 11-11PH alloy.

Chapter 4 – Composition Control and Modeling

Composition control is logically the first factor to be adjusted in CB7Cu alloys. Before processing is applied, the composition of alloys can be adjusted to influence the as-cast microstructure to dictate processing goals. The goal of this chapter was to establish the relationship between composition and phase content in CB7Cu alloys. Work performed to understand this goal includes:

- A critical experimental study of how well current constitution diagrams for stainless steels predict phase contents and trends, in terms of materials with different nickel and chromium equivalents, as well as different casting processes. In addition, determination of retained austenite content and possible effects of increased nickel/chromium equivalents in the overaged condition was examined using X-ray diffraction.
- A general design of experiments was performed to model phase stability at equalibria for the range of compositions covered by existing CB7Cu alloy specifications. By analyzing the relative stability through CALPHAD-based

modeling in FACTSage, an estimate of the effects of alloying elements and possible child phases on austenite and ferrite can be determined to a better degree than that of the Schaeffler diagram.

Chapter 5 – Process Control and Modeling

Processing represents another independent way that we can influence microstructure in the processing of CB7Cu alloys. While certain cast compositions influence the as-cast microstructure, it is the processing which dictates the ultimate influence on the final microstructure. The goal of this chapter was to investigate and characterize relationships between processing parameters and microstructure and/or mechanical properties in CB7Cu alloys after heat treatments. Investigations include:

- Differential Thermal Analysis to determine phase transformation temperatures in CB7Cu, particularly the martensite start temperature, to give a measure of austenite stability.
- Dissolution experiments to determine the effects of solutionizing/homogenizating time and temperature on delta ferrite. This includes the determination of the relationship between processing variables and the dissolution of delta ferrite at high temperatures common of the solutionizing/homogenizing cast treatments.
- The effects of quenching temperature and proceeding cryotreatment were determined in terms of hardness and tensile properties to determine possible property improvements.
- In terms of aging, multistage aging was applied as a way to get high peak-aged strength while preserving ductility. Mechanical testing was performed on these materials to determine the effects of different age hardening combinations on properties.
- CB7Cu precipitation reactions were successfully modeled using a modified Shercliff-Ashby age hardening model that was originally intended for Al-Cu alloys. Corresponding tempering effects were also taken into effect using hybrid models.

Chapter 6 – Development of a Prototype 11-11PH alloy

Because CB7Cu alloys are limited in terms of the strength of the copper precipitate, investigation into a stronger precipitate system was performed. Investigations include:

- Initial microstructure and mechanical property studies of solution treated, cast and cryoquenched processed alloys to determine basis relationships between processing and microstructure. General microstructural studies of the as-cast, quenched and aged microstructure of this material were carried out. Investigations were generally focused on developing high strength using low aging temperature.
- Investigation of the nature of secondary phases in this material through by X-ray diffractometry, OIM/EBSD analysis, and SEM microscopy and analysis. In particular, the retained austenite morphology and content were analyzed along with study of the titanium rich inclusions that are formed in the melt and solidification temperatures.
- Improved heat-treatment (HIP) and variation of cooling treatments on 11-11PH mechancal properties were also studied.

3.3 Description of Materials used in this study:

The corrosion resistant materials used in the studies included CB7Cu-1 sand castings from Andritz-Durametal in Muncy, PA. Investment castings were provided by Hitchiner Manufacturing of Milford, NH. One 300 lb investment cast heat of material was cast into 0.5 in. diameter, 3.0 in. long sub-sized tensile specimen blanks and as well as 0.6" x 0.6" cross-section Charpy blanks. For the sand cast material, a 1000 lb heat was poured into standard ASTM A370 keel block molds to guarantee complete filling and limit solidification shrinkage. Thin specimens were provided in the form of 0.5" x 1.5" thick, flat rectangular bars. The investment cast CB7Cu-1 material was melted under an inert gas blanket, while the sand cast material was poured under standard atmospheric conditions. All heats of material were deoxidized with Al + Ti using

standard practices. The compositions of the heats of CB7Cu are given in Table 10. Although aim compositions were chosen to minimize as-cast ferrite formation, the actual compositions provided resulted in Cr-equivalent and Ni-equivalent combinations expected to contain some as-cast ferrite.

Composition (wt. %)											
Material	Cr	Ni	Mn	С	Si	Cu	Ν	Nb+Ta	Р	S	Fe
CB7Cu-1 ASTM A747 (Specification Limit)	15.5- 17.7	3.6-4.6	0.7 max	0.07 max	1.0 max	2.5-3.2	0.05 max	0.15- 0.35	0.04 max	0.03 max	Bal
Inv Cast (IC)	15.73	4.18	0.56	0.055	0.73	3.00	0.02	0.23	0.005	0.006	Bal
Sand Cast (SC)	15.97	3.89	0.50	0.035	0.8	2.97	0.02	0.19	0.019	0.006	Bal
CB7Cu High C (SC)	15.36	3.78	0.51	0.11	1.48	3.18	0.026	0.04	0.023	0.005	Bal

Table 10 - Composition of test materials compared to CB7Cu-1 specified composition limits

Table 11 - Composition of test materials for 11Cr-11Ni alloys

Composition (wt. %)													
Material	Cr	Ni	Mn	С	Si	Cu	N	Nb+ Ta	Р	S	Ti	Al	Мо
11-11PH (Heat 1)	11.33	11.13	0.05	0.01	0.13	0.01	0.007	0.1213	0.005	0.003	1.52	0.09	1.13
11-11PH (Heat 2)	11.20	10.95	0.1			0.08					1.2		1.19

11-11PH alloys were cast in the form of standard ASTM investment casting blanks at Hitchiner Manufacturing in Milford, NH. Two 300lb heats were produced as the first heat contained large amounts of entrained titanium oxide dross, due to the reaction of ferrotitanium with surface atmosphere. In the case of the second heat, titanium was added in bar form to avoid excessive dross formation.

All alloys were provided in the as-cast condition and heat treated in the Penn State laboratory furnace to insure strict control of heat treatment time and temperature. High temperature treatments were performed under an argon flow $(4L^2 / hr)$ to reduce oxidation on the surface of the material during high temperature treatments.

Chapter 4 -Composition Control and Modeling in CB7Cu Alloys

4.1 Introduction

CB7Cu materials generally have an as-cast microstructure of lath martensite with vermicular delta ferrite. Delta ferrite is the first phase to form in CB7Cu as the material solidifies. The delta ferrite in CB7Cu generally forms with random orientation in castings and persists in the solidified alloy as remnants between austenite grains. These areas are rich in chromium content and are not driven to react and form austenite because of added ferrite stability due to composition differences. As cooling continues, the general disorder along these grain boundaries creates favorable nucleation and growth sites for carbides, such as $M_{23}C_6$ carbides. These carbides are stable at levels above 10% Cr and grow more rapidly into the chromium-rich delta ferrite as opposed to the austenite.

Strategic composition limits are important for microstructural control in precipitation hardening alloys. It is well known that elements often have synergistic effects in terms of phases and precipitation reactions. Most PH alloys, including CB7Cu and 17-4PH, contain chemistries that favor contributions of both dispersion hardening and precipitation hardening characteristics. In particular, the combination of elements in 17-4PH and CB7Cu control both the stability and amount of both the austenite and ferrite phases. Weldment based constitution diagrams (such as the Schaeffler Diagram) described in the literature review were developed for austenitic-ferritic alloys, rather than for the martensitic alloys or the martensitic precipitation hardening alloyed steels. There are many underlying assumptions that may possibly lead to problems when using the constitution diagrams for prediction in precipitation hardening steels. Of particular concern is chemistry ranges - most of the PH steel chemistries tend to fall out of the range or just inside the allowable chemistry ranges used to develop current predictive constitution diagrams. The original Schaeffler diagram was only developed for use with 304 stainless steel weldments. [70] Even the extended and modified constitution

diagrams were developed for use with exclusively for ferritic-austenitic steels, particularly with higher austenite-ferrite contents.[72], [74], [126]There are no constitutive diagrams developed for the use with martensitic alloys. Thus, the use of these diagrams for CB7Cu is an extrapolation. Welding researchers are currently working on merely portraying a line on empirical studies to establish an accurate "martensitic" line for constitution diagrams. [74]

In order to develop improved compositions of the Cu-PH cast systems, composition modeling and experimental verification are both important in terms of finding the best possible composition to limit secondary detrimental phases. From the literature review and predictive phase diagrams, the following is known about acceptable compositions:

- While nickel and other elements promote toughness in high chromium alloys, nickel and nickel equivalent elements need to be limited so that austenite is not stabilized to the point where the transformation of austenite to martensite becomes difficult during conventional heat treatment practice.
- Chromium is important for corrosion resistance, but other than molybdenum, very few of the other "chromium equivalent" elements promote corrosion resistance. In the CB7Cu alloys, chromium levels are very close to that of the minimal limits to promote a continuous chromium oxide passivation layer. Further reduction of chromium without molybdenum additions is expected to be detrimental to corrosion resistance. Silicon is an element that is important for castability, but also adds to ferrite stabilization. Excessive additions of chromium equivalent elements lead to excessively stable delta ferrite, which in turn, reduces strength and toughness. However, a small amount of as-cast delta ferrite is desirable as it prevents hot-tearing in the casting. The delta ferrite must be controlled in such that the remnant delta ferrite can be dissolved during subsequent heat treatment.
- Reduced amounts of both Cr and Ni equivalent alloying elements promote a fully martensitic microstructure according to Schaeffler. A fully martensitic microstructure provides maximum base matrix strength as opposed to mixed

microstructures. However, the major strengthening element in CB7Cu is copper, which also acts as a mild austenite stabilizer. In addition, there is generally always residual carbon in this steel, which behaves as potent stabilizer of austenite. It is important to note that rapid cooling to a temperature below the Ms generally eliminates the possibility of significant amounts of retained austenite, particularly in alloys such as CB7Cu.

• The measurement of retained austenite vs. "stable austenite" as predicted by the modified Schaeffler diagram is suspect at best. It is important to realize that in austenite-ferritic series steels, the martensite start temperatures are far below room temperature and austenite-stable alloys are possible at roomtemperature. In the case of PH-cast steels, significant amounts of retained austenite are unlikely to form in the composition range due to the transformation of austenite to martensite.

In terms of the alloy combination used in the study, composition limits were established using the modified Schaeffler equivalents to minimize delta ferrite. Because there is some uncertainty in terms of composition measurements, it is important to strive for the upper left-hand quadrant with a high nickel equivalent and lowered chromium equivalent. While the nickel and chromium equivalents of the alloys evaluated in this study did not fall in the targeted range (Figure 24), the amounts of predicted ferrite and actual ferrite were vastly different, even in the as cast specimens than are predicted for a Modified Schaeffler diagram.



Figure 24 - Projection of composition limits and cast PH experimental steels on Modified Schaeffler Diagram

4.2 Accuracy of Schaeffler Diagram in Predicting Delta Ferrite

Samples of both the investment cast and sand-cast CB7Cu material were heat treated according to Table 12. Samples were given treatments which followed the minimum high temperature treatment guidelines as required by ASTM A747. The later trial samples used to develop a best-practices material (denoted with a "+") were given a homogenization, a solution treatment, and then were water quenched and put in liquid nitrogen cryotreatment for 8 hours. Materials were then slowly brought up to room temperature. Both materials were age-hardened for 1 hour.

	Standard Practice	+ Practice
HIP	Not performed	2125°F / 4 hr
Homogenization	Not performed	1920°F / 1.5 hr
Solution Annealing	1925°F / 30 min	1925°F/0.5 hr
Quenching	Water Quench at 55°F	Water Quench at 55°F, then -320°F for 8 hr
Age Hardening	900°F, 1 hr.	900°F, 1 hr.

Table 12 - Standard and (+) Practice Heat Treatments, Screening Test Material

4.2.1 Results from Delta Ferrite Mitigation Investigation

A Schaeffler diagram evaluation suggests that the delta ferrite range should be between 20 and 40% delta ferrite for the as-cast samples. However, the actual amount of delta ferrite was between 13-16% in both the sand cast and investment cast alloys based on the point-count estimates. Therefore, it would seem that the Modified Schaeffler diagram appears to overpredict the amount of delta ferrite in the CB7Cu alloys. For the as-cast samples, the thin specimens had more delta ferrite on average, but the difference in ferrite content from the section size (cooling rate) between the two specimens was too small to be significant. Sand cast material, whether provided in 1" or 0.5" thick specimens, contained the most delta ferrite. When heat treated with the best practices (+) methods, all specimens showed a significant reduction in the amount of remaining delta ferrite. The investment cast CB7Cu-1 material had less delta ferrite in the processed conditions; there was very little to no delta ferrite detectable on the corresponding micrographs. This is likely due to the contents of more austenite stabilizing elements, along with the reduction in ferrite stabilizing elements. In addition, the thin investment cast specimens are in initial cast shapes that have fast cooling rates, which results in less time for ferrite element partitioning. This is consistent with prediction and theory which suggests that increasingly slow cooling rates and an insulating mold can be expected to increase the amount of stabilized delta ferrite upon cooling.

Specimen Samples	NI _{eq}	Cr _{eq}	Actual %δF (n=36)	Predicted %δF
Fe-Ni-Cr-Mo-Ti	11.7	18.1	NONE	NONE (A+M)
As Cast 0.5" Sand Cast CB7Cu-1			$15.7 \pm 1.5\%$	
As Cast 1" Sand Cast CB7Cu-1			$13.1 \pm 1.46\%$	
0.5'' (SP) Sand Cast CB7Cu-1	6.00		$8.75\pm1.87\%$	20.400
1" (SP) Sand Cast CB7Cu-1	6.08	18.17	$9.20\pm2.18\%$	30-40%
0.5" (+)			$0.68\pm0.76\%$	
Sand Cast CB7Cu-1 1" (+) Sand Cast CB7Cu-1			$2.80 \pm 1.32\%$	
IC (SP) Investment Cast	7.46	17.85	$3.77\pm2.29\%$	10-20%
IC (+) Investment Cast			$0.21 \pm 0.34\%$	

 Table 13 - Delta Ferrite, Actual and Predicted Percentages. Nickel and chromium equivalents are calculated from the modifed Schaeffler constitution diagram.

The amount of delta ferrite quantified in the micrographs is far less than predicted by the modified Schaeffler diagram. In addition, even at the same composition, delta ferrite content is influenced by the particular heat treatment performed. Similar results have been reported in terms of 17-4PH wrought material. [82]

4.2.2 Morphology of Delta Ferrite in CB7Cu

In addition, while a reduction of delta ferrite is observed in both (+) and standard practice material after heat treatment, the delta ferrite in the (+) practice material was reduced in terms of area content, and developed an insular morphology as compared to the elongated pools of the in the as-cast material. Material treated according to ASTM A747 also had the same, long morphology seen in the as-cast material, though the fraction was reduced. (Figure 25, Figure 26) The insular fields likely represent intersections of thick stringers and the last of the delta ferrite to form upon solidification. Unlike the material treated through standard practice processing, delta ferrite was less likely to be distributed in

along subpacket boundaries; rather, the remaining delta ferrite pools were concentrated in interdendritic regions of alloys.



Figure 25 – SP δ-ferrite Morphology

Figure 26 – (+)δ-Ferrite Morphology

4.3 Austenite Stability and Chemistry in the H1150 Condition

The majority of the investigation was performed on materials in the peak-aged (H900) condition. However, because CB7Cu is an age-hardening alloy, it can be treated to a number of conditions which sacrifice strength for increased toughness. In the overaged condition, temperatures can approach and exceed the point where martensite retransforms to austenite. At these temperatures, composition may play a greater role in terms of phase composition and the related mechanical properties.

In general, no retained austenite is detected at the H900 condition even with air cooling of specimens (see later studies). However, the composition may have an effect on materials that are treated in the extreme overaged condition. In order to test this, two CB7Cu-1 samples from a centrifugal cast foundry were tested with differences in the Ni/Cr equivalent chemistries. Material was supplied in small, broken-charpy samples. One version of the alloy had a Schaeffler equivalent Ni_{eq}/Cr_{eq} ratio of 0.30, providing a more ferrite stable alloy, while the other alloy had a Ni_{eq}/Cr_{eq} 0.48, which was a more austenite stable alloy. Both sections of alloy were solution treated at 1050°C for 1 hour, air cooled, and then age-hardened to the H1150 condition (1150°F). While nickel/chromium equivalents have little effect on material aged in the 900°F range, an investigation was carried out in terms of determining how much austenite stability was

induced in terms of both nickel stable and chromium stable elements. Materials were then subjected to X-ray diffractometry to determine the fraction of austenite stable in the alloy. In addition, notched impact values and Rockwell hardness were recorded.



Figure 27 - Chromium and Nickel Equivalent of CB7Cu alloys tested in this alloy.

4.3.1 Impact / XRD Results & Discussion

XRD results for the two alloys revealed the expected five strong, standard peaks for the martensite/ferrite for each of the alloys. The alloy with the higher nickel equivalent /chromium equivalent ratio showed additional peaks corresponding to that of retained austenite. XRD measurements determined that the alloy with the higher nickel equivalent and corresponding lower chromium equivalent had approximately 15% austenite in the structure. The other alloy, with the lower nickel equivalent/chromium equivalent ratio, had no measurable/detectable retained austenite in the alloy. Hardness for the alloy was also increased, but only by a relatively slight amount. At the same time,

notch impact toughness was only a fifth of that of the alloy with the large fraction of retained austenite.

Condition/ CVN (RT)	HR _C	Quench	Ni(Eq)	Cr(Eq)	Area under Austenite Peak (Intensity)	Area under Martensite Peak (Intensity)	% Estimated Austenite
CB7Cu, H1150F - 8ft-lb	30.5	Air Cool	5.7	19.2	1155	3011	Not Detectable
CB7Cu, H1150F - 47ft- lb	27	Air Cool	8.0	16.7	802	3987	%15.1

Table 14 - XRD Results of H1150 Condition

The high nickel equivalent alloy with the greater amount of retained austenite showed a distinct increase in impact toughness with little loss in strength. The larger amounts of *reverted* austenite in the nickel-stable alloy are consistent with what is expected of an alloy with a higher nickel equivalent. It can be expected that the alloy with the higher nickel equivalent contains less stable delta ferrite. Because ferrite also reduces toughness along with strength to a lesser degree than austenite, increased fractions of retained delta ferrite also negatively impact strength while greatly impacting toughness.

This small portion of the study focuses on the H1150 aged condition, which is the "lowstrength" heat treatment regime of this material. Material treated in the H1150 condition is expected to reached strengths on the order of 120 ksi (~900MPa), which is far below the aims of this material. However, this finding is significant due to the fact that while the observation of *retained* austenite may be less likely because of processing in the peak-aged condition, the composition can have a larger effect in terms of toughness on overaged samples, due to *reverted* austenite stability. Because this study mainly focuses on the high-strength regime of this alloy, and this experiment specifically examined the "low-strength" regime, further research is likely necessary in terms of examining CB7Cu in the overaged condition.







Figure 29 - XRD of CB7Cu-1 treated at H1150 - Ni_{eq}/Cr_{eq} ratio of 0.48

4.4 CALPHAD modeling for predicting stability of Delta Ferrite/Carbide in CB7Cu-1

In CB7Cu materials, the chemistry is such that upon cooling, transformation to the solid state, body centered cubic ferrite (δ -ferrite) forms initially. Upon further cooling in the solid state, the bcc structure of delta ferrite transforms to the face-centered cubic austenite. Along with these major phase constituents, small amounts of intermetallic phases such as M₂₃C₆ carbide, MC carbides, MN nitrides and MCN carbonitrides may precipitate from the matrix. Growth of these intermetallic phases is favored during slow cooling and long holds at favorable temperatures. These carbides, particularly M₂₃C₆ carbides, are detrimental to toughness in CB7Cu-1 and related alloys. Upon further cooling from the austenite field, austenite undergoes transformation to martensite. Because of the very low carbon content of the martensite phase, the tetragonality is slight enough that it resembles the bcc phase. The phase contents, as previously described, can have dramatic effects on the mechanical and corrosion properties of the alloy content.

Thermodynamic equilibrium calculations were performed with the software FACTSage 5.5 using the FStel custom database with parameters for steels in particular. Some caveats for interpreting results from FACTSage include the following:

- In castings, phase equilibrium is not fully achieved, particularly at lower temperatures. This is particularly true at lower temperatures where diffusion of substitutional elements is orders of magnitude slower than that in higher temperature situations.
- Temperature gradients within the material are not taken into account. Metal closest to the mold-interface is expected to solidify faster than that of the center of a casting. The same holds true upon cooling from high heat temperature treatments.
- The segregation of alloying elements during initial solidification is not considered in this analysis. In true solidification, alloy-rich intercelluar regions can be

expected to undergo different reactions and yield different distributions of phases as compared to alloy poor interdendritic regions.

• Results are dependent upon the data quality of the thermodynamic database, and with multicomponent systems, data must be extrapolated from established experimental data from simpler systems. The number of constituent subsystems of an n-component system is determined by the binomal function *C*(*n*,*k*) representing the number of combinations of k that can be chosen from the pool n. Hence a 10 component system can have 45 binary phase diagrams, 120 ternary diagrams, and 210 quaternary diagrams. In FACTSage and other thermodynamic programs, phase outputs can be "constrained" by excluding phase products that are known not to exist through experimental evidence as well as discounting higher-order alloy interactions.

Despite these limitations in determining phase equilibria and phase percentages, FACTSage can give a relative measure of the effects of composition on high-temperature phases. Running validation experiment studies are possible; but are also extremely expensive, require difficult setup, and can be inconclusive because of interference due to experimental limitations. Experimental results for phase stability in martensitic PH stainless steels are limited at best. Useful information on the role of nitride and carbide stabilizers and the feasibility of reactions and transformations in these multicomponent systems can lead to an understanding of how chemistry influences phase stability for expected chemistry variation in commercial CB7Cu alloys. However, calculating a single thermodynamic profile tells little information of the effect of changing chemistries, and testing all possible chemistries would require excessive amounts of time. The most efficient way of determining relationships with large amounts of factors involves using design of experiments (DOE) techniques.

4.4.1 Experimental Design and Model Inputs

In this study, the goal was to estimate the effect of composition on relative phase stability for CB7Cu alloys the austenite/ferrite high temperature field temperature ranges. In general, the more stable delta ferrite predicted to be in the austenite field, the more residual delta ferrite will be expected in the product after cooling, and the more difficult it will be to dissolve with high temperature dissolution treatments, such as solution treatment/homogenization. In order to compare chemistry variation and responses, a two-level half factorial experiment and data analysis is carried out using MINITAB software along with the results obtained from FACTSage software calculations. The use of a fractional factorial design is performed to reduce the number of runs from 32 to 16, since computational time is limited. A half-factorial design is appropriate because although second level interactions may be significant, three-factor and higher-order interactions are not typically significant.

The factors investigated include the elements Cr, Ni, C, Nb, and Cu. Cr, Ni, Nb, and Cu are elements which are assigned non-zero two-sided ranges. Carbon only has a specified maximum range in ASTM A747, however it is not possible to completely eliminate carbon in production melts. It is reasonable to assume a production range of carbon in CB7Cu between approximately 0.01 and 0.07 weight percent. Elements such as Mn, Si, and N are held constant in this analysis due to the fact that Mn and Si do not affect carbide stability. However, Mn and Si do effect austenite stability, but because of they are minor alloying elements (<1% by weight), variations were not considered. Nitrogen is an austenite stabilizer and nitride former, but is generally kept to minimum levels and picked up through atmospheric interactions rather than intentionally added.

Two-level factors input values for (for 100g CB7Cu-1)									
Run #	Cr	Ni	С	Cu	Nb	Ni(eq)	Cr(eq)		
1	-	-	+	-	-	7.2	17.2625		
2	-	-	-	+	-	5.61	17.2625		
3	+	-	-	+	+	5.61	19.8125		
4	-	-	-	-	+	5.4	17.6125		
5	+	-	+	+	-	7.41	19.4625		
6	-	+	-	+	+	6.61	17.6125		
7	+	+	+	-	-	8.2	19.4625		
8	-	+	+	+	-	8.41	17.2625		
9	+	-	+	-	+	7.2	19.8125		
10	-	+	+	-	+	8.2	17.6125		
11	-	+	-	-	-	6.4	17.2625		
12	+	+	-	-	+	6.4	19.8125		
13	-	-	+	+	+	7.41	17.6125		
14	+	-	-	-	-	5.4	19.4625		
15	+	+	-	+	-	6.61	19.4625		
16	+	+	+	+	+	8.41	19.8125		

Table 15 - Two-level half factorial design for CB7Cu alloy

* "+" and "-" refer to the high level and low level respectively.

The minima and maxima levels of Cr, Ni, Nb, Cu, and C are based on ASTM A747 composition limit guidelines for each of the alloying elements. These "+" and "-" values cover the extreme ranges of each of the elements that are to be added according to specification. Because CB7Cu is a martensitic alloy that is solution treated at temperatures above 1000°C and then quenched, only phases that exist in this "neighborhood" of temperatures should be considered for analysis. Therefore, phase contents at equilibrium are calculated for each set of conditions at temperatures from 750-1550°C at 25°C steps at 1 standard atm of pressure. It could be argued that chemistry and phase calculations should be continued below 750°C, however, alloy diffusion kinetics are highly limiting at temperatures below 700°C, severely slowing formation of equalibria phases from the parent higher temperature phases. In addition, experimental data for phases at low temperatures is relatively scarce, and CALPHAD models generally attempt to extrapolate phase data at low temperatures, which leads to questionable validity.

Phases that have not been experimentally found to exist at these temperature ranges were excluded from the analysis to reduce error and constrain the model. These included phases such as graphite, M_2C and M_6C carbides, cementite, sigma and Laves phases, which have not been found at these compositions and/or temperature ranges. Phases that were included were iron-alloy-liquid, austenite, ferrite, iron-copper, $M_{23}C_6$ carbide and NbC carbide.

Element	%wt. Input	Type of Input
Cr	15.5-17.7	Two-factor
Ni	3.6-4.6	Two-factor
С	0.01-0.07	Two-factor
Nb	0.15-0.35	Two-factor
Cu	2.5-3.2	Two-factor
Mn	0.5	Fixed-input
Si	0.75	Fixed-input
Р	0.012	Fixed-input
S	0.006	Fixed-input
Ν	0.002	Fixed-input
Fe	bal	Variable-input

 Table 16 - Factor inputs for DOE

4.4.2 Composition Modeling Results

FACTSAGE outputs are expressed as grams of phase products from reactants, though other outputs from the reactions are also possible (mols, g, etc.). The output data also provides the general activity of a phase at a given temperature along with minor, expected reaction products. However, simply comparing phase fractions at one temperature does not give a good estimate of phase stability. For example, at high temperatures (1400°C), delta ferrite may be the only stable phase, despite chemistry variations. At lower temperatures, only small amounts of the marginally stable ferrite will be present. Instead, a stability index can be created by taking stability over a whole range of temperatures from solidification to austentization temperature ranges. A stability index is calculated by taking the area of mass (grams) under the curve at 25°C steps (33 total steps) for each phase. For each equivalent, a normalized "stability" number is then created for each phase. Because the liquid phase coexists at some of the

temperatures, it has been included in the analysis in terms of understanding the effects of alloying on liquid stability and melting point. The normalized stability values for each of the runs has been calculated and shown in Table 17.

Run	Ni Eq	Cr Eq	NbC	FeCu	M ₂₃ C ₆	Austenite	Ferrite	Liquid
1	7.2	17.2625	0.066	0.09	0.13	74.54	7.47	17.67
2	5.61	17.2625	0.014	0.23	0.00	71.65	10.58	17.47
3	5.61	19.8125	0.026	0.28	0.00	58.19	22.62	18.81
4	5.4	17.6125	0.026	0.10	0.00	69.87	12.82	17.12
5	7.41	19.4625	0.065	0.27	0.15	65.97	13.98	19.54
6	6.61	17.6125	0.027	0.21	0.00	75.85	5.27	18.57
7	8.2	19.4625	0.065	0.10	0.16	71.50	8.75	19.40
8	8.41	17.2625	0.066	0.20	0.14	78.04	2.47	19.04
9	7.2	19.8125	0.200	0.12	0.05	62.85	17.63	19.10
10	8.2	17.6125	0.192	0.08	0.05	77.44	3.43	18.77
11	6.4	17.2625	0.015	0.08	0.00	76.40	6.15	17.29
12	6.4	19.8125	0.026	0.10	0.00	66.71	14.40	18.70
13	7.41	17.6125	0.189	0.23	0.04	73.70	6.76	19.04
14	5.4	19.4625	0.014	0.13	0.00	58.66	23.87	17.27
15	6.61	19.4625	0.015	0.24	0.00	68.63	11.90	19.17
16	8.41	19.8125	0.197	0.24	0.06	70.01	7.87	21.10
Highest Value (Run)			9	3	7	8	14	16
Lowest Value (Run)			2	10,11	2-4, 6,11- 12, 13-14	3	8	4

Table 17 - FACTSage Normalized Stabilities

Three dimensional stability surface graphs were constructed to represent how well chromium and nickel equivalent values from the widely used Schaeffler constitution diagram predicted general stability of elements. As per the Schaeffler equivalents, it is expected that nickel and chromium equivalents will show a "linear" stability relationship. The compositions chosen in this analysis were "extremes" in terms of acceptable composition; therefore most of the data used to develop the stability surface graph was clustered in the nickel and chromium maximums and minimums.

A complete list of the phase stability results in terms of coefficients and effects are included in Appendix A of this study. Interaction and main effects plots (Figure 30-

Figure 35) were calculated for each of the element factors and response variables, showing the magnitude of effects for each of the elements in terms of interactions and main effects. Because simulations do not have multiple runs or variations between runs, the significance of effects is estimated in terms of Lenth's PSE. The analysis of the data consists of assessing the following:

- The "main effects" where a factor is a main effect for a response when different levels cause a significantly different response based on levels.
- The "interaction effects" where the effect of one factor is dependent on the effect of another factor. Because interactions can effect and even cancel out main effects, it is important to consider them in the analysis.

Discussion of Results

Careful assessment reveals that many of the elements in the analysis have significant effects on phase composition. The following major trends can be observed from results in Table 18:

- Austenite stability is negatively influenced by chromium. Austenite stability is also significantly positively affected by nickel and carbon. The interaction between chromium and nickel reduces austenite stability somewhat because chromium has the ability to be a weak austenite stabilizer. The effect of carbon is somewhat muted by the fact that some of the carbon the CB7Cu is tied up in the form of $M_{23}C_6$ and NbC carbide. Therefore, carbon does not have as strong of an effect on austenite stability as per Schaeffler analysis indicated.
- Ferrite stability is negatively affected by nickel, carbon and copper. It is only weakly destabilized by copper, while being strongly influenced by chromium, which is known to be potent ferrite matrix stabilizer. The effects of nickel and chromium were not equal in opposition; chromium was slightly more effective in terms of stabilizing ferrite than nickel was in destabilizing ferrite.
- All alloying elements increased stability of the liquid phase. This means that the metal remained liquid at lower temperatures as more alloying content was added.
- As expected, M₂₃C₆ carbide stability was strongly affected by carbon as compared to chromium. This is true because at levels of 15.5% of chromium, the amount of chromium is such that the reaction is thermodynamically favorable enough to form the carbide in the presence of any free carbon. Niobium, because of niobium carbide formation tendencies, negatively affected the formation of M₂₃C₆ carbide; this is why it is often effective at reducing M₂₃C₆ carbide formation in slow-cooling thick sections of cast material.

Response	Factor	Magnitude of Effect	Average Stability Index Value(all runs)
Austenite Stability	Cr	-9.37	70.00
	Ni	6.14	
	С	3.51	
	Cr*Ni	1.65	
Ferrite Stability	Cr	8.23	11.00
·	Ni	-6.94	
	Cr*Ni	-1.86	
	С	-4.91	
	Cu	-0.82	
Liquid Stability	Cr	1.01	18.62
- ·	Ni	0.75	
	С	1.16	
	Nb	0.54	
	Cu	0.93	
	Cr*Ni	0.16	
	Cr*C	0.14	
M ₂₃ C ₆ Stability	Cr	0.007	0.046
	С	0.097	
	Nb	-0.047	
	Nb*C	-0.047	
	Cr*C	0.008	
NbC Stability	Nb	0.07	0.075
	С	0.11	
	Nb*C	0.06	

Table 18 - Main effects and interaction sizes (for significant responses)





Figure 30 – Normal Plot of Effects, Response is Austenite Stability

Figure 31 – Normal Plot of Effects, Response is Liquid Stability



Figure 32 - Normal Plot of Effects, Response is Delta Ferrite Stability

Figure 33 - Normal Plot of Effects, Response is M23C6 Carbide Stability

The effect of interactions in terms of alloy stability is subtle. The interaction plots between Cr and Ni show a clear interaction. At higher levels of chromium, nickel is more potent at reducing the amount of stable ferrite. (Figure 32) At higher levels of chromium, nickel is also more potent at increasing the amount of austenite, though not to the same extent as the previous example. This confirms the fact that chromium behaves as both a ferrite stabilizer and as a weak austenite stabilizer. Niobium is a strong influence in terms of preventing detrimental $M_{23}C_6$ precipitation. There is also a weak interaction between Nb and C in terms of preventing $M_{23}C_6$ precipitation.





Figure 34 - Interaction Plots for Delta Ferrite Stability

Figure 35 - Interaction Plot for Austenite Stability



Figure 36 - Surface graph of Austenite Stability vs. Nickel and Chromium Equivalents in Runs. Most of the data is clustered around extremes due to the design of the experiment.

When plotting nickel equivalent and chromium equivalent on a surface graph, it becomes apparent that nickel and chromium equivalent additions have interactions that are not linear and independent as portrayed in many constitution diagrams. For example, adding carbon to an alloy with high levels of Nb (a ferrite stabilizer) may not further stabilize austenite simply because of the fact that carbon can readily form NbC, and is removed from the matrix so that it no longer behaves as potently as an austenite stabilizer. At the same time, adding chromium in the presence of excessive carbon leads to formation of $M_{23}C_6$ carbide, which somewhat reduces the effectiveness of chromium stabilizing the austenitic matrix. This "saddle shaped" curve further indicates that although the Schaeffler diagram provides good general guidance in terms of alloying effect, it may ignore the effects of important interactions.



Figure 37 - Surface graph of Ferrite Stability vs. Nickel and Chromium Equivalents in Runs.

In a sense, this analysis has provided a measure of average stability across the 750-1550°C temperature ranges for equilibrium conditions. While the predicted amount of delta ferrite represented in this alloy may not strictly represent the actual amount of delta ferrite for the alloy, it is likely that the predictions could be scaled to the real amounts of delta ferrite found in the alloy.

Run	Ni Eq	Cr Eq	Austenite (Area %)	Ferrite (Area %)	Schaeffler Predicted Ferrite (%)
1	7.2	17.2625	74.54	7.47	15
2	5.61	17.2625	71.65	10.58	35
3	5.61	19.8125	58.19	22.62	70
4	5.4	17.6125	69.87	12.82	40
5	7.41	19.4625	65.97	13.98	25
6	6.61	17.6125	75.85	5.27	20
7	8.2	19.4625	71.50	8.75	19
8	8.41	17.2625	78.04	2.47	8
9	7.2	19.8125	62.85	17.63	40

Table 19 - Schaeffler Prediction versus Ferrite Stability Calculations from FACTSAGE FStel

10	8.2	17.6125	77.44	3.43	10	
11	6.4	17.2625	76.40	6.15	20	
12	6.4	19.8125	66.71	14.40	50	
13	7.41	17.6125	73.70	6.76	15	
14	5.4	19.4625	58.66	23.87	70	
15	6.61	19.4625	68.63	11.90	35	
16	8.41	19.8125	70.01	7.87	19	

Effect of Intermetallic and Precipitation Phases on Austenite and Ferrite Stability

Interestingly enough, the effect of the minor intermetallic phases themselves are significant in terms of predicting ferrite and austenite stability. A simple multiple regression equation shows that the presence of niobium carbide strongly affects austenite stability, even more than the presence of ferrite or fcc FeCu content. Ferrite affects austenite in the regression equation because it is strongly dependent and correlated. Note that the presence of NbC also has a negative effect on the amount of ferrite as well, likely due to the removal of niobium from the matrix. The precipitation of FeCu (copper precipitate) has a negative effect on both ferrite and austenite formation; this is due to the fact that it is a separate phase formed at low temperatures that reduces the stability of both austenite and ferrite.

Table 20 - Significant Factors as Linear Estimators of Ferrite

The regression equation is							
g-l-BCC = 83.1 - 10.2 g-NbC(s) - 1.00 g-l-FCC - 8.05 g-FeCu							
Predictor C	oef SE Coef	T F					
Constant 83.	114 2.731	30.43 0.000					
g-NbC(s) -10.	175 3.043	-3.34 0.006					
g-l-FCC -0.99	985 0.03695	-27.06 0.000					
g-FeCu -8.	053 3.031	-2.66 0.021					
S = 0.857985 R	-Sq = 98.5%	R-Sq(adj) = 9	8.2%				
Analysis of Vari	ance						
Source	DF SS	MS F	P				
Regression	3 592.20 19	97.40 268.16	0.000				
Residual Error	12 8.83	0.74					
Total	15 601.04						

Source	DF	Seq SS
g-NbC(s)	1	43.59
g-l-FCC	1	543.42
g-FeCu	1	5.20

Austenite stability is also negatively affected by niobium carbide and iron. In this discussion, austenite stability does not necessarily refer to the stability of austenite in terms of transformation to martensite. While the composition will affect the martensite start temperature (the temperature in which the martensite first forms); and while a lower M_s will correspond to a lower M_f (martensite finish) temperature, processing in terms of final quench temperature and cooling rate will have an equally marked effect on the final martensite content in the CB7Cu-1 alloys. The hardenability (quench stability of austenite) is influenced in the similar way by other nickel and chromium equivalent elements and is not predicted by this phase stability diagram.

Fable 21 ·	 Significant 	Phases a	s Predictors	s of Austenite
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The regression equation is g-l-FCC = 82.9 - 9.80 g-NbC(s) - 0.984 g-l-BCC - 8.23 g-FeCu
PredictorCoefSE CoefTPConstant82.94990.7073117.280.000g-NbC(s)-9.8053.097-3.170.008g-1-BCC-0.984020.03636-27.060.000g-FeCu-8.2252.954-2.780.017
S = 0.851165 R-Sq = 98.5% R-Sq(adj) = 98.1%
Analysis of Variance
Source DF SS MS F P Regression 3 573.80 191.27 264.00 0.000 Residual Error 12 8.69 0.72 Total 15 582.49
Source DF Seq SS g-NbC(s) 1 13.80 g-1-BCC 1 554.38 g-FeCu 1 5.62

Chapter 5 – Heat Treatment & Processing Control in CB7Cu Alloys

As much as composition control plays a part in terms of developing good microstructural elements, processing is equally important to final microstructure and properties. High temperature treatments act to both ensure dissolution of delta ferrite and secondary detrimental intermetallic phases, particularly in castings, where delta ferrite is likely to be found in the as-cast microstructure. Proper quenching from high temperature treatments ensures complete transformation from austenite to martensite. The subsequent age hardening reaction strengthens the alloy, but also must be carefully controlled in such that the distribution of the precipitate ensures adequate toughness.

5.1 - DSC/DTA Analysis of Phase Reactions in CB7Cu

5.1.1 Introduction/Detailed Methodology

Complex phase reactions occur during both heating and cooling in precipitation hardening alloys. In general, the reactions that happen during heating are likely to be more complex and numerous than reactions that occur during cooling of these alloys. The results of a DTA (Differential Thermal Analysis) trace for heating and cooling were recorded for investment cast CB7Cu. An alumina standard was used as the comparative specimen for the DTA analysis. The temperature differences (or energy differences) were plotted as a function of the specimen temperature over time. Non-linear slopes that do not match that of the linear increases in temperatures are considered to represent exothermic and/or endothermic reactions. Phase reactions are also dependent upon heating and cooling rate of the specimen. This is particularly true with diffusion controlled transformation processes. Therefore, in most cases, the exact peaks, starts and end times of these reactions are only approximations. In this study, the behavior of the investment cast CB7Cu alloy was investigated to determine reactions, particularly to quantify the Ms temperature.

The sample was heated in an atmosphere of argon at a rate of 5°C/min, held at 1100°C for 10 minutes, and then cooled at 15°C/min to approximately 50°C. The rate of heating was likely rapid enough to mask some of the diffusional processes, but at high temperatures, even some reactions of these reactions were noted.

5.1.2 Results /Discussion of Differential Thermal Analysis

Upon initial heating, a complex set of reactions was evident from 468°C to 644°C. This included exothermic peaks amongst a large slow endothermic reaction. The endothermic reaction likely indicates resolution of the martensite (α) phase to fcc-austenite (γ). The reaction is broadened likely due to the interfering precipitation of copper into the matrix (exothermic reaction) and at slightly higher temperatures, the redissolution of copper precipitate into the stabilizing austenite matrix. Resolving the two reactions is somewhat more difficult in CB7Cu-1 than in related 18Ni maraging steels, because the ranges of the two reactions overlap, where they do not in the 18Ni maraging steels. In the 18Ni maraging steels, the resolution of the precipitate often does not occur until *after* a good deal of the matrix has reverted to austenite.

A small exothermic reaction was detected at about 1050°C in the material, which is possibly identified as an exothermic reaction involving the dissolution of residual delta ferrite. Because delta ferrite is a metastable product at those temperatures, the resolution of delta ferrite into the austenite field is expected to exothermic. The other possibility is the dissolution of Nb-rich carbonitrides, which are formed upon initial cooling, and also dissolve to some extent at temperatures above 1050°C. However, the reaction to dissolve these carbides is still relatively sluggish at those ranges. Further study is warranted in high temperature reactions to clarify the sequence of reactions taking place during heating.



Figure 38 - DTA Heating for CB7Cu-1 showing resolution of precipitate and austenite reversion

Upon cooling, reactions were much less, as the thermal analysis cooling rate (15° C/min) likely exceeded the rate for many diffusion controlled processes. In these low-carbon steels, the reactant levels for carbon are likely very low, and therefore unlikely to undergo major intermetallic phase reactions ($M_{23}C_6$ formation). Such minor reactions at fast cooling rates would be difficult to detect at intermediate temperatures. The martensite formation reaction was very evident in the cooling cycle, forming a strong, sharp exothermic peak. The start of martensite formation (M_s) temperature was measured at approximately 170°C. This value is in line with estimates for similar copper stainless precipitation steels (such as 17-4PH) [10] and also in line with estimates from empirical equations. This also suggests that standard quenching guidelines currently used in practice (90°F in 1 hour) are likely sufficient to guarantee complete transformation from martensite to austenite upon quenching. It is important to note that even at these modest cooling rates (15°C/min), the martensitic transformation was nearly complete at 70°C.



Figure 39 - DTA Cooling curve for CB7Cu-1 showing beginning and end of martensitic transformation

5.2 High Temperature Process Control of Delta Ferrite

Delta ferrite dissolution occurs during homogenization in CB7Cu alloys and is used to control the amount and morphology of delta ferrite. In wrought alloys, homogenization of duplex austenitic-ferritic and martensitic-ferritic alloys is important to mitigate residual stresses and subsequent tearing that can be caused by differences in hardness between delta ferrite and other phases during deformation. Some delta ferrite in castings is useful because of the varying section sizes and the accompanying contraction gradients that may occur upon cooling. The ability to retain some delta ferrite upon initial cooling and subsequent removal of delta ferrite by homogenization-heat treatment would be ideal in terms of castings.

In high strength CB7Cu castings, ferrite needs to be dissolved due to the reduced strength and toughness of the ferritic matrix as compared to martensite. This portion of the thesis describes an attempt to quantify and control the ferrite dissolution reaction.

5.2.1 Experimental Investigation of Delta Ferrite Dissolution

Samples of CB7Cu-1 were homogenized for different times and temperatures to determine the effect of homogenization on the delta ferrite content in CB7Cu-1. Material was cut into approximately 0.75" x 0.75" x 0.5" blocks and homogenized at either 1925°F or 2125°F for 1, 2, 4, or 8 hours. (Table 22) A "double" homogenization was also performed. This double homogenization consisted of a high temperature heat treatment for 4 hours, interrupting the homogenization and air cooling to room temperature, and then placing the sample in the furnace for a second homogenization. Following the heat treatment, samples were tested for hardness, then polished, etched in Fry's Reagent, and subjected to a standard point count to estimate the amount of delta ferrite. It should be noted that magnetic techniques are commonly used to measure ferrite content in austenitic alloys and will not work in the presence of martensitic alloys. This is because the presence of martensite will generally lead to incorrect results when using magnetic methods to assess ferrite percentages due to the fact that martensite is also magnetic. Although there is no upper limit to homogenization temperature, higher temperatures leads to dissolution of grain boundaries, which may result in grain coarsening. This leads to lowered strength and impact toughness if intermetallic segregation products are present in the alloy.

Table 22 - Homogenization Conditions for CB7Cu-1 material

Time
1 hr, 2 hr, 4 hr, 4hr + 4hr, 8 hr
1 hr, 2 hr, 4 hr, 4hr + 4 hr, 8 hr

The use of hot isostatic processing and homogenization prior to a solution annealing treatment can effectively reduce the amount of detrimental ferrite in castings. The two temperatures used in the study were the typical upper and lower limits of homogenization of CB7Cu-1; 1900°F was used because it is the lower-bound value for ASTM A747 specified values for homogenization. 2125°F was also used, as it represents a relatively high temperature for homogenization treatment; homogenization temperatures at

temperatures greater than 2150°F are generally not recommended due to excessive grain growth and possible stabilization of delta ferrite.

5.2.2 Experimental Results

Figure 40 shows the results of homogenization of sand-cast material at different times and temperatures. Note that in all cases, there was some form of delta ferrite reduction. At 1900°F, the dissolution of delta ferrite appears is more sluggish than that of 2125°F. At the 1900°F 4+4 hour treatments, there is still about 20% of the original delta ferrite remaining. At 2125°F, nearly all of the δ -ferrite appeared to be dissolved in the material by 4 hours. The long 8 hour (4+4 aging) cycle reduced both the variance and amount of delta ferrite measured.

Even at the ASTM A747 (1050°C/1925°F 1 hr) minimum solution treatment, modest delta ferrite reductions are probable. After relatively short holds, delta ferrite is reduced by greater than 50% after relatively short holds at both temperatures. The change in ferrite morphology during long time, high temperature treatments is notable. Elongated ferrite stringers present in the as-cast microstructure can be reduced to a more rounded, island morphology during homogenization, minimizing the detrimental effects of ferrite on strength.

As-Cast Specimen



15.7 ± 1.7%

1900F/1037C



Figure 40 - Delta Ferrite Concentration vs. Homogenization Treatment micrographs (1900F -2125F)

5.2.3 Discussion and Comparison with Analytical Solution for Dissolution of Delta Ferrite

From the observations collected along with an understanding of dissolution kinetics, a model for reduction of delta ferrite in 17-4PH can be developed. First, the diffusion symmetry must be considered. Delta ferrite in castings is not influenced by martensitic reactions and retains a non-preferred orientation barring thermomechanical treatment. Stringers of delta ferrite are remnants of alloy-rich ferrite regions which remain upon the periphery of austenite grains formed during cooling after solidification. In CB7Cu, the interface between delta ferrite and austenite is usually carbide rich, with carbides precipitating in the range of 500-700°C (900-1300°F). It has been suggested that these carbides precipitate in a eutectoid reaction where delta ferrite decomposes to M₂₃C₆ and austenite end products. [127] $M_{23}C_6$ boundary carbides have been reported to grow into the delta ferrite phase rather than into the interface austenite phase due to the rapid diffusion of chromium in delta ferrite as compared to austenite. These phase boundaries are less than 0.5µm in thickness and the carbide matter contained in these boundaries (generally $M_{23}C_6$) quickly dissolves into solution at homogenization temperature treatments (>1040°C). This proposed mechanism suggested to be the "fast dissolution" step which occurs within the first hour, as the initial alloy-poor delta ferrite along the interface rapidly transforms, reducing the fraction of delta ferrite significantly at the beginning of high temperature thermal cycles.



Figure 41 - Graph showing Delta Ferrite Dissolution Fraction compared to Time and Temperature

Because of the simple morphology and relatively small amounts of delta ferrite content in CB7Cu-1, development of a dissolution model for reduction of delta ferrite can be modeled using a few assumptions. Because CB7Cu-1 is cast and not subjected to wrought thermomechanical treatments, directionality of formation is much more random and does not form in anisotropic plates. Using long sine-wave dendritic modeling is inappropriate due to the globular child-austenite structure forming upon cooling. Delta ferrite is often in the shape of long plates, with a reasonably constant diameter, which can be modeled with a simple planar model. Copper, nickel and chromium have all been observed in study to segregate in CB7Cu castings; though chromium and nickel represent the major segregation prone elements and elemental stabilizers. Delta-ferrite (bcc), which is metastable at solution treatment temperatures and below, is usually rich in chromium (bcc, ferrite stabilizer), but poor in nickel (fcc, austenite stabilizer) and copper (fcc, austenite stabilizer) as compared to the nominal composition.

RegionCrNiCuγ16.5-17.53.1-4.12.4-3.1δ-ferrite21.5-22.51.6-2.11.3-2.2

Table 23 - Measured Composition Ranges of Cr, Ni, and Cu in CB7Cu-1[41]

Measurements for chromium, nickel and copper ranges were taken from an ongoing study performed at Missouri University of Science and Technology involving investigations on cast CB7Cu alloy. These measurements were used to estimate initial and interface compositions for delta-ferrite and austenite. Because of the low solidification cooling rates in the alloy, a concentration gradient is expected within the phases themselves. In the case of delta ferrite, the diffusion of substitutional elements (Cr, Ni) has been measured to be at least 30 times faster than the diffusion of elements in austenite. [128] The concentration of elements across the delta ferrite stringers from the interface to the center will become small compared to concentration gradients in the austenite. Therefore, the delta ferrite concentration between center and interface is taken to be constant. The austenite grains in cast CB7Cu are very large, on the order of 50-100µm, which is more than 10 times the size of the thickest delta ferrite. It can be assumed that delta ferrite dissolution will behave similarly to dissolution in a semiinfinite field, and that field gradients from neighboring delta ferrite structures will not overlap.

The analytical solution [129-131] for Fe-Cr-Ni alloys in terms of the position of the moving boundary on a semi-infinite field is described by the following four equations:

$$C_{Cr}^{\delta/\gamma} - C_{Cr}^{\gamma/\delta} = \frac{(C_{Cr}^{0\gamma} - C_{Cr}^{\gamma/\delta}) \exp\{(K_{Cr}^{\gamma})^{2}\}}{K_{Cr}^{\gamma}(\pi)^{0.5}\{1 - \operatorname{erf}(K_{Cr}^{\gamma})\}}$$
$$C_{Ni}^{\delta/\gamma} - C_{Ni}^{\gamma/\delta} = \frac{(C_{Ni}^{0\gamma} - C_{Ni}^{\gamma/\delta}) \exp\{(K_{Ni}^{\gamma})^{2}\}}{K_{Ni}^{\gamma}(\pi)^{0.5}\{1 - \operatorname{erf}(K_{Ni}^{\gamma})\}}$$
$$\frac{\Delta f}{f_{0}} = \frac{(z - z_{0})}{z_{0}} = \frac{K_{Cr}^{\gamma}}{z_{0}}\{2(D_{CrCr}^{\gamma}t)^{0.5}\}$$

$$\frac{\Delta f}{f_0} = \frac{(z - z_0)}{z_0} = \frac{K_{Ni}^{\gamma}}{z_0} \{ 2(D_{NiNi}^{\gamma} t)^{0.5} \}$$

Where $C_X^{\delta/\gamma}$ represents the concentration of element X at the δ -ferrite->austenite interface, $C_X^{\gamma/\delta}$ represents the concentration of element X at the austenite delta ferrite interface, and D represents the main diffusion coefficient of a particular phase, K is the dimensionless diffusion parameter and z is the half width of the secondary phase plate (δ -ferrite), and Δf / f_0 represents the dissolved fraction of δ -ferrite.

Phase	Initial Comp	oosition	Interface Composition		K_{Cr}^{γ}	D_{CrCr}^{γ} (cm ² s ⁻¹)
	wt. Cr (%)	Wt. Ni (%)	Wt. Cr (%)	Wt. Ni (%)		
δ-ferrite	22	1.85	22	1.85	-0.113	3.6 x 10 ⁻¹¹
γ (austenite)	16.5	4.1	17.5	3.1		

Table 24 - Values used for interface / initial composition based on CB7Cu segregation profile

An interdiffusion coefficient for chromium in a ternary Fe-Cr-Ni system found in previous research was used in the calculation. [129] The diffusion parameter K was determined through calculation with the estimated boundary and matrix concentrations found by EDAX measurement and found to be -0.113.

The remaining volume fraction of delta ferrite was plotted as a function of the square root of time. The function was calculated after an hour of dissolution time due to the effects of rapid dissolution during the first hour. It was found that after the first hour of heat treatment, dissolution of delta ferrite generally followed a linear trend in relation to the square root of time for both the high temperature and low temperature heat treatment conditions. It was also found that the analytical solution for dissolution of delta ferrite in CB7Cu fit well with the results from the dissolution experiment at 2125°F (1163°C). (Figure 42)



Figure 42 - Delta Ferrite Dissolved vs. Square Root of Time in CB7Cu-1

In all cases, it is safe to assume that at most practical heat treatment temperatures, delta ferrite dissolution occurs very quickly at the first hour - likely more than a 60% reduction is expected after that first hour. Following the first hour, delta ferrite dissolution is relatively slow, controlled by the reduced driving force and weak gradient of reactant (chromium) across the boundary to austenite. Therefore, in both cases, relatively small fractions of delta ferrite are expected to be dissolved over long periods of time.

It might be suggested that further increases in temperature may increase the rate of dissolution in terms of delta ferrite content. However, above 1300°C, in many composition combinations of CB7Cu actually begin to *promote* reformation of ferrite. Increasing temperatures only benefits dissolution to a certain point. Therefore, while mobility in terms of diffusion must be considered, so must the stability of phases at high temperatures.

5.3 Retained/Reverted Austenite Phase Dependence on Heat Treatment in CB7Cu-1

5.3.1 Introduction/Methodology

While composition in the CB7Cu-1 alloy influences the M_s temperature, the processing of the alloy determines how fast the M_f temperature is reached. As determined by DTA analysis and corroborated in the literature review, CB7Cu-1 has an M_s temperature of about 170°C in an alloy with a near center composition in terms of content. Because of the low martensite start temperature and lack of drive for diffusion-driven processes (such as autotempering), guidelines suggest that reaching near room temperature (90°F/32.2°C) within an hour is sufficient to prevent excessive retained austenite.

Samples of CB7Cu material were exposed to different forms of high temperature treatments. All samples were solution treated for 1 hour and then quenched in specific media. Samples 1, 2 and 6 were quenched in water after solution treatment. Samples 3 and 4 were quenched in water and then cooled in liquid nitrogen for 24 hours. Sample 5 was cooled in still air. Samples 1 and 3 were exposed to hot isostatic pressure treatments prior to solution treatment for 4 hours at 1162°C/2125°F with a pressure of 15 ksi. Retained austenite was measured by XRD diffactrometry by taking the area under the (200) martensite peak and comparing it to the (200) austenite peak.

5.3.2 Results/Discussion

There was no retained austenite detected in any of the CB7Cu in specification composition investment cast samples, despite the different cooling treatments performed after solution treatment. (Table 25) Therefore, in section sizes up to $\frac{1}{2}$ " of CB7Cu material, it is unlikely that significant amounts of retained austenite will form in properly balanced compositions, with cooling rates up to those seen in still air.

If the alloy is significantly out of balance, particularly in carbon, there will be some retained austenite formed upon quench, even in thin sections. However, it must be noted

that the amount of carbon is over 50% of the specified maximum allowable amount. Even with this extreme amount of austenite stabilizer in the alloy, retained austenite still only presents itself as a small fraction of the overall base matrix.

Sample	Material	Conditioning	Cooling	Retained
Sample	wateria	Conditioning	Treatment	Austenite (y)
1	CB7Cu-1 IC	HIP 1162°C / 4 hr / 15	Water (RT)	Austennie (7)
		ksi		
		SA 1050°C / 1 hr		
2	CB7Cu-1 IC	SA 1050°C / 1 hr	Water (RT)	
3	CB7Cu-1 IC	HIP 1162°C / 4 hr /	Water (RT)	
		15ksi	$LN_2 - 24$ hr (-	None Detected
		SA 1050°C / 1 hr	180°C)	
4	CB7Cu-1 IC	SA 1050°C	Water (RT)	
			$LN_2 - 24$ hr (-	
			180°C)	
5	CB7Cu-1 IC	SA 1050°C	Still Air (RT)	
6	CB7Cu-1 + High	SA 1050°C / 1 hr	Water (RT)	9.12%
	Carbon (0.11)			

Table 25 - Retained Austenite Measurements from Quenched Samples of CB7Cu-1



 Perin State
 [NNUNDERLING/ment/10]/suc/Modele's work/Rachel Arnhams (0-24.000) Thursday, September 25, 2000 02.23(h) (MULADEB)

 Figure 43 - XRD Spectra for IC CB7Cu-1 Material corresponding to H900 treatments. There are no retained austenite lines in any of these treatments.



Penn State (AVAL/SISTINAT50742-Wednesday, April 14, 2010 03 42p (MDUADE5) Figure 44 - XRD Spectra for CB7Cu-1-0.11C Material corresponding to H900 treatments. Minor austenite peaks are lined with blue overlays.

5.4 Effects of Cryotreatment on Hardness

5.4.1 Detailed Methodology

Initial heat treatment screening tests were performed on small sand cast 0.5" x 0.5" x 0.5" samples to evaluate the hardness response upon aging versus heat treatment. Conventional 'standard practice' processing as prescribed by ASTM A747 was compared to '+ practice' (e.g. best practice) processing on sand cast materials.

Samples were solution annealed at 1925°F (1050°C) for .5 hrs, quenched, and then heat treated for various times and temperatures to develop a baseline aging response curve. (Table 12) Both standard water quenching from the solutionizing temperature and cryoquenching (water quenching immediately followed by holding in liquid nitrogen - 180°C/-320°F for 8 hours) were evaluated. All samples were also water quenched after aging. Samples were evaluated for both hardness (HRC) and microstructural content. All samples were etched using Fry's Reagent, which can differentiate martensite (etches dark) from retained austenite (jagged boundaries and no etch) and delta ferrite (rounded and darkly bounded).

The goal of the initial screening tests was to determine the effect of specialized processing techniques on the hardness of sand cast 17-4PH. Because the goal is to maximize strength of the alloy, temperatures that represented peak-aged conditions were chosen. Four measurements were taken from each screening sample and averaged.

5.4.2 Results

The initial hardness screening tests gave a good indication of the aging response of high strength cast 17-4PH alloys aged at low aging temperatures. The aging behavior of cast Cb7Cu-1 generally mimics that of wrought 17-4PH grades of material. Like 17-4PH, measured hardness appears to peak close to 850°-900°F, (450-482°C) which is consistent with previous research results for 17-4PH. The highest hardness values measured were obtained after aging at 850°F (450°C) at 24 hours (Figure 45, Figure 46). However, the

material may not have reached peak hardness after 24 hours of aging, which is consistent with previous peak-aging studies. At aging temperatures of 875°F (468°C), peak hardness was achieved at much shorter aging times. Final aged hardness values for samples aged at 875°F (468°C) were similar to that of samples aged at 900°F (482°C). Material aged at 900°F (482°C) for 30 minutes showed a large increase in hardness that was unexpected as compared to the samples aged at 850°F/875°F.

Cryotreatment of the '+ practice' material assured complete transformation of any retained austenite present in the solutionized to martensite and therefore can be expected to affect the as-quenched hardness. Material that was cryotreated generally showed a slightly higher as-quenched hardness and higher hardness after subsequent aging. These hardness increases were minor because the Cb7Cu-1 composition chosen was not expected to have significant amounts of stable austenite present in the structure even after 'standard-practice' room temperature quenching. The modest but consistent hardness gains from cryoquenching were accompanied by a slight decrease in the amount of aging time necessary to reach peak hardness.



Figure 45 - Hardness vs. Aging Time and Temperature, Standard Practice Material



Figure 46 - Hardness vs. Aging Time, (+) Practice Cb7Cu-1

5.5 Effects of Improved Processing on High Strength Mechanical Properties and Microstructure

5.5.1 Detailed Methodology

Two sets of heat treatment conditions were performed on the investment cast and sand cast materials previously described in the materials section. The first treatment was a "standard practice" heat treatment schedule which conformed to the practices set forth in ASTM A747 for Cb7Cu grades 1 and 2. This heat treatment consisted of solution annealing at 1925°F for .5 hours/in, followed by quenching below 90F in water, followed by aging at 900F for 1.5 hours. The '17-4PH + practice' heat treatments were chosen to reflect possible improvements in processing that are attainable using best commercial practices of wrought producers and investment casters. Prior HIP processing was performed by Bodycote Thermal Processing using standard HIP cycles used for 17-4PH investment casting densification. Test bars were hot isostatic pressed at 2125°F for 1.5

hours followed by air cooled. Homogenizing was followed by solution annealing at 1925°F, water quenching to 55°F and then cryoquenching in liquid nitrogen at -320°F with an 8 hour hold. After cryoquenching, the material was then allowed to return to room temperature, and was cleaned before aging to remove deposits and scale. The material was then aged at 875°F-900°F for either 1.5, 2 or 4 hours. After aging, the gage length of the material was polished to ensure no complications from scale. The '+ practice' material was HIPed, solutionized, and cryoquenched prior to aging at various times and temperatures.

	Standard Practice	+ Practice
HIP Treatment	-	2125°F / 4 hrs / 15 ksi
Homogenization	-	1920°F / 1.5 hr
Solution Annealing	1925°F/.5 hr	1925°F / 1 hr
Quench/Cryogenic Treatment	Water Quench at 55°F	Water Quench - 55°F
		Liquid Nitrogen -320°F, 8 hr
Age Hardening	900°F, 1.5 hr	875-900°F, 2.5-4 hr

Table 26 - Heat Treatments for Fe-Cr-Ni-Cu Materials

5.5.2 Results

Standard practice heat treatments of thin section sand material resulted in high tensile/yield strength (~190ksi/170ksi) in most specimens. The elongation in the tensile specimens was relatively low, but was in most cases above the minimum 5% elongation requirements for Cb7Cu grade 1 (H900 condition) in ASTM A747. The tensile strength of the investment cast materials, after the same standard practice heat treatments, was significantly lower, developing strengths just above the H900 specification limits but with tensile elongations generally over 10%.

Specimen	Tensile Strength (ksi)	Yield at 0.2% Offset (ksi)	% Elongation	Impact Energy (ft-lbs)
As Cast	95.9	95.8	10%	5.1
SP/IC	173.1	145.4	15%	1.6
SP/SC-1"	194.6	176.0	12%	1.6
SP/SC-0.5"	190.0	167.6	7%	2.9
+/IC	184.2	163.1	14%	1.5
+/H900-2.5hr	171.0	152.3	6.3%	2.4
+/H900-4.0hr	180.5	166.3	23.6%	5.7
+/H875-2.5hr	183.9	168.9	11.8%	2.2
+/H875-4.0hr	194.5	173.6	19.1%	3.6

Table 27 – Average Results Summary, Preliminary and Improved Experiments

The '+ practice' material aged at 900F had tensile and yield strength properties similar to the standard practice material; however the percent elongation was significantly higher. Specimens aged for 4 hours at 875°F showed the best combinations of strength and elongation. Tensile strengths of greater than 190 ksi were achieved. While strength increases were modest from '+ practice' processing, the elongation differences were more pronounced.

The room temperature Charpy impact toughness for all heat treatments was generally poor. (Table 27) Impact toughness values observed were typically less than 5 ft-lbs. Somewhat improved toughness was observed for materials that were aged for longer periods of time, possibly due to further tempering of martensite. The results of these Charpy impact test must be questioned because of methods used to create the v-notch in the Charpy specimens. Notches were produced by electro-discharge machining (EDM) which resulted in a poor notch surface finish and possible thermal damage to the notch root which may have adversely affected the impact energy measurements. In addition, while HIP treatment at high temperatures and pressures may have closed microporosity in the samples and dissolved all delta ferrite, the fact that the material is held at high temperatures for a long period of time may have led to the promotion of excessive grain growth. Nonetheless, all HIP treatments lead to significant increase in elongation over non-HIP samples.

It is important to note that in all of the (+) cases, the aging time is significantly longer than what is called for in ASTM A747. ASTM A747 dictates an aging time of only 1.5 hours for peak-aged specimens. Yet, in the previous results, significantly better ductility, and slightly better impact toughness result from aging for longer periods of time at the lower aging temperatures. At the lower temperatures, the material has a higher peak and kinetics dictate that the material does not reach the true peak for longer times as compared to higher temperatures. In addition, at 1.5 hours, it is likely that the martensite is only lightly tempered. Longer aging times appear to result in more heavily tempered martensite, and as a result, better ductility and impact properties. At the higher range of aging temperatures, a longer aging time has the consequence of excessive coarsening of precipitates and the corresponding loss of strength. At the 850°-900°F range, impractically long times are required to develop incoherency of Cu-precipitates, and generally little loss of strength/hardness is seen in slightly prolonged aging times (t < 24hours, etc.). Variance amongst the samples could not be well-quantified; in all but the +/ H900-4.0hr (n=8) & +/H900-4.0hr (n=4), samples were only machined and pulled in double replicates. In general, the (+) H900 material showed a great deal of variance, but also showed the best elongation values per specimen.



Figure 47 – Charpy V-Notch Impact Values from CB7Cu "+" and SP (standard practice) material

5.6 Enhanced Strengthening through Multistaged Age Treatments

5.6.1 Mechanical Testing - Detailed Methodology

A separate study was performed to determine whether multistage aging improved properties of cast CB7Cu-1 material. As in previous tests, material was homogenized, solution annealed and cleaned before aging. Material was aged at 850-950°F for 4 hours, interrupted, and then aged again from 850-950°F for 1-4 hours. (Table 28) Since there is prior knowledge about certain combinations (e.g. aging at 950°F for long periods of time will limit strength – therefore no doubling of long treatments), some combinations were not tested. In particular, the ordering of the aging was of interest; Al-Cu systems with GP-zones generally favor starting with a lower precipitation temperature to favor fine precipitate growth first, and then a slightly higher temperature to control growth of precipitates. Sample investment cast material was heat treated and cleaned, before being

sent to Westmoreland Mechanical Testing & Research, Inc. for final sample preparation and testing. Generally, samples were aged in a condition for 1 or 4 hours, and then stepped up or down 50°F and aged for an additional 1 or 4 hours. After aging was complete, samples were removed from furnace and quenched to prevent further aging. As in the previous study, material was characterized using optical light microscopy using Fry's Reagent and scanning electron microscopy.

Specimen	HIP	Homogenization	Solution	Aging Step 1	Aging Step 2
Description		Conditions	Treatment		
			Conditions		
SP	no	Not performed	1925°F, 1 hr	900°F / 1 hr	Not performed
850-1/900-4	no	2000 °F / 2 hrs	1925°F, 1 hr	850°F / 1 hr	900°F / 4 hrs
850-1/950-4	no	2000 °F / 2 hrs	1925°F, 1 hr	850°F / 1 hr	950°F / 4 hrs
850-4/900-1	no	2000 °F / 2 hrs	1925°F, 1 hr	850°F / 4 hrs	900°F / 1 hr
950-1/850-4	no	2000 °F / 2 hrs	1925°F, 1 hr	950°F / 1 hr	850°F / 4 hrs
850-1/900-4	yes	2000 °F / 2 hrs	1925°F, 1 hr	850°F / 1 hr	900°F / 1 hr
+ HIP					

Table 28 - Multistaged Heat Treatment Study

Because multistage aging had shown promise in terms of increased ductility with a limited wrought study, a similar, but smaller study was performed on the investment cast CB7Cu-1 bars. Unlike the cast study performed, the wrought study advocated underaging at temperatures below or around peak-aging temperatures. Increases of about 10% in ductility were seen over H900 samples, but impact data and other properties were not available. Because precipitation is a nucleation and growth process, the literature is mixed in terms of high-to-low temperature stepping, as opposed to low-to -high temperature stepping. Some literature advocates overaging the sample and then aging the sample at a lower temperature to improve properties by encouraging remaining copper to precipitate out of solution, which provides small improvements in strength. This is stated in particular for the "overaged" condition. Other literature suggests stepping temperature in the opposite step order; aging is first performed at a lower temperature to promote fine precipitation, and then at a slightly higher temperature, promoting an intermediate distribution of multiple precipitate sizes.

5.6.2 Mechanical Testing Results

The baseline measurement represents the standard heat treatment as per "standard practice" treatment. This gives a baseline to compare the rest of the sample. Overall, there was little difference in measured elongation for the samples. Aging at extended times at 850°F led to high strengths, but poor toughness values, independent of step order. Conversely, aging at 950°F for extended amount of time appeared to favor relatively strong growth of the precipitating agent and led to better fracture toughness values at the expense of strength. The best combination of strength, ductility and impact properties occurred when the material was aged for a short duration at 850°F for 1 hour and 900°F for 4 hours. Presumably by limiting the time at peak age, the distribution of precipitates was established. By growing the precipitate at a slightly higher temperature for a longer period of time, the martensite was further tempered, and precipitate coarsening/interspacing was limited as compared to a four hour age at 900°F alone. Further investigation would be necessary by atom probe analysis to confirm this. To see if the properties could be further improved, HIP processing was applied to material treated at 850°F -1hr/900°F-4hr material. Material that was treated in this fashion developed better mechanical properties than previously treated materials.

Specimen Description	UTS (ksi)	0.2% YS (ksi)	% Elongation	Impact (ft-lbs)
SP	182	167	14	3
850-1/900-4	190.4	170.9	14	4
950-1/850-4	190.7	171.7	14	2
850-4/900-1	194.5	170.6	14	2
950-1/850-4	181.0	163.0	15	5
850-1/900-4	196.0	176.1	14	6
+ HIP				

Table 29 - Effects of Multistaged aging on mechanical properties of Investment Cast CB7Cu-1

5.6.3 Micrograph/Fracture Surface Evaluation of Multistage Aged Material

The microstructures of investment cast CB7Cu-1 are similar to those of the sand cast material, with both containing a large secondary fraction of delta ferrite within low-carbon lath martensite. Material that was minimally processed with only a solution treatment and age shows remaining elongated regions of delta ferrite. Material that was HIP treated and/or solution treated at 2000°F for 2 hours was nearly delta ferrite-free, with only minor regions of ferrite showing up as small isolated globules within the microstructure. Small, sparsely dispersed niobium carbides are also seen in this material, as expected in all heat treatments.



Figure 48 - As Cast Investment Cast Cb7Cu-1, Fry's Reagent (50X)



Figure 49 - As Cast Investment Cast Cb7Cu-1, Fry's Reagent (200X)



Figure 50 - SP Investment Cast CB7Cu-1, H900 Condition, Fry's Reagent (500X)



Figure 51 - CB7Cu-1, Treatment - HIP 850-1/900-4, Fry's Reagent (500X)



Figure 52 –CB7Cu-1, Treatment 850-1/950-4, Fry's Reagent (200X)



Figure 53 - Cb7Cu-1, Treatment – HIP + 850-1/900-4, Fry's Reagent (200X)



Figure 54 - CB7Cu-1, Treatment 950-1/850-4, SEM 1000X



Figure 55 - CB7Cu-1, Treatment HIP + 850-1/900-4, SEM 1000X



Figure 56 - CB7Cu-1, Treatment 950-1/850-4 SEM 5000X



Figure 57 - CB7Cu-1, Treatment HIP + 850-1/900-4 SEM, 5000X

The copper-rich particulate responsible for age-hardening is impossible to observe by light microscopy in these alloys, so precipitate distribution and size could not be measured. However, the response in mechanical properties seems to indicate that there is some difference in the age-hardening particulate distribution and size between each of the conditions.

Fracture surfaces were also observed to determine the nature of the different impact toughness values that were observed with each treatment. Both standard practice treated and multistage aged material specimens were observed to have fracture surfaces with general quasi-cleavage fracture, corresponding to the low impact toughness measurements. Material which had been double-aged and hot isostatically pressed developed mixed modes of ductile and cleavage fracture surfaces in some areas. No evidence of hydrogen embrittlement was detected in any of the specimens tested.

5.7 Effect of Double Solution Treatments on Peak-Aged Material

5.7.1 Detailed Methodology

Three additional conditions were added after the best combination of mechanical properties was determined from the screening conditions. HIP was added, followed by the addition of double solutionizing at two different temperatures. As previously described, mechanical testing and specimen machining were carried out at Westmoreland Mechanical Testing & Research. Double solution annealing was also investigated as a possible way to further increase properties of the material. Early ARMCO studies on wrought materials suggested that double solution treatments provided an increase in properties by further refining grain and subgrain structure. This may be particularly true in the case of these low carbon cast materials, which have relatively little to pin grain boundaries.

Treatment	HIP	Homogenize	Solution	Age Step 1	Age Step 2
			Treatment		
850-1/900-4	Yes	2000 °F / 2 hrs	1700°F, 1 hr* x2	850°F / 1 hr	900°F / 1 hr
+ HIP	+				
DBL1700F					
850-1/900-4	yes	2000 °F / 2 hrs	1925°F, 1 hr* x2	850°F / 1 hr	900°F / 1 hr
+ HIP	+				
DBL1900F					

 Table 30 - Conditions Table of Double Solution Treatments

*Material was double solution treated

5.7.2 Results

The addition of a second solution treatment further improved the impact properties of the Cb7Cu alloy at peak-aging temperature. Both lower temperature and higher temperature solution treatments were tested. There was little difference between the two treatments in terms of ductility and impact measurements; however, the low temperature solution treatment was significantly less strong than that of the standard temperature solution treatment. In both cases, ductility was consistently improved as compared to all other treatments.

Treatment	Ultimate	Yield Strength (ksi)	Elongation	Charpy Imapct
	Tensile		(%)	Toughness (ft-lbs)
	Strength(ksi)			
SP	182	167	14	3
850-1/900-4	196.0	176.1	14	6
+ HIP				
850-1/900-4	190.5	172.1	17	8
+ HIP + DBL1700F				
850-1/900-4	199.5	179.5	17	7
+ HIP + DBL1900F				

Table 31 - Double Solution Treatments

5.8 Modeling Age Hardening in CB7Cu Alloys

The precipitation sequence in Fe-Cu related alloys has been well-documented. There is relatively good agreement on the precipitation structure evolution. Copper is retained in the solution upon cooling from austenite to martensite. Early precipitate is rich in both iron and copper, and proceeds from a (1) coherent bcc spherical to (2) an intermediate low-strain structure, denoted as 9R, and finally to (3) a larger, incoherent ε -copper precipitate. In general, the precipitate is spherical in shape, and remains generally spherical (though oblong in some cases). This is as opposed to structures such as found in zinc-magnesium precipitation structures and phases which do not share similar morphologies.

When precipitates first form, they are small and dislocations that are moving through the matrix shear across these particles. As age-hardening proceeds, more precipitates form from the solid solution, causing the material to increase in strength. As the precipitates grow, more energy must be absorbed to allow dislocations in the matrix to shear or bypass the particle. The stress required to shear the increasing size of the precipitates also becomes greater, even as the interparticle spacing also continues to grow. There comes a point where the precipitates become so large that it becomes energetically favorable for the precipitate to simply flex around the precipitates as compared to shearing across them. As the interparticle spacing continues to increase, the strength begins to decrease until the precipitates redissolve back into the matrix at the metastable solvus temperature.

5.8.1 Methodology and adaptation of the Model for Martensitic Cu-PH Steels

Ashby and Shercliff originally denoted this general model to relate hardness (or strength) to the following components, all as a function of time:

$$\sigma(t) = \sigma_i + \Delta \sigma_{ss} + \Delta \sigma_{ppt}$$
Where $\sigma(t)$ is the strength at time t, σ_i is the intrinsic, constant strength of the matrix, $\Delta\sigma_{ss}$ is change in strength due to solid solution strength and is the $\Delta\sigma_{ppt}$ is change in strength due to precipitation. Because hardness changes in precipitation hardening materials are proportional to strength, both strength and hardness measurements can be used within the constraints of this model for prediction.

In Shercliff and Ashby's model, the intrinsic strength is estimated to be the same as pure aluminum for most aluminum alloys. Using the intrinsic strength term of pure iron (YS = 34-54 ksi, 234-372MPa) would result in a poor fit, considering the structure of pure iron is a soft, unstrained ferritic matrix. While the martensite in 17-4PH materials is relatively low in carbon, the strength of the untempered martensite (>690MPa, 100ksi) far exceeds that of pure iron-ferrite. Like the copper particulate itself, the martensite exists as a metastable structure. When exposed to the same heating that causes the precipitate to come out of solution, the martensite itself is tempered to ferrite and carbide, remaining strain in the matrix is relaxed, which leads to the loss of strength as well as a significant increase in ductility, all dependent upon the extent of tempering.

The tempering reaction can be far more complex, governed by not just the tempering of the martensite, but the formation of mixed, secondary carbides. The extent of tempering in families of alloys is modeled by using a plot curve of time-temperature relationship.



Figure 58 - Tempering Curve for 13Cr Low Carbon Steels[56]

The extent of tempering is denoted by a Hollomon-Jaffe heat treatment parameter - T(20 + log t) x 10^{-3} , allowing for multiple time and temperature combinations to be used. We remove the solid solution contribution in this investigation because the 2-3% Cu contributes very little to the solid solution strengthening. However, to add this term would not be very difficult in other steel alloy materials where the strengthening mechanism is much more important. Therefore the correction term $\Delta\sigma_{tempering}$ must also be added. The low-carbon martensite found in 10-20Cr steels generally does not soften much at low-tempering temperatures, but begins to show appreciable softening/tempering at 500°C and 1 hour and above. The correction term $\Delta\sigma_{tempering}$ is dependent on time and temperature. Because 17Cr-4Ni steels are not produced, a tempering curve from 13Cr-0.068C steel is used, as the behavior is likely to be most similar to 17-4PH steel without copper. The final curve for CB7Cu-1 steel then becomes:

$$\sigma(t,T) = \sigma_{quenched} + \Delta \sigma_{ppt} + \Delta \sigma_{tempering}$$

Where:

$$S_o^2(t,T) = S_{o,max}^2 \left[1 - exp\left(-\frac{Q_s}{R}\left(\frac{1}{T} - \frac{1}{T_s}\right)\right] \times \left[1 - exp\left(-\frac{t}{\tau_1}\right) \right] + \Delta H(T,t)$$

Where $\Delta H(T,t)$ is defined by difference of hardness between the initial hardness and final hardness as predicted by the Holloman-Jaffe parameter.

5.8.2 Experimental Work

Aging curves for CB7Cu were developed using the investment cast CB7Cu material. Materials were first homogenized for 2 hrs at 2000°F, air cooled, and then solution treated at 1950°F for 1 hour before being water quenched to assure a near delta-ferrite free structure. Samples were then aged at four temperatures: 850°F, 925°F, 950°F and 1000°F (454-538°C) for times between 0 and 960min. Rockwell Hardness (Scale C) tests and multiple indents (n=4) were used and averaged to reduce variation in the hardness curves. Hardness results from the heat treatment are detailed in Figure 59.



Figure 59 - Actual Age Hardening Curves - CB7Cu-1 IC

To set up the Shercliff-Ashby relationships, we require a number of terms to properly form the hardness function. The methodology and values for the curves are detailed in the following section.

5.8.3 Model Assumptions and Inputs

A) Activation Energy of Precipitation: The activation energy to form copper precipitate from a supersaturated matrix of martensite is calculated by taking the plots of $\ln(t_p/T)$ vs. the plot 1/T x 10⁻³. (Figure 60) The slope of the line is Q_a/R. Q_A is calculated to be about 114.11kJ/mol. This is in good agreement with other investigations which found ranges from 112-120kJ/mol for copper precipitating from martensite. This is far less than the value of copper precipitating from ferrite (>200kJ/mol), likely due to ability of copper precipitate to nucleate on dislocation tangles in the lath martensite.



Figure 60 - Calculation of Activation energy from Temperature Corrected Time Measurements

B) The as-quenched hardness was measured for this material. An average of four measurements yielded 31.3 HRC as the average hardness. This value is used as the $\sigma_{quenched}$ value.

C) The metastable solvus temperature was estimated from data from previous investigations as well as DTA measurements from this investigation. A value of 600°C was chosen as the metastable solvus, the temperature of dissolution of copper in martensite.

D) The solvus boundary enthalpy, was estimated through best-fit with $S(o)_{max}$ and the metastable solvus. The solvus boundary enthalpy was a good fit at an estimate value of 40kJ.

E) S_0 max, (the maximum absolute hardness increase)was estimated to be 18 HRC; this is the estimate of the maximal possible hardening that was possible with the current composition. This is consistent with previously established peak-age hardening data from 17-4PH curves.

F) K, the time decay constant, was fitted to the data, and established to fit well with a value of 0.4.

G) The extent of tempering was estimated by using the tempering curve for 13Cr-0.068C steel. While this steel is not identical to 17Cr-4Ni-0.04C, the tempering curve is likely to be reasonably similar in behavior to that of 17-4PH steel without copper precipitate.

H) P_p (the temperature adjusted time peak average) was estimated by taking the average P_p value from each temperature. The calculated value of P_p is 1.201 x 10⁻⁷ s/K.

5.8.4 Model Results and Discussion

Results for the model for several different aging temperatures are demonstrated in Figure 61-Figure 64. Curves for the model with the tempering term and without the tempering term are included. In many cases, during early stages of tempering, the model without tempering fits well with the actual age hardening data, which is expected as the extent of tempering is limited. As the age-hardening proceeds and more energy is added to the

reaction, the model without tempering deviates further from the actual data, particularly at the higher tempering temperatures, where more energy is being introduced to the system, and increasing the extent of tempering. At 850°F, the tempering reaction proceeds slowly enough that no significant change of hardness is evident even after long-term holds at this temperature. Therefore, in this model, there is no apparent change of hardness in the tempering regime selected. At 850°F, tempering would proceed, but likely in a range past the realm of industrial tempering times. Note that in the actual data, there is also little change in terms of hardness over time. In terms of the aging precipitate, 850°F represents a temperature as to which peak-aging in CB7Cu alloys has been realized. At this temperature, there is little driving force to influence the coarsening of precipitates and a small radius and distribution of the precipitate is maintained. This is also mirrored in the actual hardness measurements, which show little change over long periods of time.

At intermediate temperatures (925°F-950°F), the precipitation strength increases quickly to a peak, and then slowly decreases. The incremental rate of softening increases with the temperature, along with the peak hardness, as expected with spherical age hardening precipitates. As the temperature increases, the tempering parameter value also increases, which correlates to the amount of tempering in the martensite. This eventually has a marked effect on the final bulk strength of the material, while the precipitate strength alone does not decrease substantially. At 1000°F, there is enough energy that relaxation of the martensitic matrix occurs within a relatively short time, precipitating into metal carbide and relaxed ferrite. Without the addition of the tempering parameter and the effect of tempering, the bulk hardness prediction would deviate substantially from that of the modeled hardness, due to the fact that the precipitate only marginally decreases in strength.



Figure 61 - Graphical Results for Model with Tempering, without Tempering, and the Actual Data. CB7Cu-1 tempered at 850F

Table 32 –Numerical	Results for Model with	Tempering, without	Tempering, and t	he Actual Data.	CB7Cu-1
tempered at 850F					

time (sec)	Strength PPT	Model w/ Tempering	Actual Data	Model Error	SSR
0	0.0	31.3	31.3	0.0	0.0
600	5.1	36.4	36.6	-0.2	0.0
1200	7.4	38.7	40.7	-2.0	4.0
1800	8.9	40.2	42.6	-2.4	5.8
3600	11.7	43.0	44.1	-1.1	1.2
5400	13.2	44.5	44.7	-0.2	0.0
7200	14.1	45.4	45.4	0.0	0.0
9000	14.5	45.8	43.9	1.9	3.7
10800	14.8	46.1	43.5	2.6	6.8
14400	15.0	46.3	43.2	3.1	9.4
28800	14.3	45.6	42.8	2.8	7.6
57600	12.8	44.1	41.9	2.2	4.9
				SSR	43.4
				χ^2	0.99
		Test Statistic at $\alpha=0$.	05,df=10	χ^2 (test)	18.31



Figure 62–Graphical Results for Model with Tempering, without Tempering, and the Actual Data. CB7Cu-1 tempered at 925F

Table 33 – Numerical Results for Model with Tempering, without Tempering, and the Actual Data. CB7Cu-1 tempered at 925F

Time (sec)	Strength from Precipitate	Adjusted Loss in Hardness	Model w/o Tempering	Model w/ Tempering	Actual Data	Model w/o Temper Error	Model w/ Temper Error	w/o Temper SSR	w/ Temper SSR
0	0.0	0.0	31.3	31.3	31.3	0.0	0.0	0.0	0.0
600	7.1	0.0	38.4	38.4	36.2	2.2	2.2	4.8	4.8
1200	9.4	0.0	40.7	40.7	41.9	-1.1	-1.1	1.3	1.3
1800	10.7	0.0	42.0	42.0	44.7	-2.6	-2.6	6.9	6.9
3600	12.3	0.0	43.6	43.6	44.6	-1.0	-1.0	1.0	1.0
5400	12.5	0.0	43.8	43.8	42.5	1.4	1.4	1.9	1.9
7200	12.4	0.0	43.7	43.7	42.0	1.7	1.7	2.9	2.9
9000	12.2	0.0	43.5	43.5	40.3	3.2	3.2	10.2	10.2
10800	11.9	0.8	43.2	42.4	38.7	4.5	3.7	20.4	13.8
14400	11.5	1.1	42.8	41.7	37.4	5.4	4.3	29.2	18.6
28800	10.2	2.3	41.5	39.2	36.2	5.3	3.0	28.2	9.1
57600	8.9	3.4	40.2	36.8	36.9	3.3	-0.1	10.6	0.0
						χ^2 (w/o t	empering)	3.09
						χ^2 (with	tempering	g)	1.81
				Test Statist	ic at α=0	.05,df=10	χ^2 (test)		18.31



Figure 63 - Graphical Results for Model with Tempering, without Tempering, and the Actual Data. CB7Cu-1 tempered at 950F

Time (sec)	Strength (Precipitate)	Tempering Loss of Hardness	Model w/o Tempering	Model w/ Tempering	Actual Data	Model w/o Error	Model w/ Tempering Error	w/o Temper SSR	w/ Temper SSR
0	0.0	0.0	31.3	31.3	31.3	0.0	0.0	0.0	0.0
600	7.6	0.0	38.9	38.9	31.5	7.4	7.4	54.7	54.7
1200	9.8	0.0	41.1	41.1	33.5	7.6	7.6	58.0	58.0
1800	10.9	0.0	42.2	42.2	38.5	3.8	3.8	14.1	14.1
3600	11.9	0.0	43.2	43.2	40.8	2.3	2.3	5.5	5.5
5400	11.8	0.0	43.1	43.1	42.0	1.1	1.1	1.2	1.2
7200	11.5	0.0	42.8	42.8	41.9	0.9	0.9	0.9	0.9
14400	10.4	0.8	41.7	40.9	41.5	0.3	-0.5	0.1	0.3
28800	9.2	1.1	40.5	39.4	41.5	-1.0	-2.1	1.0	4.3
57600	7.9	3.4	39.2	35.8	40.8	-1.6	-5.0	2.5	24.9
							SS Residuals	137.9	163.8
						χ^2	(w/o temperi	ng)	4.09
						χ^2	(with temper	ing)	4.73
					Test St	tatistic at	α=0.05,df=8	χ ² (test)	15.51

Table 34 - Numerical Results for Model with Tempering, without Tempering, and the Actual Data. CB7Cu-1 tempered at 950F



Figure 64 - Graphical Results for Model with Tempering, without Tempering, and the Actual Data. CB7Cu-1 tempered at 1000F

Time	Strength (Proginitate)	Temper	Model w/o	Model w/	Actual	Model	Model w/	w/o Tompor	w/ Tompor	
(sec)	(Trecipitate)	Hardness	Temper	Tempering	Data	LIIUI	Error	SSR	SSR	
0	0.0	0.0	31.3	31.3	31.3	0.0	0.0	0.0	0.0	
600	8.8	0.0	40.1	40.1	35.2	-40.1	0.0	1611.3	0.0	
1200	10.6	1.1	41.9	40.8	40.9	-39.7	1.1	1572.7	1.2	
1800	11.1	2.3	42.4	40.1	39.4	-37.8	2.3	1427.2	5.3	
3600	10.9	3.4	42.2	38.8	37.6	-35.4	3.4	1255.6	11.6	
5400	10.4	3.8	41.7	37.9	35.4	-34.1	3.8	1165.0	14.4	
7200	10.0	4.6	41.3	36.7	35.2	-32.1	4.6	1030.2	21.2	
9000	9.6	5.2	40.9	35.7	35.1	-30.5	5.2	932.4	27.0	
10800	9.3	5.9	40.6	34.7	34.1	-28.8	5.9	831.2	34.8	
14400	8.8	5.9	40.1	34.2	34.2	-28.3	5.9	803.1	34.8	
28800	7.6	6.3	38.9	32.6	34.4	-26.3	6.3	693.2	39.7	
57600	6.5	6.3	37.8	31.5	33.3	-25.2	6.3	632.8	39.7	
							SSR	11954.8	229.7	
					χ^2 (v	v/o temp	ering)		8.08	
	χ^2 (with tempering)									
				Test	Statistic a	at α=0.05	,df=10 χ ² (t	est)	18.31	

Table 35 – Numerical Results for Model with Tempering, without Tempering, and the Actual Data. CB7Cu-1 tempered at 1000F

In all cases, while the deviations are relatively small, fits are not perfect, both because of the variation in the data and the differences in temper behavior between the 13Cr-0.06C steel and the CB7Cu-1. Overall, when testing for Chi-squared goodness of fit, all models fit well with the actual data. In particular, the model with the tempering effect added fits the data better than the model without the temper data. In the 850°F prediction, there is no inclusion for tempering data, because tempering proceeds at a very slow rate at low tempering temperatures. Note that in some higher carbon steels, there is actually an increase in hardness in terms of low-tempering temperature regimes. However, this alloy appears to be so low in carbon that there is an insignificant increase in hardness and lack of a distinct transition carbide strengthening effect, which appears as an increase in hardness during early tempering. Indeed, in many materials, there has been lack of a detection of a transition carbide stage of tempering, particularly in low carbon steels. CB7Cu-1 has a more complex chemistry than that of a ternary Fe-Cr-C steel, leading to high-temperature NbC carbides as well as $Cr_{23}C_6$ carbides, which would be seen in the aforementioned alloy. This would further influence kinetics of transformation to be sluggish as these stable carbides remain free of the matrix and do not redissolve at such low temperatures. These carbides are capable of sequestering carbon from the matrix, and will cause the martensite to be depleted of carbon. In this case, the steel will temper as if it was of a lower carbon content. Of course, with less carbon, the base strength of the martensite is lower than with significant carbon tied up in the matrix. For example, a significant addition of niobium may increase the amount of NbC and increase the apparent solution treated hardness, but it may cause the tempering response to flatten out. Therefore, it is important to note that while carbon content is relatively low, the difference in form and temperature stability can have a significant effect on the temper behavior.

Chapter 6 -The Development and Properties of a Prototype Ultrahigh Strength Precipitation Hardening Cast Steel

Although the improved processing techniques developed for CB7Cu in this investigation can be used to successfully increase the strength of these alloys, the copper precipitation system appears to be limited in castings to yield strengths of 190ksi (1310MPa). From the previous investigations, we have established:

- Delta ferrite is detrimental to both strength and ductility and can be avoided through proper composition control and processing. The amount of delta ferrite must be limited to achieve high strength and good toughness.
- Retained austenite is found to be nearly absent with good processing techniques in properly specified CB7Cu-1 alloys. Austenite does not appear to be a problem within the CB7Cu composition level, but may be a problem in more nickel stabilized compositions.
- Even with the best aging combinations, ultimate tensile strengths of an deltaferrite and retained austenite free CB7Cu alloy are limited to an ultimate tensile strength of 200ksi. Therefore, the copper precipitation system has limits in terms of strengthening the alloy.

It has already been established that ultimate tensile strengths of 220 ksi are required to reach the levels of specific strength of titanium alloys. High strength low-alloy castings are capable of reaching strength levels that match titanium, but are not corrosion resistant. Therefore, an alloy that exceeds the strength limitations of CB7Cu is required. Therefore, movement to a higher strength, nickel-titanium or nickel-aluminum precipitate system is required. The use of the nickel precipitate system is a natural evolution from CB7Cu:

- Because of the high nickel and lowered chromium contents, a nickel precipitation system is likely to be delta ferrite free after solidification. Therefore, processing to remove delta ferrite will be reduced.
- The nickel-titanium precipitate systems have been proven to reach strengths exceeding 260ksi in terms of ultimate tensile strength, which provides a better strength to weight ratio than that of cast titanium-6-4.
- While nickel-titanium alloys contain 1-2% titanium, the amounts are small enough that the formation of alpha-case (titanium-oxygen rich phase) on the surface is not a problem. However, the surface area of additions must be limited to avoid loss of titanium to surface oxidation on the melt.

However, there are some new challenges with this material:

- While this material is likely to be near delta-ferrite free, austenite is likely to be stabilized beyond the extent of what is encountered in CB7Cu alloys. Because the Schaeffler does not give clear guidance in terms of martensitic + austenitic alloys, there is little guidance in terms of the amount of retained austenite (or if retained austenite exists in an alloy such as this).
- Solidification of this alloy (particularly in complex sections) may lead to
 problems such as solidification tearing in thick sections due to the material
 primarily solidifying as austenite. Because this is prototype material, we have
 mainly focused on heat-treatment and leave the solidification investigation for
 future work with this material.
- While not as reactive as pure titanium, the titanium in this material is highly reactive and can be lost to the environment (known as fade) over a short period of time. Therefore melting under argon is used, and the titanium is added to the melt as a late addition.
- Aging behavior is likely to differ from copper precipitation material as the composition of the precipitate and shape are much different. Because the

behavior of these materials is unknown, estimates from similar wrought-maraging materials will be used.

6.1 Introduction and Casting Process

With appropriate compositions and processing, nickel precipitation systems can be expected to be far stronger than Fe-Cu precipitation systems. Since the Ni-Mo-Ti system alloy is a prototype casting material, guidelines for heat treating wrought maraging materials were used in the development of the initial heat treatment procedure. While similar wrought specifications and CALPHAD modeling results serve as a starting point, there was no guarantee that these guidelines would be optimal due to the fact that wrought materials do not suffer from the same solidification segregation profiles as castings. There also may be other unknown problems that are unforeseen with castings, due to the mode of solidification and processing. Schaeffler Equivalents predict the material will generally be martensitic with a minor fraction of stable austenite at room temperature. This limited stability is necessary to ensure that adequate nickel is present to participate in the precipitation hardening reaction and to prevent excess stable ferrite formation after solidification. Because the processing and composition ranges are unknown in this material, the focus of these studies is to develop a recommended composition and heat treatment schedule for this prototype alloy.

An 11-11PH Fe-Cr-Ni-Mo-Ti alloy which uses a $Ni_3(Ti,Mo)$ precipitation hardening system was adapted for casting using specialized processing. The initial heat of the 11-11PH alloy was produced at Metal Casting Technologies, Inc. and melted under an inert (argon) environment using the CLI³ process. This method employs counter gravity pouring under an argon gas blanket to assure smooth filling and lowered reactivity for sensitive alloys that may combine with gases contained in the atmosphere. The initial composition of the alloy is given in

Table 36.

														_
Composition (wt. %)														
Material	Cr	Ni	Mn	С	Si	Cu	Ν	Nb+ Ta	Р	S	Ti	Al	Мо	
11-11PH/1	11.33	11.13	0.05	0.01	0.13	0.01	0.007	0.1213	0.005	0.003	1.52	0.09	1.13	
*Fe balan	20													

Table 36 - Composition of Experimental Next Generation Casting Alloy

Fe balance

6.2 Property Screening

6.2.1 Approach to Property Development

Using the previously stated empirical Eichelmann-Hull [76] and Pickering equations [56] for predicting martensite start, the values for Ms calculated are 83°C and -3.8°C respectively. While there is a wide variance, either case roughly agrees with the Schaeffler prediction for at least some retained austenite at room temperature. Predictive CALPHAD transformation models suggest that the alloy transforms from liquid to solid in a ferrite + austenite mode, leading to a ferrite free casting upon cooling.



Figure 65 - Major Phases in NiTiMo Steel at Equilibrium, including precipitate Ni3Ti Phase as calculated by **CALPHAD Modeling**

In order to reduce or eliminate the amount of retained austenite, samples were first water quenched in 55-60°F water and then immersed in liquid N_2 for 12-24 hours. Because of the athermal nature of the transformation, the transformation from austenite to martensite is expected to viable 12-24 hours after the initial drop from the solution treatment temperature to that of room temperature. In addition, a lower solutionizing temperature was chosen in line with wrought alloy processing, as higher solutionizing temperatures have a tendency to dissolve austenite stabilizing elements within the grain and increase grain size, which both further depress the M_s. The material was then allowed to warm to room temperature, bead-blasted to remove oxide and aged at 950°F for 4 hours. Both Charpy V-notched samples and tensile samples were prepared and tested. Because of the experience with sample preparation and testing of hard materials, final machining and testing of samples was performed at Westmoreland Mechanical Testing and Research, Inc. Bars were machined and then heat treated according to the following schedules:

- Initial Q&T Test Condition (Heat 1): Solution Annealed at 982°C for 1 hr, direct LN2 Quench (-196°C/-321°F) for 8 hours, and then aged for 4 hours at 950°F/510°C.
- Q&T with HIP & Homogenization (Heat 2): Hot Isostatic Pressed at 2125°F for 4 hours, 15 ksi. Solution Annealed at 1800°F (982°C) for 1 hour, and direct LN2 quench - 8 hours of cryotreatment in LN₂ for 8 hours. After being allowed to warm to room temperature, the bars were then heat treated for 4 hours at 950°F.

6.2.2 Results

In the case of this alloy, no delta ferrite was detectable in any stage of the alloy precipitation. In the case of the initial of experiments, the original trial samples failed to age-harden effectively and resulted in yield strength levels of below 155 ksi (1070MPa) and contained large visible fractions of retained austenite within the low-carbon primary lath martensite matrix. (Figure 66) The retained austenite, formed due to insufficient cooling rates in LN2, has a strong propensity to dissolve critical age-hardening precipitates, while also negatively impacting the base strength of the material matrix. The initial cooling rate to room temperature is particularly important as relatively short holds at temperatures close to the M_s are more effective at leading to retained austenite than holds closer to the M_s as per the tangential nature of the martensite formation curve.

Even with the 8 hour hold in LN2, little further reduction in retained austenite was attained if the initial cooling rate was too sluggish.

Treatment	Homogenization	Iomogenization Solution (Aging
	/Hot Isostatic	Anneal		
	Pressing			
1800/1hr-950/4hr	None	1800°F/1 hr	LN ₂ /24 hr	950°F / 4hr
1800/1hr-LN2-	2125°F / 4hr / 15	1800°F/1 hr	LN ₂ /24 hr	900°F / 4hr
900/4hr (HIP)	ksi			
1875/1hr-LN2-	2125°F / 4hr / 15	1875°F/1 hr	LN ₂ / 24 hr	850°F / 4hr
850/4hr (HIP)	ksi			

 Table 37 - Treatment, 11-11PH Experiment #1 Results

Table 38 - 11-11PH Alloy Experiment #1 Results

Treatment	Tensile Strength	0.2% Offset Yield	Elongation
		Strength	
1800/1hr-950/4hr	165	155	6%
1800/1hr-LN2-	166	156	12%
900/4hr (HIP)			
1875/1hr-LN2-	169	153	7%
850/4hr (HIP)			

These specimens were cooled through a direct LN_2 quench. Unfortunately, liquid nitrogen behaves as a poor conductor of heat (and therefore quenchant), particularly in terms of direct quenching of a sample. At such high temperatures (much above room temperature), liquid nitrogen is superheated and forms a vapor blanket around the casting. [132] Because there is no direct liquid content, nitrogen gas is a very poor coolant, and slow cooling occurred causing long holds between the M_s and M_f temperatures, relaxing the strain and promoting large amounts of stable retained austenite. This retained austenite is of a blocky irregularly spaced morphology and does not contribute as much to ductility and impact properties as evidenced by the elongation numbers.

In light of the results, a second experiment was run on the remaining bars of material. With this second experiment, hot isostatic processing was not applied to the bars, but rapid quenching prior to cryotreatment was applied by a direct water quench. LN_2 times and solution treatment temperatures were varied. Solution treatment temperatures were

reduced in order to destabilize austenite by slowing down dissolution of TiN and TiC carbides.



Figure 66 - Retained Austenite (Light Phase) Visible in 11-11 Alloy, Fry's Reagent (250X)

6.3 Revised Processing of 11-11PH

6.3.1 Detailed Methodology – Mechanical Testing & Microstructural Investigation of 11-11PH

This early study limited heat treatments to solution treatment, liquid nitrogen cooling, and kept aging times and temperatures constant. Initial trials resulted in materials with large amounts of retained austenite and poor mechanical properties. In general, large amounts of retained austenite limits age-hardening by retaining age hardening elements within the matrix. In order to reduce or eliminate the amount of retained austenite in the sample, samples were first water quenched in 55-60°F water and then immersed in liquid N₂ for 12-24 hours. In addition, a lower solutionizing temperature was chosen in order to promote less retained austenite, as in similar wrought materials higher solutionizing temperatures have a tendency to more effectively dissolve austenite stabilizing elements. This in turn, further depresses the M_s temperature. Specimens were then allowed to warm to room temperature, then cleaned and aged at 950°F for 4 hours, which is common for

Fe-Ni precipitation hardening materials. Both Charpy V-notched samples and tensile samples were tested.

6.3.1 Mechanical Property Results

The results of the second study and conditions are detailed in Table 39. Duplicate replicates for each of the conditions were heat treated. Tensile strengths were on the order of 50-75 ksi greater than the same material aged in the earlier heat treatment with insufficient quenching. All strengths and impact values were generally improved over the cast 17-4PH material. Solution treatment of the material at the reduced temperatures below 1800°F led to slight increases in the strength of the materials at the expense of fracture toughness. Whether or not there was an appreciable change in terms of properties due to hold time in liquid nitrogen is unclear; while the deviations between in-condition samples were small (± 1 ksi of each other), the differences between each of the responses was also small. The literature regarding cryotreatment of stainless steels is unclear in terms of time-temperature responses in terms of mechanical properties. [133]

Sequence	Solution Treatment	Cooling	Aging	<pre> ó_{UTS} / 0.2% ό_{YS} (ksi) </pre>	Elongation (%)	Impact Energy (ft-lbs)
1	1700°F / 1 hr	Water Quench \rightarrow LN ₂ (24 hrs)	950°F / 4 hrs	210/198	10	5.9
2	1800°F / 1 hr	Water Quench \rightarrow LN ₂ (24 hrs)	950°F / 4 hrs	206/192	8.5	7.4
3	1800°F / 1 hr	Water Quench \rightarrow LN_2 (12 hrs)	950°F / 4 hrs	209/195	9	6.5

Table 39 - Results of Preliminary Study (n=2, each condition)

Results from this study were far more encouraging than the initial trials. The material appeared to properly age harden, increasing hardness over the earlier test samples by more than 50 ksi. This likely is related to the fact that the final material contained much less retained austenite than the previous samples. Because retained austenite readily

dissolves age-hardening elements, such as nickel, precipitation is limited. Elongation and impact toughness numbers were comparable and/or greater than best practices peak aged CB7Cu-1 alloys with + processing. Further improvements in impact toughness in particular are expected with the addition of hot isostatic processing in the heat treatment cycle.

6.3.2 Microstructural Results

When examined for microstructural characteristics, the sample appeared to be nearly fully martensitic and delta-ferrite free. No large austenitic pools were seen in this sample as compared to the samples which previously did not age-harden. A few titanium carbide particles were visible in both the as-cast and age-hardened specimens, though the occurrence was relatively rare and limited to scattered appearances on prior austenite grain boundaries.



Figure 67 - 11-11PH, As Cast, Fry's Reagent, 50X



Figure 68 - NPH-1800-24, Fry's Reagent, 200X

Gross fracture surfaces showed evidence of long dendritic arm structure with some limited microporosity. Fracture surfaces appeared to show evidence of mixed dimple rupture and quasicleavage fracture. Even though the material contained relatively low amounts of carbon and nitrogen, some evidence of Ti(C,N) formation was observed in SEM fractography. In many cases, these particles were observed to be centered within fracture dimples. Small titanium carbonitrides are typically observed in low-carbon maraging steels, which use the same precipitation hardening systems as compared to this

cast alloy.[4] A few rounded MnS particles were also observed in the alloy at the center of fracture dimples, though the number was relatively small, likely due to the low manganese and sulfur content. However, TiSCN particles were adjacent to TiCN particles along prior austenite grain boundaries.



Figure 69 - Fe-Ni-Cr-Mo-Ti Alloy, Gross Image showing dendritic structure, SEM 50X



with some scattered TiCN, 2000X



Figure 71- Likely TiCN inclusions in Fe-Ni-Cr-Mo-Ti Figure 72 - Detail of Inclusions, TiCN , SEM 10000X Alloy (5000X)

6.4 Microstructural Investigation of the role of Ti(C,N) inclusions in 11-11PH

The use of a Ni-Ti-Mo precipitation system, rather than the Cu precipitation system used in CB7Cu alloys, introduces other alloy complexities. Carbonitrides are observed in many of the wrought stainless maraging styles, because of the high driving force associated with the reaction of titanium to combine with free carbon and nitrogen. These carbonitrides are highly stable at temperatures below the melting point of steel and do not dissolve appreciably during solid state treatment. Large carbonitrides are extremely detrimental, essentially behaving as brittle intermetallic inclusions. These act as initiation sites for void nucleation upon stress/fracture, which in turn, lower both fracture toughness and strength.





Figure 73 - Carbonitrides visible in as-cast structure of 11-11PH alloys (500X)

 15.00 kV ETD112.6 mm400 x
 1532 AL2

 Figure 74 - SEM image of (Ti,Mo)C,N and (Ti,Mo)S(C,N) (400X)

Wrought Ni-Mo-Ti maraging alloys are melted and deformed at high temperatures and are generally cooled quickly, which tends to be effective at producing a finer distribution of carbides. Conversely, investment castings cool slowly in a ceramic mold, exposing the material to long temperature holds, which promote carbide growth and increase interparticle spacing. Titanium carbonitrides in the prototype alloy were measured to be between 1-5µm in diameter in the cast material using ImageJ particle analysis software. While the carbonitrides tend to dissolve at austenizing temperatures, they are still stable enough that they will dissolve slowly. Table 40shows measured areas of titanium carbonitrides on micrographs, demonstrating the change in carbonitride size with changes in heat treatment during HIPing or solutionizing.

Table 40 - Measured areas of Ti(C,N) Particles in 11-11PH material (n=20 measurements)

High Temperature Treatment	Average Ti(C,N) Particle Size
As Cast	$11.175 \pm 1.63 \mathrm{im}^2$
1- 1700°F / 1 hr	$9.778 \pm 1.53 \text{ im}^2$
1 - 1800°F / 1 hr	$9.52 \pm 4.49 \text{ im}^2$
1- HIP 2125°F / 4 hr	$7.07 \pm 3.69 \text{ im}^2$
2- 1800°F / 1 hr	

Even with high temperature, long-term temperature treatments, carbonitride size remains relatively large ($<1\mu$ m). Similar results have been seen in other alloy systems where titanium has been added to high strength, low-alloy steels as a carbide forming element. [59], [134], [135] Further treatment would likely continue to decrease the size/area of precipitates; however, extending heat treatment to these relatively long times may not be practical.



Figure 75 - SEM of TiMoS(C,N) and Ti(C,N) particles on lath & packet boundaries (1600X)

Figure 76 - Detail of SEM of TiMoS(CN) and TiMo(CN) particles (12000X)

Upon closer examination using SEM and SEM-EDS, it becomes more evident that the carbonitrides are rich in titanium, molybdenum, carbon and nitrogen. Using the SEM, two different particles were identified:

• A Ti(C,N) particle, generally cubic in shape, measuring from 9-25µm² in size, located at grain and subgrain boundaries. These were far more numerous in terms of distribution.

• A Ti,Mo,S(C,N) particle, generally rod shaped, measuring 3-10µm² in length, located at favoring prior austenite grain boundaries. (Figure 78-Figure 82)

The second type of CN-rich particles is rich in sulfur as well as titanium and, in some cases, molybdenum. This is consistent with wrought materials that contain little manganese. With little manganese, some of the sulfur in the alloy forms TiS(C,N) instead of the typical MnS found in cast materials. Segregation of sulfur to grain and subgrain boundaries has been determined to decrease fracture and impact toughness, even at very low levels of sulfur. [136-138]What is particularly problematic is the size of the titanium carbonitride particles. The TiSCN rods are on the order of 1-10µm in size, and are large inclusion sized particles, which are likely to disrupt grain and subgrain boundary cohesion as well as limit toughness.





Figure 77 - Secondary Election Image of TiS(C,N) Figure 78 - TiK Map (EDS) for TiS(C,N) Particle Particle



Figure 79 - NK Map (EDS) for TiS(C,N) Particle



Figure 80 - MoL Map (EDS) for TiS(C,N) Particle



Figure 81 - FeK Map (EDAX) for TiS(C,N) Particle



Figure 82 - SK Map (EDS) for TiS(C,N) Particle

6.5 Hot Isostatic Processing & Quench Treatment Variation of 11-11PH Alloy

6.5.1 Detailed Methodology

A second 300 lb investment cast heat of 11-11PH material was cast at Metal Casting Technologies in Milford, NH. The alloy composition was measured and detailed in Table 41. The composition was similar to the previous heat #2 alloy; however, no entrainment of dross was observed through radiographic inspection. Bars were provided in the standard 4" x 0.5" tensile investment cast blanks and 3" x 0.5" x 0.5" charpy specimens.

Table 41 - Composition of 11-11PH Alloy, Heat 2

Mn	Cr	Ni	Мо	Cu	Co	Ti	Fe	
0.10	11.20	10.95	1.07	0.08	0.21	1.19	bal	

Specimens were heat treated using multiple heat treatment schedules (Table 42), with particular variation in terms of cooling holds and temperatures to influence the amount of retained austenite. All specimens, except for the as-cast sample, were hot-isostatic pressed at 2125°F (1160°C) for 4 hours at 15 ksi (103 MPa). No homogenization was performed as it was expected that the 4 hour HIP treatment itself would provide sufficient

high-temperature homogenization treatment. Samples were furnace cooled to 700°F (370°C) and then air cooled to room temperature to prevent surface oxidation. Following hot isostatic pressing, samples were solution treated at 1800°F (982°C) for 1 hour, and then cooled using a number of conditions. Two samples were quenched in water and deep-cooled using liquid nitrogen for 4 or 24 hours. One sample was left to air cool from solution treatment temperatures to ambient temperature, and the last sample was quenched in water and stored at 20°F (-6.6°C) for 24 hours. After cold treatment was complete, samples in liquid nitrogen were brought up to room temperature over 12 hours. All samples were then peak-aged at 950°F (510°C) for 4 hours. Testing of samples was performed on standard investment cast tensile and v-notched impact specimens according to ASTM E8.

Test	Ref. Name	HIP	Homogeniz e	Solution Treatment	Quench	Cryo	Aging Treatment
1	AL2-ASCAST	None	None	None	None	None	None
2	AL2-24LN	2125/4hr/ 15 ksi	None	1800°F/1 hr	Water	LN ₂ , 24 hrs	510C/950F, 4 hrs
3	AL2-4LN	2125/4hr/ 15 ksi	None	1800°F/1 hr	Water	LN ₂ , 4 hr	510C/950F, 4 hrs
4	100109AL2-1-T	2125/4hr/ 15 ksi	None	1800°F/1 hr	Forced Air Cooled (60°F)	None	510C/950F, 4 hrs
5	100109AL2-2-T	2125/4hr/ 15 ksi	None	1800°F/1 hr	Water	20°F, 24hrs	510C/950F, 4 hrs

Table 42 - Test Conditions, 11-11PH Experiments, Heat #2

6.5.1 Mechanical Property Results

Mechanical property results are detailed in Figure 83 and Figure 84. In this second experiment, strength levels for all treatments were greatly improved over samples in the previous experiments. Strength levels generally increased with the hold time and increments of decrease in temperature. The sample that was air cooled appeared to harden less, and showed a loss of 10ksi over other treatments, suggesting that some retained austenite remained untransformed. The sample which was refrigerated to only 20° F developed the highest levels of strength, which seems to indicate that the M_f was

above that temperature, and cryotreatment may be unnecessary to develop a fully martensitic microstructure.



Figure 83 - Tensile and Yield Strength Results from Cast 11-11PH Alloy



Figure 84 - Charpy Impact and Elongation Results from HIP and Cast 11-11PH Alloy

Elongations and V-notch impact values were all appreciably reduced compared to the previous samples with excessive amounts of retained austenite. The sample which was air-cooled showed the greatest elongation and impact values, likely due to increases in the amount of retained austenite. However, the increases (~ 2 ft-lbs) are relatively small as compared to the equivalent losses in strength. It is important to realize that the sample with the lowest strength (221 ksi UTS/1524 MPa) exceeds the highest realized strength of CB7Cu by over 20 ksi, with similar room temperature V-notch toughness values. Also note that these samples were peak-aged, and likely suffered from some aging brittleness. The nature of maraging steels is that increasing aging temperatures (slightly overaging) often leads to increases in toughness, without the dramatic loss in strength that is typical in copper precipitation alloy. Time appears to play little role in terms of strength of the material; rather, final temperature reached appears to play the most important role. However, the increase in strength only exist to a certain point; cooling the sample under forced air showed lower strength (and more retained austenite) in the alloy. Once 20°F $(-6^{\circ}C)$ was reached, there were no further increases in strength. (Figure 85) This suggests that the final temperature plays more of a role than the absolute time that the part is held.



Further aging studies are needed to identify best conditions for high strength with adequate toughness.

Figure 85 - Charpy Impact vs. Yield Strength in 11-11NiMoTi. Reduced yield strengths and higher levels of retained austenite produce higher impact toughness measurements.

Therefore, once we can assure complete cooling of a part to a temperature near or below the acceptable M_f , further cooling is unnecessary. This is in contrast to certain highstrength low alloys which benefit from low temperature holds for long periods of time, even once the temperature of the part has reached equilibrium with the cooling media. To understand why this holds true for the PH hardening steels has to do with the nature of the PH strengthening particle. In HSLA materials, particularly those tempered at lowtempering temperatures, it is a carbon-rich precipitate (η or ε -carbide) that is responsible for the increased strengthening of the alloy. The behavior of these carbide precipitates is inherently different than those of nickel-rich and copper-rich precipitates.

6.6 Retained Austenite Characterization in 11-11PH by XRD and OIM (EBSD)

Unlike CB7Cu-1, 11-11PH is expected to contain small remnants of retained austenite in the solution treated and quenched condition. OIM (Orientation Imaging Microscopy) and XRD (X-ray diffraction) was used to characterize and determine the phase content of 11-11PH. In particular, the analysis was focused on detecting and determining the morphology of the retained austenite content.

A section of the charpy sample associated with the AL2-24LN treatment was sectioned prepared and polished with 0.04 μ m alumina to EBSD standards. A 40 μ m x 40 μ m sample was scanned at 3000X with a .05 μ m (50nm) step size. Phases for detection included alpha-iron, gamma-iron, and M₂₃C₆ carbide. Figure 86-Figure 89 show various results for OIM imaged material.

6.6.1 OIM (EBSD) Analysis Results

In OIM imaging, coloration represents the orientation (directionality) of crystallographic structures. The cast 11-11PH structure consists of laths which are about 2-3µm wide in random orientations, as represented by the random colors in each of the laths sub-packets. The prior austenite grain boundary is visible, and becomes more apparent when the alpha-iron (martensite/ferrite) is excluded from the analysis. Unlike the more randomly oriented martensite, retained austenite within each grain contains the original orientation of the parent austenite. In properly heat-treated 11-11PH, the austenite is interlath in nature, as compared to the more detrimental reverted 'blocky' austenite. The amount of austenite measured by OIM was estimated to be 9%. It is likely that this retained austenite contributes to the toughness of the 11-11PH material even when high precipitation strengths and age particle induced embrittlement is a factor. It is theorized that upon impact and fracture, localized stresses at the crack tip are at sufficiently high strain rates (>200s⁻¹) so that the austenite transforms to martensite. The transformation from austenite to martensite is an endothermic reaction (the reverse transformation has been well observed to be exothermic in nature in this study, along with many other

studies. [139]) and is responsible for some absorption of the impact energy upon breakage. No $M_{23}C_6$ carbides were detectable with any confidence in this EBSD study.



Figure 86 - OIM Image, AL2-24LN, 3000X, All Data



Figure 87 OIM Image, AL2-24LN, 3000X, Image Quality Nearest Neighbor Filtered



Figure 88 - OIM Image, AL2-24LN showing Martensite (Alpha-iron) only



Figure 89 - OIM Image, AL2-24LN showing Retained Austenite (Gamma-Iron)

6.6.2 Results from Retained Austenite Quantification by XRD

Two samples of the 11-11PH alloy were analyzed using X-ray diffraction to determine differences in retained austenite between water quenched and refrigerated material versus material that was air-cooled in still air. Peaks for austenite are apparent in both conditions, with the air cooled alloy containing about twice as much austenite as that of the material that was refrigerated at 20°F for 24 hours.



Figure 90 - XRD Spectra showing representative 7% Retained Austenite

Table 43 - Retained Austenite Differences between Air Cooled and Refrigerated Samples

Homogenization / Austenization	Quench	Area under Austenite Peak (Intensity)	Area under Martensite Peak (Intensity)	% Estimated Retained Austenite
HIP - 2125°F / 4hr / 15 ksi 1800°F / 1 hr	Air Cool	1155	3011	%13.0
HIP - 2125°F / 4hr / 15 ksi 1800°F / 1 hr	Water Quench / 20°F Refrigeration 24 hours	802	3987	%7.04

Chapter 7 -Research Contributions and Future Directions

7.1 Research Contributions

Research contributions on the development of high strength cast precipitation steels include:

- An understanding of the effect of composition on the general stability of ferrite and austenite (martensite), established through equilibrium calculations and thermodynamic modeling.
- A thermokinetic model which predicts the amount of delta ferrite dissolution based on heat treatment time and temperature conditions.
- An age hardening model for a martensitic cast precipitation hardened steel which predicts hardness over time for different times and temperatures. This model also takes into account the effect of tempering on the castings.
- An understanding of the role that multistaged heat treatment, quenching, and peak-aging has on the strength and toughness of CB7Cu-1 and the corresponding microstructural evaluation responsible for property development.
- Successful casting and processing of a very high strength prototype 11-11PH alloy based on principles from the previous investigations from CB7Cu. The 11-11PH material (Ni-PH) material was successfully cast under an argon atmosphere and analyzed to develop initial processing guidelines to produce a material with a higher specific strength than CB7Cu and cast titanium alloys.

7.2 Conclusions

CB7Cu-1 Composition Studies

- From the analysis of the equilibrium FACTSage modeling, along with the experimental model, it has been determined that the commonly used Schaeffler constitution diagram likely overestimates the amount of secondary phases present in CB7Cu and related alloys. FACTSage thermodynamic modeling gives reasonable estimates of the relative stability of delta ferrite, as delta ferrite forms during slow cooling. While FACTSage allows us to estimate austenite stability, non-equalibrium processing steps play a large role in the martensite formation, and we cannot directly predict the amount of martensite and retained austenite from FACTSage. The FACTSage model suggests about 2-20% average stability of delta ferrite across all temperatures. The "scaling" stability estimates better agree with delta ferrite measurements from selected alloys.
- Interactions between chromium and carbon in the material, as well as between niobium and carbon, can influence the austenitic stability of CB7Cu. Carbides forming at high temperatures (near the melt temperature) reduce the effective stability of high temperature austenite, and therefore, influence the temperature range and stability of delta-ferrite as a consequence. In terms of niobium carbides, NbC will always form at high temperatures if niobium is available, even if low levels of carbon are in the alloy.
- The Schaeffler diagram cannot be used to directly estimate the amount of delta ferrite in CB7Cu alloys. Experiments suggest that the Schaeffler diagram overestimates the amount of delta ferrite in as-cast and heat treated CB7Cu-1. However, both the FACTSage model and experimental results suggest that Schaeffler style diagrams provide good "trend" descriptions. Also, despite the fact that Schaeffler calculations suggest that there should be some form of detectable retained austenite in most CB7Cu alloy compositions, analysis in this investigation suggests that significant amounts of retained austenite are typically not present after usual heat treatments. However, increasing the nickel equivalent

with high out-of-specification limits of carbon (0.11% vs. 0.07 maximum) led to about 9% of detectable retained austenite in the alloy.

CB7Cu -1 Processing Studies

- Double solutionizing at 1900°F increases the impact toughness as well as the ductility of the alloy. Double solutionizing at 1700°F also increases ductility, but with a slight decrease in strength. High solutionizing temperatures are necessary to solutionize detrimental secondary phases that inhibit ductility and fully dissolve and desegregate elements contribute to age hardening.
- In CB7Cu, retained austenite appears to be less of a concern than delta ferrite. Because the M_s temperature is above 150°C, and the M_f is estimated to be about 70°C even at relatively slow quenching rates (15°C/second), fully martensitic structures can be achieved. Current guidelines of cooling the material (90°F in 1 hour) are adequate to assure a martensitic material in properly balanced CB7Cu alloys. Only extreme out of balance, high nickel equivalent alloys (0.11C - nearly 150% of maximum specified carbon) show significant amounts of austenite upon quenching. Because of this, cryotreatment is likely unnecessary for properly-balanced CB7Cu alloys that are cooled within guidelines.
- Multistaged aging above the peak aging temperature (850°F x 1 hr/900°F x 4 hrs) leads to the best properties in terms of strength/toughness combinations in properly balanced CB7Cu alloys. Aging at a near peak-aging temperature for a short time, followed by a growth period at a slightly higher temperature, leads to increased strength through precipitation size and distribution control. Aging at too high of a temperature leads to precipitate coarsening along with significant tempering of the martensite, which lowers the tensile strength.
- Friedel-based precipitation models by themselves can be used to predict the behavior of age-hardening in precipitation hardening steels, but deviations from the model increase at higher temperatures. By adding a tempering "correction" factor along with the equation, the hardness response during aging can be more accurately modeled. This is the first time that a martensitic Fe-Cu alloy has been

modeled using the age-hardening macromodel concepts popularized by Shercliff and Ashby.

11-11PH Prototype Alloy

• A stronger precipitation system has been successfully cast, and exceeds the strength to weight (specific strength) ratio of CB7Cu. This alloy is capable of competing on strength to weight ratio with cast Ti-6Al-4V. Ductility and impact toughnesses are greater or comparable to cast CB7Cu in the peak-aged condition with strength levels greater than 20ksi in difference. Ni-Mo-Ti PH alloys also have the benefit of being delta ferrite free upon cooling to room temperature. This material was observed to have small amounts of interlath retained austenite (as opposed to "blocky" morphology retained austenite). Fracture surfaces and SEM microscopy reveal that titanium-carbonitrides and titanium-sulfur-carbonitrides are often found at void initiation points. Homogenization and HIP treatment reduces the size of these inclusions rather slowly.

7.3 Future Work

In terms of improving CB7Cu, work needs to be performed to determine the kinetics of formation of $M_{23}C_6$ in CB7Cu alloys. In this work, equilibrium amounts of $M_{23}C_6$ are used in the FACTSage analysis; consistent with conditions that may be encountered at high temperatures. Learning the kinetics and finding the time-temperature-transformation curves for $M_{23}C_6$ in CB7Cu will help casters of thick sections to adjust niobium contents in such that niobium is not added if $M_{23}C_6$ does not precipitate out of the alloy.

Further investigation into the role of hot isostatic processing needs to be performed. In all of the investigations, hot isostatic processing appeared to improve performance of each of the alloys, even when delta-ferrite was not an issue (such as in 11-11PH). This is likely due to the healing of microporosity caused by shrinkage during solidification and/or gas removal. The optimization of time-temperature combinations decrease the possibility of excessive grain/growth, reduce energy use, and increase production while still providing adequate pressure and temperature to produce the beneficial effects, likely due to yield of the material and healing.

While 11-11PH has exceeded titanium in terms of strength to weight ratio, toughness of the material needs to be improved. Further investigation into the overaged condition (H1000-1150) needs to be performed, along with methods to reduce inclusion size and preserve some retained austenite for toughness. In addition, there are other alloys which present opportunities, such as alloys that use alternative systems, such as β NiAl alloys (PH13-8Mo). PH13-8Mo provides intermediate levels of strength between the titanium system and copper system, but may be easier to cast into complex shapes because it solidifies in a ferrite mode (rather than an austenite-ferrite mode of 11-11PH). However, this alloy may present challenges in that aluminum reacts strongly with oxygen and surface media upon pouring. PH13-8 has been successfully investment cast under a vacuum, but in the investigation did not reach the levels of strength of the analogue wrought material. Reasons for this were not fully explored in the investigation, and whether or not the material could be poured under atmosphere was not covered.

Modification or combination of the CB7Cu alloy may be prudent based on the previous studies. CB7Cu is easier to cast than the next generation systems due to the high levels of silicon (fluidity promoting element). Whether 11-11PH or other alloys are capable of being modified with high levels of silicon is unknown. Whether or not Laves phase (an undesirable, brittle material) will be promoted is also unknown.
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Appendix A – Minitab Output from Composition Control Statistical Analysis

This data represents the direct output from the design of experiments section of the composition processing of CB7Cu section. In particular, this section shows the organization of aliases, significant factors and interactions, and other items that may be of interest to the reader.

Welcome to Minitab, press F1 for help. Executing from file: C:\Program Files (x86)\Minitab 15\English\Macros\Startup.mac This Software was purchased for academic use only. Commercial use of the Software is prohibited. Alias Information for Terms in the Model. Totally confounded terms were removed from the analysis. I + Cr*Ni*C*Cu*Nb Cr + Ni*C*Cu*Nb Ni + Cr*C*Cu*Nb C + Cr*Ni*Cu*Nb Cu + Cr*Ni*C*Nb Nb + Cr*Ni*C*Cu Cr*Ni + C*Cu*Nb Cr*C + Ni*Cu*Nb Cr*Cu + Ni*C*Nb Cr*Nb + Ni*C*Cu Ni*C + Cr*Cu*Nb Ni*Cu + Cr*C*Nb Ni*Nb + Cr*C*Cu

Factorial Fit: g-NbC(s), g-NbN(s), g-FeCu, g-I-M23C, g-I-FCC, g-I-BCC, g-I-FE-L

Factorial Fit: g-NbC(s) versus Cr, Ni, C, Cu, Nb

Estimated Effects and Coefficients for g-NbC(s) (coded units)

Term	Effect	Coef
Constant		0.075248
Cr	0.001566	0.000783
Ni	0.000124	0.000062
С	0.109560	0.054780
Cu	-0.000658	-0.000329
Nb	0.070330	0.035165
Cr*Ni	-0.000884	-0.000442
Cr*C	0.001992	0.000996
Cr*Cu	-0.000303	-0.000152

C*Cu + Cr*Ni*Nb C*Nb + Cr*Ni*Cu Cu*Nb + Cr*Ni*C

Cr*Nb	0.002102	0.001051	
Ni*C	-0.000241	-0.000121	
Ni*Cu	0.002295	0.001148	
Ni*Nb	-0.000290	-0.000145	
C*Cu	-0.000758	-0.000379	
C*Nb	0.058381	0.029191	
Cu*Nb	-0.000708	-0.000354	

S = * PRESS = *

Analysis of Variance for g-NbC(s) (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	Ρ
Main Effects	5	0.06781	0.06781	0.013562	*	*
2-Way Interactions	10	0.01370	0.01370	0.001370	*	*
Residual Error	0	*	*	*		
Total	15	0.08151				

Estimated Coefficients for g-NbC(s) using data in uncoded units

Term	Coef
Constant	0.0492921
Cr	0.00153557
Ni	-0.00417312
С	-0.971596
Cu	-0.0173139
Nb	-0.155449
Cr*Ni	-8.03973E-04
Cr*C	0.0301753
Cr*Cu	-3.93916E-04
Cr*Nb	0.00955332
Ni*C	-0.00803480
Ni*Cu	0.00655742
Ni*Nb	-0.00289756
C*Cu	-0.0361121
C*Nb	9.73020
Cu*Nb	-0.0101102

Factorial Fit: g-NbN(s) versus Cr, Ni, C, Cu, Nb

Estimated Effects and Coefficients for g-NbN(s) (coded units)

Term	Effect	Coef
Constant		0.02250
Cr	-0.00279	-0.00140
Ni	-0.00047	-0.00023
С	-0.02360	-0.01180
Cu	0.00060	0.00030
Nb	0.00873	0.00437
Cr*Ni	-0.00023	-0.00011
Cr*C	-0.00084	-0.00042
Cr*Cu	-0.00005	-0.00002
Cr*Nb	-0.00098	-0.00049
Ni*C	0.00034	0.00017
Ni*Cu	-0.00169	-0.00084
Ni*Nb	-0.00043	-0.00022
C*Cu	0.00003	0.00001
C*Nb	-0.00314	-0.00157
Cu*Nb	0.00049	0.00024

S = * PRESS = *

Analysis of Variance for g-NbN(s) (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	Ρ
Main Effects	5	0.00256577	0.00256577	0.00051315	*	*
2-Way Interactions	10	0.00005996	0.00005996	0.00000600	*	*
Residual Error	0	*	*	*		
Total	15	0.00262573				

Estimated Coefficients for g-NbN(s) using data in uncoded units

Term	Coef
Constant	-0.0549280
Cr	0.00136365
Ni	0.0173195
С	-0.100242
Cu	0.0198075
Nb	0.136440
Cr*Ni	-2.05228E-04
Cr*C	-0.0127601
Cr*Cu	-5.85737E-05
Cr*Nb	-0.00445260
Ni*C	0.0111999
Ni*Cu	-0.00482236
Ni*Nb	-0.00434458
C*Cu	0.00133538
C*Nb	-0.523857
Cu*Nb	0.00697908

Factorial Fit: g-FeCu versus Cr, Ni, C, Cu, Nb

Estimated Effects and Coefficients for g-FeCu (coded units)

Term	Effect	Coef
Constant		0.16897
Cr	0.03068	0.01534
Ni	-0.02573	-0.01287
С	-0.00290	-0.00145
Cu	0.13932	0.06966
Nb	0.00323	0.00162
Cr*Ni	-0.00358	-0.00179
Cr*C	-0.00162	-0.00081
Cr*Cu	0.00648	0.00324
Cr*Nb	0.00134	0.00067
Ni*C	0.00166	0.00083
Ni*Cu	-0.00514	-0.00257
Ni*Nb	-0.00015	-0.00008
C*Cu	-0.00009	-0.00005
C*Nb	0.00001	0.00000
Cu*Nb	0.00180	0.00090

S = * PRESS = *

Analysis of Variance for g-FeCu (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	Ρ
Main Effects	5	0.0841255	0.0841255	0.0168251	*	*
2-Way Interactions	10	0.0003669	0.0003669	0.0000367	*	*
Residual Error	0	*	*	*		
Total	15	0.0844924				

Estimated Coefficients for g-FeCu using data in uncoded units

Term	Coef
Constant	-0.487123
Cr	0.00276266
Ni	0.0683578
С	0.146011
Cu	0.113306
Nb	-0.152103
Cr*Ni	-0.00325581
Cr*C	-0.0245987
Cr*Cu	0.00841683
Cr*Nb	0.00611178
Ni*C	0.0552647
Ni*Cu	-0.0146913
Ni*Nb	-0.00154454
C*Cu	-0.00451973
C*Nb	0.00119061
Cu*Nb	0.0256507

Factorial Fit: g-I-M23C versus Cr, Ni, C, Cu, Nb

Estimated Effects and Coefficients for g-1-M23C (coded units)

Term	Effect	Coef
Constant		0.04840
Cr	0.00766	0.00383
Ni	0.00242	0.00121
С	0.09680	0.04840
Cu	0.00099	0.00049
Nb	-0.04687	-0.02343
Cr*Ni	-0.00047	-0.00024
Cr*C	0.00766	0.00383
Cr*Cu	-0.00085	-0.00043
Cr*Nb	-0.00272	-0.00136
Ni*C	0.00242	0.00121
Ni*Cu	-0.00272	-0.00136
Ni*Nb	-0.00085	-0.00043
C*Cu	0.00099	0.00049
C*Nb	-0.04687	-0.02343
Cu*Nb	-0.00047	-0.00024

S = * PRESS = *

Analysis of Variance for g-1-M23C (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	Ρ
Main Effects	5	0.046530	0.046530	0.0093060	*	*
2-Way Interactions	10	0.009115	0.009115	0.0009115	*	*
Residual Error	0	*	*	*		
Total	15	0.055645				

Estimated Coefficients for g-1-M23C using data in uncoded units

Term	Coef
Constant	-0.249324
Cr	0.00686125
Ni	0.0306445
С	1.17509
Cu	0.0515066
Nb	0.337720
Cr*Ni	-4.31511E-04
Cr*C	0.116080
Cr*Cu	-0.00110933
Cr*Nb	-0.0123651
Ni*C	0.0805235
Ni*Cu	-0.00777236
Ni*Nb	-0.00854182
C*Cu	0.0470141
C*Nb	-7.81125
Cu*Nb	-0.00678088

Factorial Fit: g-I-FCC versus Cr, Ni, C, Cu, Nb

Estimated Effects and Coefficients for g-l-FCC (coded units) Term Effect Coef 70.000 Constant -9.370 -4.685 Cr Ni 6.144 3.072 С 3.509 1.755 0.509 0.254 Cu -1.348 -0.674 Nb 1.648 0.824 Cr*Ni Cr*C 1.026 0.513 0.131 0.261 Cr*Cu -0.404 -0.202 -1.162 -0.581 -0.389 -0.194 Cr*Nb Ni*C Ni*Cu 0.206 0.103 Ni*Nb -0.162 -0.081 C*Cu -0.165 -0.083 -0.287 -0.143 C*Nb Cu*Nb

S = * PRESS = *

Analysis of Variance for g-l-FCC (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	Ρ
Main Effects	5	559.77	559.77	111.954	*	*
2-Way Interactions	10	22.72	22.72	2.272	*	*
Residual Error	0	*	*	*		
Total	15	582.49				

Estimated Coefficients for g-l-FCC using data in uncoded units

Term	Coef
Constant	212.216
Cr	-11.5311
Ni	-14.5324
С	-11.8474

Cu	0.984225
Nb	28.0801
Cr*Ni	1.49844
Cr*C	15.5392
Cr*Cu	0.338987
Cr*Nb	-1.83738
Ni*C	-38.7339
Ni*Cu	-1.11027
Ni*Nb	2.06465
C*Cu	-7.69364
C*Nb	-27.5144
Cu*Nb	-4.09890

Factorial Fit: g-I-BCC versus Cr, Ni, C, Cu, Nb

Estimated Effects and Coefficients for g-l-BCC (coded units)

Term	Effect	Coef
Constant		10.998
Cr	8.258	4.129
Ni	-6.936	-3.468
С	-4.905	-2.453
Cu	-1.634	-0.817
Nb	0.705	0.353
Cr*Ni	-1.862	-0.931
Cr*C	-1.236	-0.618
Cr*Cu	-0.437	-0.218
Cr*Nb	0.300	0.150
Ni*C	1.105	0.552
Ni*Cu	0.330	0.165
Ni*Nb	-0.280	-0.140
C*Cu	0.083	0.042
C*Nb	0.054	0.027
Cu*Nb	0.193	0.097

```
S = * PRESS = *
```

Analysis of Variance for g-l-BCC (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	Ρ
Main Effects	5	574.12	574.12	114.823	*	*
2-Way Interactions	10	26.92	26.92	2.692	*	*
Residual Error	0	*	*	*		
Total	15	601.04				

Estimated Coefficients for g-l-BCC using data in uncoded units

Term	Coef
Constant	-145.976
Cr	12.7192
Ni	17.7079
С	64.4309
Cu	2.37588
Nb	-15.8738
Cr*Ni	-1.69282
Cr*C	-18.7204
Cr*Cu	-0.567513
Cr*Nb	1.36419
Ni*C	36.8277

Ni*Cu	0.941647
Ni*Nb	-2.80038
C*Cu	3.97577
C*Nb	8.98601
Cu*Nb	2.76348

Factorial Fit: g-I-FE-L versus Cr, Ni, C, Cu, Nb

Estimated Effects and Coefficients for g-l-FE-L (coded units)

Term	Effect	Coef
Constant		18.6281
Cr	1.0155	0.5077
Ni	0.7532	0.3766
С	1.1561	0.5781
Cu	0.9274	0.4637
Nb	0.5445	0.2723
Cr*Ni	0.1590	0.0795
Cr*C	0.1403	0.0701
Cr*Cu	0.1107	0.0553
Cr*Nb	0.0394	0.0197
Ni*C	-0.0120	-0.0060
Ni*Cu	0.0038	0.0019
Ni*Nb	0.0128	0.0064
C*Cu	0.0179	0.0090
C*Nb	0.0428	0.0214
Cu*Nb	0.0299	0.0149

S = * PRESS = *

Analysis of Variance for g-l-FE-L (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	Ρ
Main Effects	5	16.3667	16.3667	3.27334	*	*
2-Way Interactions	10	0.2485	0.2485	0.02485	*	*
Residual Error	0	*	*	*		
Total	15	16.6152				

Estimated Coefficients for g-l-FE-L using data in uncoded units

Term	Coef
Constant	22.1064
Cr	-0.670423
Ni	-1.69288
С	-18.5869
Cu	-1.24640
Nb	-2.27369
Cr*Ni	0.144534
Cr*C	2.12526
Cr*Cu	0.143748
Cr*Nb	0.178887
Ni*C	-0.399386
Ni*Cu	0.0107832
Ni*Nb	0.128057
C*Cu	0.853011
C*Nb	7.13207
Cu*Nb	0.426824

Alias Structure
I + Cr*Ni*C*Cu*Nb
Cr + Ni*C*Cu*Nb
Ni + Cr*C*Cu*Nb
C + Cr*Ni*Cu*Nb
Cu + Cr*Ni*C*Nb
Nb + Cr*Ni*C*Cu
Cr*Ni + C*Cu*Nb
Cr*C + Ni*Cu*Nb
Cr*Cu + Ni*C*Nb
Cr*Nb + Ni*C*Cu
Ni*C + Cr*Cu*Nb
Ni*Cu + Cr*C*Nb
Ni*Nb + Cr*C*Cu
C*Cu + Cr*Ni*Nb
C*Nb + Cr*Ni*Cu
Cu*Nb + Cr*Ni*C

Appendix B - Tensile Data

This table gives a detailed summary of each of the tensile specimens tested in for use in Chapter 4. In particular, this data cover the specimens that were tested in-house at Pennsylvania State University.

Specimen	Tensile Strength (ksi)	Yield at 0.2% Offset	% Elongation
		(KSI)	Measured
As Cast Specimen	95.9	95.8	10%
SP/IC-1	173.1	145.4	15%
+/IC -2	184.2	163.1	14%
SP/SC-1-THK	196.1	174.9	16%
SP/SC-2-THK	196.6	178.8	12%
SP/SC-3-THK	191.1	174.3	8%
Average	194.6	176.0	12%
+/ SC-2-TN	190.4	166.3	6%
+/ SC-3-TN	189.6	168.7	8%
Average	190.0	167.6	7%
+/SC-1-THK	178.5	156.0	6%
+/SC-1-TN	197.7	176.5	6%
+/SC-1-TN	189.8	169.7	7%
+/SC-1-TN	185.1	169.7	8%
Average	191.0	172.0	7%

*TN = Thin 0.5 in. Specimen

*THK = Thick 1.0 in. Bar Specimen

Table 2 – Heat Treated Specimens, All Better PracticesHIP: 2125°F, 4 hours, 15 ksi + Cryotreatment at -320°F, 8 hoursFormat: (Aging Time)-(Aging Time)-(Replicate Number)

Specimen	Tensile Strength (ksi)	Yield at 0.2% Offset	% Elongation
		(ksi)	Measured
H900-4.0hr-1	183.1	181.1	25.2%
H900-4.0hr-2	184.9	161.5	30.5%
H900-4.0hr-3	183.3	171.3	27.4%
H900-4.0hr-4	175.7	172.2	23.4%
H900-4.0hr-5	180.5	163.0	22.6%
H900-4.0hr-6	181.8	159.4	21.4%
H900-4.0hr-7	180.1	162.9	14.6%
H900-4.0hr-8	176.9	159.3	23.7%
Average	180.5	166.3	23.6%
Specimen	Tensile Strength (ksi)	Yield at 0.2% Offset	% Elongation
~	g ()	(ksi)	Measured
H875-2.5hr-1	183.3	161.8	9.8%
H875-2.5hr-2	184.4	176.0	13.9%
Average	183.9	168.9	11.8%
Specimen	Tensile Strength (ksi)	Yield at 0.2% Offset	% Elongation
H000 2 5hr 1	170.6	(KSI) 152.0	7 5%
H000-2.5hr-2	170.0	152.0	5.0%
11900-2.5111-2 A versee	171.0	152.7	6 30 / ₀
Average	1/1.0	132.3	0.570
Specimen	Tensile Strength (ksi)	Yield at 0.2% Offset	% Elongation
	102.0	(ksi)	Measured
H8/5-4.0hr-1	193.2	172.9	16.5%
H875-4.0hr-2	187.1	166.3	22.8%
H875-4.0hr-3	199.6	180.8	16.9%
H875-4.0hr-4	198.3	174.2	20.4%
Average	194.5	173.6	19.1%

Appendix C - Age Hardening Calculations

Description

This section gives a summary of calculations used for calculating the age-hardening precipitation reaction model in Chapter 5. Included in this table are the parameters for each of the following:

Strength PPT = Strength due to precipitation

P(normalized) = Is the current temperature adjusted time of the alloy

P/p = The proportion of actual temperature-adjusted time has passed as compared to the peak-temperature adjusted time for the temperature.

Q(s) = Is the estimated metastable boundary solvus enthalpy. The value was estimated to be a 40kJ.

T = is the temperature of the reaction in K.

Tables are given for values from 850-1000°F, the usual high-strength range for tempering CB7Cu.

For 850°F (454°C	For	850°F	(454°)	C)
------------------	-----	-------	-----------------	----

Strength PPT	P(norm)	P/(p)	Q(S)	Q(A)	T (temp K)
0	0	0	40000	114110	727.59
4.83699827	5.62835E-09	0.046842509	40000	114110	727.59
6.950847388	1.12567E-08	0.093685017	40000	114110	727.59
8.414821812	1.68851E-08	0.140527526	40000	114110	727.59
11.0776952	3.37701E-08	0.281055052	40000	114110	727.59
12.49237302	5.06552E-08	0.421582578	40000	114110	727.59
13.29662295	6.75402E-08	0.562110104	40000	114110	727.59
13.75395661	8.44253E-08	0.702637631	40000	114110	727.59
14.00058407	1.0131E-07	0.843165157	40000	114110	727.59
14.14472712	1.3508E-07	1.124220209	40000	114110	727.59
13.47514926	2.70161E-07	2.248440418	40000	114110	727.59
12.13678616	5.40322E-07	4.496880836	40000	114110	727.59

For	1000°F	(538°C)
-----	--------	---------

Strength PPT	P(norm)	P/(p)	Q(S)	Q(A)	T (temp K)
0	0	0	40000	114110	810.93
8.106626613	3.49E-08	0.290240909	40000	114110	810.93
9.680977554	6.97E-08	0.580481819	40000	114110	810.93
10.1582242	1.05E-07	0.870722728	40000	114110	810.93
10.02663889	2.09E-07	1.741445457	40000	114110	810.93
9.566292363	3.14E-07	2.612168185	40000	114110	810.93
9.166592981	4.18E-07	3.482890913	40000	114110	810.93
8.835576503	5.23E-07	4.353613642	40000	114110	810.93
8.556196078	6.28E-07	5.22433637	40000	114110	810.93
8.104282713	8.37E-07	6.965781826	40000	114110	810.93
6.995368955	1.67E-06	13.93156365	40000	114110	810.93
5.918523876	3.35E-06	27.86312731	40000	114110	810.93

For 950°F	(510°	C)
-----------	-------	----

Strength PPT	P(norm)	P/(p)	Q(S)	Q(A)	T (temp K)
0	0	0	40000	114110	783.15
7.594334163	1.98E-08	0.165198	40000	114110	783.15
9.813648739	3.97E-08	0.330396	40000	114110	783.15
10.90741443	5.95E-08	0.495594	40000	114110	783.15
11.87215982	1.19E-07	0.991187	40000	114110	783.15
11.78727213	1.79E-07	1.486781	40000	114110	783.15
11.49788481	2.38E-07	1.982375	40000	114110	783.15
10.42613343	4.76E-07	3.964749	40000	114110	783.15
9.173717183	9.53E-07	7.929499	40000	114110	783.15
7.886515761	1.91E-06	15.859	40000	114110	783.15

For 925°F (496°C)

Strength PPT	P(norm)	P/(p)	S(T, t)	Q(S)	Q(A)	T (temp K)
0	0	0		40000	114110	770
7.060385213	1.5E-08	0.12468		40000	114110	770
9.412902751	3E-08	0.24936		40000	114110	770
10.72202701	4.49E-08	0.374039		40000	114110	770
12.27293119	8.99E-08	0.748079		40000	114110	770
12.53216033	1.35E-07	1.122118		40000	114110	770
12.41440474	1.8E-07	1.496157		40000	114110	770
12.18811762	2.25E-07	1.870197		40000	114110	770
11.94165579	2.7E-07	2.244236		40000	114110	770
11.48236503	3.6E-07	2.992315		40000	114110	770
10.21208606	7.19E-07	5.983698		40000	114111	770
8.858514187	1.44E-06	11.96553		40000	114112	770

Vita

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Education

Ph.D, Industrial and Manufacturing Engineering, Expected December 2010 The Pennsylvania State University, University Park, PA Dissertation: Development of High Strength Corrosion Resistant Stainless Steels. Advisor: Dr. Robert Voigt

BS, Manufacturing Engineering/Industrial Engineering, May 2005 The Pennsylvania State University, University Park, PA Thesis: Time Transformation Behavior for Sigma Phase in CE3MN Cast Stainless Steel. Advisor: Dr. Victor Okhuysen

Publications

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