

Cast high Nickel containing austenitic alloys for paper and pulp industry

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ABSTRACT

High nickel-containing alloys find applications as engineering materials in the paper and pulp industry since they can be used in a wide variety of environments necessitating aqueous or high temperature corrosion resistance. These alloys are available in the wrought form as well as the cast form. High carbon containing cast nickel alloys find applications where high temperature resistance (for e.g. creep resistance, oxidation and carburization) are required whereas low carbon containing cast high nickel alloys find usage where wet corrosion is a challenge. Depending on the application and given the fact that nickel is an element which has an excellent metallurgical compatibility over a wide composition range with a variety of alloying elements, it is not uncommon to see a variety of alloys with different elemental additions being used to impart the desired properties necessary for the right application and intended performance. This paper shall review the existing knowledge on metallurgy and new innovations in terms of developments in cast high nickel alloys for high temperature and aqueous corrosion resistance.

INTRODUCTION

The paper and pulp industry offers a significant metallic material selection challenge due to the spectrum of possible corrosive environments. As an example of one end of the spectrum is the bleaching stage in pulp manufacture which removes brown lignin from cooked wood pulp by chemically breaking lignin molecules [1]. Bleaching process starts with an oxidizing, acidic stage using chlorine dioxide (D-stage) as the bleaching agent and is subsequently followed by an alkaline, caustic extraction (E-stage) to remove the soluble lignin. Material selection depends on the corrosiveness of the acidic oxidizing chloride containing solutions (especially in the D-stage). The operational temperatures are about 70-90 °C and the pH can be between 2.5 -3.5. This process necessitates the usage of aqueous corrosion resistant alloys for providing reliable service. On the other side of the spectrum a contrasting example of corrosive service is one which demands high temperature corrosion resistance. Lime kilns form part of the chemical recovery system in pulp mills where lime mud is converted to lime by calcination process [2]. The hot end of the kilns is typically experiencing temperatures of about 1150 -1250 °C. The calcined lime leaves the kiln through lump crushers and grizzlies and such conditions necessitate the usage of heat resistant alloys.

The paper and pulp industry is a highly capital and energy intensive one. Global paper production has crossed 400 million tons per year but has also coincided with stronger demands from society to have a more environmental friendly process since the industry has substantial climate change impacts [3]. This necessitates a change to cleaner production by using best possible technology to minimize the usage of primary raw materials, water, energy and chemicals. Given the fact that stricter regulation and enforcement by authorities becomes rightfully the new normal in this industry, the industry is under constant cost pressure to ensure a reliable operation. Since the process environments encountered are highly aggressive, materials costs as well as maintenance costs can be significant. This can be reduced as well as equipment reliability can be increased by upgrading to corrosion resistant materials.

The paper and pulp industry has got wide range experience with various corrosion resistant metallic alloys. An excellent treatise on this subject matter is available for mill engineers [4]. Among the various alloys for aqueous corrosion resistance, low carbon (0.03 - 0.15 wt. % C) containing metallic materials find applications. Conventional austenitic stainless form the majority usage followed by various grades of duplex stainless steels (lean, standard as well as superduplex). Martensitic stainless steels as well as precipitation hardening steels also find usage. Superaustenitic stainless steels (Fe-based austenitic) as well as high nickel-containing alloys (Ni-based austenitic) are used for the most aggressive conditions. Majority usage of low carbon high alloy corrosion resistant materials (in terms of tonnage) is still dominated by wrought materials than that for castings. This trend is reversed when high temperature corrosion resistance is the requirement. Alloys for such a service have high carbon (0.40 - 0.75 wt. % C) in order to have carbides in their microstructure to realize the necessary mechanical strength at elevated temperatures. A higher carbon containing alloy is easier to cast and difficult to work due to its inherent brittleness.

Casting as a metal working process offers the simplest form of converting a liquid metal into a solid shape and offers design and composition freedom which is unparalleled. However, it is also a challenging manufacturing method which necessitates a good understanding of alloy metallurgy, solidification, microstructure development, influence of various process variables, heat treatment as well as quality control processes. It is also a process where early stage involvement of end user and foundry is necessary to arrive at a common understanding to realize an engineering product which will have the desired functionality. Alloy castings made of superaustenitic stainless steels as well as high nickel alloys increase the challenge due to the influence of various alloying elements, which though necessary for the realization of properties, add to the complexity due to the multicomponent solidification and generation of phases which are not necessarily desirable. Notwithstanding these challenges, there are numerous cast high performance alloys consisting of low carbon stainless steels (superaustenites as well as Ni-Cr-Mo alloys) as well high carbon variants (Ni-Cr-Fe alloys with other additions). This article shall focus on the metallurgy, microstructure, mechanical properties as well as corrosion resistance of cast superaustenitics, Ni-Cr-Mo alloys as well as heat resistant Ni-Cr-Fe alloys. Each cast material type is unique and the role of various alloying elements in deriving the functional properties and are reviewed. Microstructural features necessary for the required properties and performance are identified. Some new innovation in cast metallic materials is introduced and their properties are compared with the existing cast high performance alloys.

CAST SUPERAUSTENITIC STEELS FOR AQUEOUS CORROSION RESISTANCE

Superaustenitic steel are a group of Fe-based alloys and can be described as a sub-group of austenitic stainless with higher amount of chromium, nickel, molybdenum and nitrogen than the conventional austenitic stainless steel. They contain chromium (19-38 wt. %), Ni (17-24 wt. %), molybdenum (2-8 wt.%) and nitrogen from 0.15-0.55 wt% [5,6]. Table 1 summarizes the chemical composition of the cast superaustenitic stainless steels. As the name indicates, they have an austenitic microstructure and have a face-centered cubic (fcc) crystal structure whereby atoms are located at the corners and face centers of the cubic lattice. Elements like Cr, Mo, Ni, Mn, Cu occupy the crystal lattice on substitutional sites whereas elements like C, N occupy the interstitial sites. The individual contribution from each of the alloying elements is briefly described here. Chromium, a ferrite stabilizer is the alloying element which makes the steel stain resistant. At Cr > 10.5 wt.%, a surface film is formed which is passive and thus effective in protecting the stainless steel from harsh environments like acids, oxidizing high temperature gases. Nickel is a major alloying element and its primary purpose is to stabilize the austenitic microstructure. Nickel aids in improving the corrosion resistance in certain reducing acids as well as leads to increase in stress corrosion cracking resistance. Molybdenum, another ferrite stabilizer, increases the localized corrosion resistance i.e. pitting and crevice corrosion resistance, especially in chloride containing environment. It also increases corrosion resistance in reducing environments like hydrochloric acid and dilute sulfuric acid. Carbon strengthens austenite interstitially but is limited to the lowest practical levels since it is

detrimental to corrosion resistance. This is due to the readiness for carbon to combine with chromium to form carbides. Formation of carbides results in chromium depletion in the matrix and thereby contributes to reduction in the corrosion resistance. Hence, carbon content is normally kept below 0.03 wt.%.

Table 1: Chemical composition (in wt.%) for cast superaustenitics.

High performance fully austenitic and superaustenitic castings								
DIN EN 10213/ 10283								
ACI Designation Generic Designation	Ni	Cr	Mo	N	Cu	Mn	C	Si
1.4584	24.00-26.00	19.00-21.00	4.00-5.00	0.20	1.00-3.00	2.00	0.025	1.00
1.4587	28.00-30.00	24.00-26.00	4.00-5.00	0.15-0.25	2.00-3.00	2.00	0.030	1.00
1.4416	24.00-26.00	19.00-21.00	4.50-5.50	0.12-0.20	-	1.00	0.030	1.00
1.4588	24.00-26.00	19.00-21.00	6.00-7.00	0.10-0.25	0.50-1.50	2.00	0.025	1.00
1.4557	17.50-19.50	19.50-21.50	6.00-7.00	0.18-0.24	0.50-1.00	1.20	0.025	1.00
ASTM A743/ A 744/ A351								
CK3MCuN	17.50-19.50	19.50-20.50	6.00-7.00	0.18-0.24	0.50-1.00	1.20	0.025	1.20
CN3MN	23.50-25.50	20.00-22.00	6.00-7.00	0.18-0.26	0.75	2.00	0.030	2.00
CK35MN	20.00-22.00	22.00-24.00	6.00-6.80	0.21-0.32	0.40	2.00	0.035	1.00
Other alloys (not indexed in cast standards but produced as castings)								
Alloy 28	30.00-32.00	26.00-28.00	3.00-4.00	-	0.70-1.50	2.00	0.02	0.70
904L	23.00-28.00	19.00-23.00	4.00-5.00	0.10	1.00-2.00	2.00	0.02	0.70
Alloy 24	16.00-19.00	24.00-26.00	4.00-5.00	0.30-0.60	-	5.00-7.00	0.030	1.00
Märker® MARESIST®G 4565 S	17.00-19.00	23.00-25.00	4.00-5.60	0.40-0.50	-	5.00-7.00	0.03	0.50
Märker® Alloy 31	30.00-32.00	26.00-28.00	6.00-7.00	0.15-0.25	1.00-1.40	2.00	0.020	0.30
Alloy 926	24.00-26.00	20.00-21.00	6.00-7.00	0.15-0.25	0.50-1.50	1.00	0.02	0.50
654 SMO	21.00-23.00	23.00-25.00	7.10-7.50	0.40-0.55	0.30-0.70	2.00-4.00	0.025	0.50
Single values denote maximum, balance is Fe 654SMO: Outokumpu Märker® MARESIST®G 4565 S: Schmidt + Clemens ACI: Alloy Casting Institute								

Nitrogen is a well-known austenite strengthening interstitial. Nitrogen alloying offers an opportunity but is also a demanding challenge in that the solubility of nitrogen in liquid Fe is limited at atmospheric pressure. This can be increased by increasing the nitrogen gas pressure above the melt and also via alloying addition. The nitrogen solubility is increased by increasing the Cr, Mn, Mo in steel whereas increase in Ni, Si, C and Cu decrease the solubility. Nitrogen improves resistance to chloride pitting and crevice corrosion. Manganese, an austenite stabilizer is used to deoxidize the molten steel but also serves as an alloying element. It increases the solubility of nitrogen and hence the superaustenitic materials normally have higher manganese content relative to conventional austenitic stainless steels. The cast G 4565 S, Alloy 24 as well as 654 SMO are some of the alloys which have more than 2% Mn. Copper, an austenite stabilizer, is alloyed to impart corrosion resistance of superaustenitic stainless steels in reducing acids like sulfuric acid and phosphoric acid mixtures. Silicon, a ferrite stabilizer, is used to deoxidize the steel and hence is always present as inclusions. Even though silicon is favored by casters as it increases the fluidity of the metal, it is kept to low levels since it also stabilizes unfavorable phases which are detrimental to the mechanical properties as well as the corrosion resistance. Trace elements like sulfur, phosphorous are kept to the absolute minimum level so that fabricability of these steels is not negatively affected.

Table 2 summarizes the cast superaustenitic stainless steels and their wrought equivalents [7,8]. It is evident that there are numerous alloys available within the family of cast superaustenitic stainless steels. Seven of them are also covered by the international standards for corrosion resistant castings. Six of these grades have been directly adopted by foundries based on the wrought composition but are not indexed in the standards and one of them is a standalone cast alloy (G 4565 S). Table 3 summarizes the mechanical

properties as well as the Pitting Resistance Equivalent (PREN) for the cast superaustenitic stainless steels. One definition of superaustenitic stainless is an austenitic stainless steel having a PREN value equal to or larger than 40. The PREN is based on material chemistry i.e. the Cr, Mo and N content, and this can vary based on the specific chemical composition of the heat which is, in turn, determined by the minimum and maximum specified within the governing specification.

Table 2: Cast superaustenitics and their wrought equivalents [7, 8].

ACI Designation Generic Designation	CAST STANDARDS		WROUGHT STANDARDS	
	ASTM	DIN EN	ASTM	DIN EN
Alloy 24	-	-	S34565	1.4565
Alloy 28	-	-	N08028	1.4563
Alloy 31	-	-	N08031	1.4562
654 SMO	-	-	S32654	1.4652
904L	-	-	N08904	1.4539
254SMO/CK3MCuN	J93254	1.4557	S31254	1.4547
CK35MN	-	-	-	-
AL-6XN/CN3MN	J94651	~ 1.4588	N08367	-
1.4458	-	1.4458	-	-
1.4584	-	1.4584	-	-
1.4416	-	1.4416	-	-
1.4587	-	1.4587	-	-
Alloy 926		1.4588	N08926	1.4529
Märker® MARESIST® G 4565 S	-	-	S34565	1.4565
254 SMO, 654 SMO : Outokumpu				
AL-6XN : ATI				
Märker® MARESIST® G 4565 S: Schmidt + Clemens				

Table 3: Mechanical properties (minimum requirements) at room temperature and

PREN values for cast superaustenitics [9,10].

ACI Designation Generic Designation	0.2% Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	Impact energy (J)	PREN (%Cr +3.3Mo+16N)	
					min.	max.
1.4584	185	450	30	60	32	41
904L	200	460	25	70	32	41
1.4416	185	450	30	60	36	42
Alloy 28	200	460	30	70	36	41
1.4587	220	480	30	60	40	47
1.4588	210	480	30	60	40	48
Alloy 24	340	600	35	140	42	52
CK3MCuN	260	550	35	120	42	47
Alloy 926	260	550	35	120	42	48
CN3MN	260	550	35	120	43	49
G 4565 S	325	600-750	35	100	43	51
1.4557	260	500	35	50	43	48
CK35MN	280	570	35		45	52
Alloy 31	285	450-650	40	120	48	55
654 SMO	340	620	35	120	53	59

Based on the PREN data available in Table 3 it can be realized that the alloys 904 L, 1.4584, 1, 4416, Alloy 28 can be at best described as a marginal superaustenitic. The true superaustenitics from the first generation are the CK3MCUN, CN3MN and 1.4588. The mechanical properties and corrosion resistance of these superaustenitic castings are superior to that of conventional austenitic castings (i.e. CF3, CF3M and CF3MN) due to the increased amount of nickel, molybdenum and nitrogen. Molybdenum and nitrogen also contribute significant to the localized corrosion resistance. The second generation superaustenitic castings like Alloy 31, G 4565 S, 654 SMO, Alloy 24 demonstrate further increase in the mechanical properties as well as corrosion resistance. Alloy 24 as well as G 4565 S are very similar in chemical composition and are essentially cast variants of the wrought UNS S34565 and demonstrate that marginal changes in chemistry can lead to changes in the mechanical properties. The development of these cast alloys has been possible by continuous research and development activities by innovation driven foundries. Unlike in case of wrought superaustenitic materials where melt purification is possible using special melting processes like argon oxygen decarburization (AOD), vacuum oxygen decarburization (VOD) and electroslag remelting (ESR) processes, castings are typically made by melting the liquid steel of desired composition in an air induction melting furnace. There is no secondary melting step in foundries. The production of castings requires careful selection of raw materials as well as specific metallurgical considerations to realize the low carbon, low silicon and low sulfur contents. Lower carbon and lower silicon pose challenge in terms of fluidity, shrinkage, furnace lining, solidification range, casting temperature and deoxidation practices.

The ideal and desired microstructure for superaustenitic castings is a 100% austenitic microstructure. However, higher alloying content coupled with slow solidification leads to undesirable effects in the as-cast microstructure. Casting is a liquid to solid transformation and is dendritic in nature. The initial solid that forms upon solidification leads to change in the chemical composition of the remaining liquid. This is because the liquid that is freezing rejects solutes as the solid has less solubility for them as compared to the liquid. This effect is known as segregation and leads to enrichment of solute in the remaining liquid which is then prone to other reactions like for e.g. formation of oxides, nitrides as well as other phases during its solidification. Solute segregation in superaustenitic castings is essentially due to Mo. This leads to the formation of undesirable phases in the interdendritic regions (regions which are the last to solidify). It is not untypical for an as-cast microstructure to have carbides as well as undesirable intermetallic phases like sigma, chi [11,12,13]. These phases as well as carbides are undesirable since they impair the mechanical properties as well as the corrosion resistance. It is for this reason that superaustenitic castings need to be solution heat treated prior to application. The solution heat treatment serves a two-fold purpose. One is to homogenize the austenite and remove the effects of segregation and the other is to bring into solution the undesirable phases. Solution heat treatment temperature of more than 1200 °C is normally needed for superaustenitic castings. Additionally, the duration of the solution heat treatment also needs to be optimized based on the thickness of the casting as well as due to the fact that solid state diffusion in austenite is a slow process requiring time. Cooling of a solution heat treated casting need to be accomplished in a rapid way i.e. by rapid quenching in water. This is necessary to avoid the reformation of undesirable phases like for e.g. chi phase which can form at much shorter times for a high Mo containing alloy as well as chromium carbides along austenite grain boundaries. This requires proper understanding of the kinetics of secondary phase formation as is normally described by the time-temperature-transformation (TTT) curves. For lower nitrogen alloying content, the addition of nitrogen pushes back the onset of formation of carbides and chi phases but there is a limit and this is not easy for very high Mo containing superaustenitics. This necessitates extensive testing of the heat treatment parameters.

The mechanical properties of cast superaustenitic steels are essentially derived by solid solution strengthening. This is in difference to wrought superaustenitic steels where cold working as well as strain ageing can lead to further enhancements in the mechanical properties due to grains size reduction. Substitutional solid solution strengthening is provided by addition of nickel and molybdenum whereas interstitial solid solution strengthening of the austenite is provided by the addition of nitrogen. The

increase in yield strength of the cast superaustenitics over cast standard austenitic is due to the additional molybdenum and nitrogen. The ductility (in terms of elongation) of cast superaustenitic is also similar to that of standard austenitic. In general, an austenitic structure displays good ductility. Also shown in Table 3 are the minimum impact toughness requirements at room temperature for cast superaustenitics. Unlike ferritic and duplex stainless steels, there is no ductile to brittle transition as temperature is reduced. The impact toughness is also an indicator for the quality of heat treatment and is negatively influenced if the heat treatment parameters (temperature, time, transfer time and quenching medium) are not correct.

General corrosion resistance for cast superaustenitics is generally better than that of cast standard austenitic grades due to the presence of increased molybdenum in the passive film. For oxidizing environment, a grade having more chromium gives better performance. For reducing media, grades with higher chromium, nickel, molybdenum and copper are superior. Localized corrosion, especially in chloride containing environments i.e. pitting resistance increased with higher Cr, Mo and N. The critical pitting temperature (CPT) as per ASTM G48 for cast CK3MCuN is at 50 °C whereas that for G 4565 S is 80 °C. While no data exists in open literature for the CPT of cast 654 SMO, which has the highest alloying content in terms of nitrogen and molybdenum, it is expected that this value shall be even higher than 80 °C. This is the reason for Fe-based superaustenitics are, as a family, being considered as a more economic but functionally equal alternative to high Ni-Cr-Mo alloys for highly corrosive applications. The localized corrosion resistance is also negatively influenced due to the presence of undesirable phases like sigma, chi, carbides as well as oxides and sulfide inclusions. The presence of these phases on the steel surface represents discontinuities and thus can facilitate pitting or crevice corrosion. A pickling or passivation can remove them from the surface and minimize their negative effect. Cast superaustenitic stainless steels are also more resistant to stress corrosion cracking, especially to chloride induced stress corrosion cracking as well as caustic cracking than the standard cast austenitic. This is also due to the higher chromium, molybdenum and nickel content. Limited corrosion resistance data (weight loss in mm/a) is available for cast austenitic and the literature reporting this data are cited here [14]. The corrosion resistance of cast Alloy 31 matches that of wrought UNS N08031 in 54% phosphoric acid with 20000 ppm chloride at 100 °C, 20% sulfuric acid at 100 °C, 8% hydrochloric acid at 20 °C as well as at 70% hydrofluoric acid at 20 °C. These results demonstrate that the by proper control of metallurgy, alloy chemistry as well as right foundry practice, it is possible to have a cast superaustenitic alloy which matches the wrought properties in terms of corrosion resistance.

Weldability of cast austenitic stainless steel needs considerable expertise since the high alloying content as well as repeated weld cycles create microstructural variations in the heat affected zone. This results in formation of undesirable phases as well as microsegregation due to the use of high molybdenum containing weld metal. It is common to weld using an overalloyed filler material. Post weld heat treatment is necessary in case of autogenous welding (no filler material used). Some of the covered welding electrodes are E NiCrMo-3, E NiCrMo-4, E NiCrMo-10, E NiCrMo-12, E NiCrMo-13 and E NiCrMo-14 whereas the bare welding electrodes and rods are ER NiCrMo-3, ER NiCrMo-4, ER NiCrMo-10, ER NiCrMo-13 and ER NiCrMo-15.

CAST HIGH NICKEL ALLOYS FOR AQUEOUS CORROSION RESISTANCE

Low carbon high Ni-Cr-Mo alloys offer the highest corrosion resistance amongst stainless steels and related alloys to oxidizing agents such as chlorine dioxide, especially when it comes to pitting, crevice and stress corrosion cracking. Cast alloys are covered by the ASTM standards [15]. Most alloys have been developed as cast equivalents of well-known wrought Ni-Cr-Mo alloys. However, there are also proprietary grades which have been successfully employed for various applications [16]. These alloys are usually selected only for the most severe service conditions where less costly stainless steels have proven their inadequacy in terms of their engineering functionality. Table 4 shows a list of cast Ni-Cr-Mo alloys.

Table 4: Chemical composition (in weight %) for cast Ni-Cr-Mo alloys.

Cast Nickel based alloys used for wet corrosion environments									
ACI Designation (UNS)	Wrought Grade Generic Designation (UNS)	Cr	Mo	Fe	Cu	C	Si	Mn	Others
CW6MC (N26625)	Alloy 625 (N06625)	20.00-23.00	8.00-10.00	5.00	-	0.06	1.00	1.00	3.15-4.50 Nb
CX2MW (N26022)	Alloy C-22 (N06022)	20.00-22.50	12.50-14.50	2.00	-	0.02	0.80	1.00	2.50-3.50 W 0.35 V
Centralloy® G 45Mo	-	34.00-36.00	9.00-10.00	5.00-9.00	1.00-3.00	0.015	0.20	0.40	0.24 N 1.50 W 1.50 Ta
CW2M (N26455)	Alloy C-4 (N06455)	15.00-17.50	15.00-17.50	2.00	-	0.02	0.80	1.00	1.00 W
Euzonit G 60	-	18.00-21.00	15.00-16.50	1.00	-	0.02	0.50	1.00	-
CW12MW (N30002)	Alloy C-276 (N10276)	15.50-17.50	16.00-18.00	4.50-7.50	-	0.12	1.00	1.00	3.75-5.25 W 0.20-0.40 V
CX2M (N26059)	Alloy 59 (N06059)	22.00-24.00	15.00-16.50	1.50	-	0.02	0.50	1.00	-
CW6M (N30107)	Alloy C	17.00-20.00	17.00-20.00	3.00	-	0.07	1.00	1.00	-
Single values denote maximum, balance is Ni Centralloy® and EUZONIT: Schmidt + Clemens									

The atomic structure of the Ni-Cr-Mo alloys is face-centered cubic (fcc). In this respect, they are similar to the austenitic stainless steels and the superaustenitics. Due to the high alloying content, they are more susceptible to the formation of deleterious phases during cooling. They are normally supplied in the solution annealed condition. Figure 1 shows the columnar grain macrostructure of a centrifugally cast corrosion resistant alloy. This is a result of the directional solidification process.



Figure 1: Grain macrostructure of cast corrosion resistant alloy.

Figure 2 (a and b) shows the as-cast microstructure of CW6MC. The microstructure reveals the presence of austenite matrix and another intermetallic phase which is formed as a result of the segregation of alloying elements like Nb and Mo during the solidification. The final microstructure of solution annealed CW6MC is a mixture of austenite and a small volume fraction of this Nb₃Mo- rich intermetallic phase. It is not possible to realize a intermetallic precipitate free microstructure for this alloy in both the wrought and cast form. One can only minimize it using strong experience. This requires understanding of the complex interplay between composition, heat treatment practice as well as solidification parameters.

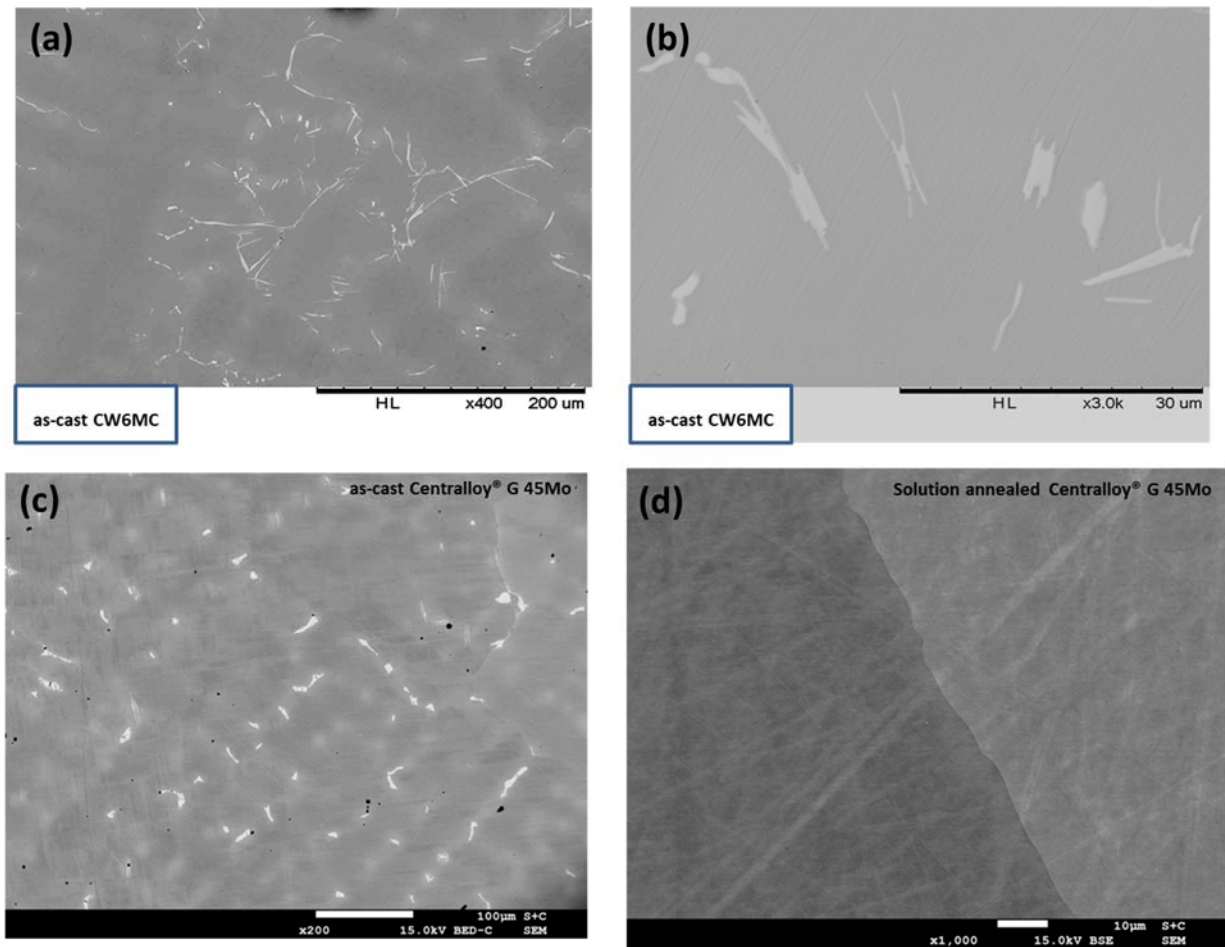


Figure 2: Microstructural features of cast Ni-Cr-Mo alloys.

An new Ni-Cr-Mo alloy developed as a standalone cast alloy is the Centralloy® G 45Mo. Figure 2(c) shows the as-cast microstructure of Centralloy® G 45Mo. It reveals an austenitic matrix with intermetallic phases formed during solidification. In case of this alloy, the intermetallic case is enriched in Cr and Mo relative to the matrix [16]. Solution heat treatment results of dissolution of this phase and results in a precipitate free microstructure as in Figure 2(d). The microstructure is mostly intermetallic precipitate free. The microstructure of cast Ni-Cr-Mo alloys also has oxide inclusions particles of 7-10 μm in size due to the air induction melting process [16]. One approach of testing the quality of heat treatment is to have impact toughness testing specified as a part of the quality control. The impact toughness values are severely impaired due to the presence of significant fraction of intermetallic phase present, which is normally a result of improper heat treatment procedure. The mechanical properties of Ni-Cr-Mo castings (Table 5) are similar to cast superaustenitic given that the microstructure is austenitic and the only way to strengthen the alloy is by solid solution strengthening. In case of Ni-Cr-Mo alloys, Cr, Mo, Nb and W are substitutional solid solution strengthener. Interstitial solid solution strengthening by nitrogen is difficult since the solubility of nitrogen in an iron-based alloy (superaustenitic) is higher than in a nickel-based alloy. To increase the solubility of nitrogen in an nickel based alloy, one needs to increase the Cr, Mo, Mn and Fe which essentially shifts the chemical composition towards superaustenitic. In terms of mechanical properties, Ni-Cr-Mo alloys have a yield strength of about 275 MPa at room temperature A new alloy which is essentially a bridge alloy between the superaustenitic and Ni-Cr-Mo alloy is the

Centralloy® G 45Mo. With yield strength of 350 MPa at room temperature it has the highest mechanical properties amongst the known cast superaustenitic and cast Ni-Cr-Mo alloys [17]. Additionally, it has corrosion resistance similar or exceeding that of existing Ni-Cr-Mo alloys like the CW6MC, CW12MW and CX2MW as well as superaustenites in the solution annealed condition. It also offers an economical alternative to the aforementioned Ni-Cr-Mo alloys [17]. The PREN of Ni-Cr-Mo alloys are in the range of 46-86. The high (and almost twice) the value over superaustenitics is due to the increased amount of molybdenum in these alloys. Ni-Cr-Mo alloys are used in service conditions with the highest risk for localized corrosion and perform under conditions where superaustenitics fail to deliver. CW6M can be used in most D stage environments due to the higher chromium in addition to molybdenum and this imparts resistance to chlorine dioxide. CM12W can have the same corrosion resistance but has inferior mechanical properties i.e. the ductility is very low and this also has a negative impact on the weldability of the alloy. It is expected that the CW2M, CX2MW as well as the Centralloy® G45 Mo alloy, all of which have high values of Cr + Mo, are extremely suitable for chloride service. Summarizing, the mechanical properties as well as corrosion resistance of Ni-Cr-Mo castings is realized by closer control on the chemistry of the melt as well as proper heat treatment practices.

Table 5: Mechanical properties (minimum requirements) at room temperature and PREN values for cast Ni-Cr-Mo alloys [15,17].

ACI Designation (UNS)	0.2% Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	PREN (%Cr +3.3Mo+16N)	
				min.	max.
CW6MC (N26625)	275	485	25	46	56
CX2MW (N26022)	310	550	30	61	70
Centralloy® G 45Mo	350	550	35	64	69
CW2M (N26455)	275	495	25	65	75
Euzonit G 60	265	550	35	68	75
CW12MW (N30002)	275	495	4	68	77
CX2M (N26059)	270	495	40	72	78
CW6M (N30107)	275	495	25	73	86

CAST HIGH NICKEL ALLOYS FOR HIGH TEMPERATURE RESISTANCE

Cast heat resistant nickel alloys are primarily composed of nickel, chromium and iron with smaller amounts of other elements [18]. The elements that mainly contribute towards the high temperature properties are the chromium and nickel. Castings for heat resistance applications need to fulfill two key material property requirements. One is to have a good oxidation resistance by having a surface layer which is stable and the other is to demonstrate sufficient mechanical strength and ductility at elevated temperatures. A brief contribution on the role of individual alloying elements is mentioned here. Nickel, an austenite stabilizer, contributes to formation of austenite. Austenite is stronger than ferrite at elevated temperatures. Nickel also contributes towards increasing the resistance to oxidation, carburization and thermal fatigue. Chromium, a ferrite stabilizer, contributes to oxidation by the formation of chromia scale on the surface. Chromia scales enable surface stability to about 1150 °C. Chromium also contributes to the strengthening of the austenitic alloy by aiding in the formation of chromium carbides which offer

resistance to the movement of dislocations at elevated temperature. Carbon, an austenite stabilizer, promotes the formation of carbides which are necessary for the high temperature strength. However, too much of it also leads to impairment of ductility. Silicon, a ferrite former, positively influences the oxidation resistance and the fluidity of the metal. Manganese, an austenite former, has no significant effect on the mechanical properties. There have been numerous innovations by foundries in the heat resistant alloy segment since castings having a coarser grain structure have superior high temperature deformation property i.e. creep resistance relative to a fine grained wrought alloy. The alloys used for high temperature service derive their strength by a combination of solid solution strengthening as well as precipitation hardening. Cast high carbon containing Fe-Cr-Ni alloys solidify in the austenitic mode. However, due to the rapid solidification process, a major portion of the alloyed carbon gets supersaturated in the austenite since the diffusion is not able to keep in pace with the falling temperature. This comes to a significant benefit when these alloys are exposed to the service temperatures i.e. 900-1150 °C. At these temperatures, diffusion becomes easier and aids in the formation of secondary carbides which impart the necessary creep strength. It has been shown that minor additions of alloying elements like niobium, titanium, and zirconium can result in even superior creep resistance. This has led to the development of numerous microalloyed grades. Table 6 shows the chemical composition of cast heat resistant alloys used for lime kiln applications within the paper and pulp industry.

Table 6: Chemical composition of cast heat resistant alloys [9,19,20].

Cast high nickel alloys used for high temperature applications in the paper and pulp industry								
ACI Designation	UNS (W. Nr.)	Cr	Ni	C	Mn	Si	Mo	Other
HD	J93005	26.00-30.00	04.00-07.00	0.50	2.00	2.00	0.50	-
HE	J93403	26.00-30.00	08.00-11.00	0.20-0.50	2.00	2.00	0.50	-
HF	J92603	19.00-23.00	09.00-11.00	0.20-0.40	2.00	2.00	0.50	-
HH	J93503	24.00-28.00	11.00-14.00	0.20-0.50	2.00	2.00	0.50	-
HI	J94003	26.00-30.00	14.00-18.00	0.20-0.50	2.00	2.00	0.50	-
HK	J94224	24.00-28.00	18.00-22.00	0.20-0.60	2.00	2.00	0.50	-
HL	J94604	28.00-32.00	18.00-22.00	0.20-0.60	2.00	2.00	0.50	-
HN	J94213	19.00-23.00	23.00-27.00	0.20-0.50	2.00	2.00	0.50	-
HP	J95705	24.00-28.00	33.00-37.00	0.35-0.75	2.00	2.00	0.50	-
HP + Nb	(1.4852)	24.00-27.00	33.00-36.00	0.30-0.50	2.00	1.00-2.50	0.50	0.80-1.80 Nb
HP + Nb (MA)	Centralloy® G 4852 MICRO	24.00-27.00	33.00-36.00	0.30-0.50	2.00	1.00-2.50	0.50	0.80-1.80 Nb Ti, Zr
Single values denote maximum, balance is Fe Centralloy® G 4852 MICRO: Schmidt + Clemens								

Fig. 3 shows the microstructure of as-cast heat resistant HP + Nb (MA). The solidification mode is austenitic and the final solidified microstructure is an austenitic matrix and an interdendritic distribution of eutectic carbides. The presence of microalloying elements like Ti,Zr lead to formation of primary Ti-rich carbonitrides $[M(C,N)]$ in addition to the primary Cr- rich M_7C_3 carbides as well as carbides of the type MC which are Nb-rich. Upon exposure to the service application temperature, fine distribution of secondary carbides is realized due to the precipitation from the matrix and results in the formation of Cr-rich $M_{23}C_6$ carbides. An example of such a microstructural state is shown in Figure 3 (b). These carbides as well as the complex form of the primary interdendritic carbides help in realizing the required high temperature strength.

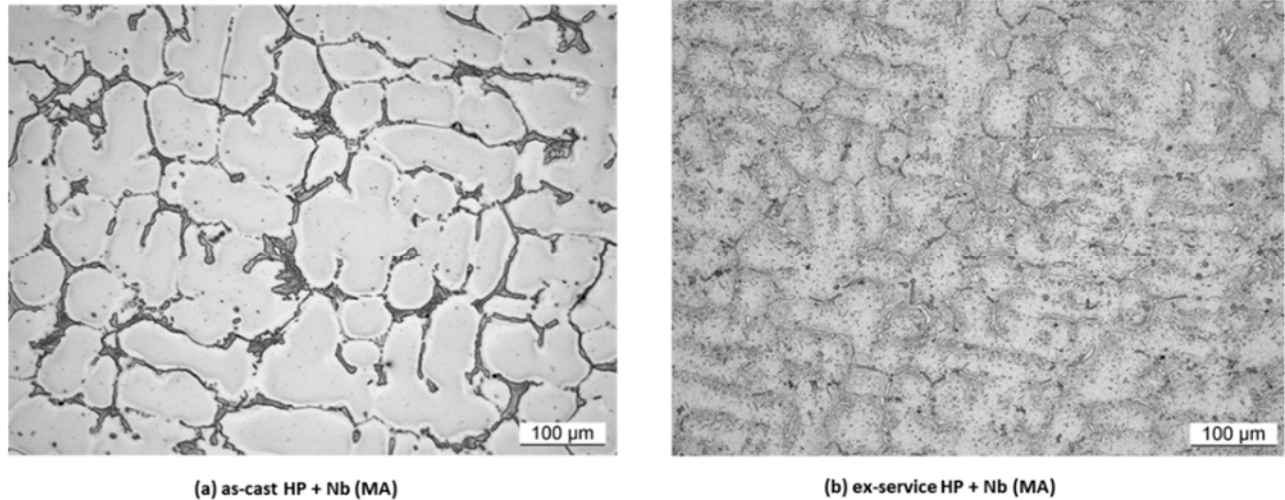


Figure 3: Optical microscopy structure of cast heat resistant alloy.

The most important mechanical property for high temperature application is the creep resistance. Table 7 shows the mechanical properties at elevated temperature for selected cast heat resistant high nickel alloys. To compare different alloys, the stress required to have 1% creep in 10,000 h at a specified temperature is used as the yardstick. This creep data is normally obtained by conducting elevated temperature testing under a constant load and temperature. Table 7 shows stress required to cause failure in 10,000 h for some of the cast alloys. Increase in the nickel leads to significant improvement in the creep resistance. However, the addition of niobium as well as microalloying elements like Ti and Zr lead to further increase in the stress necessary to cause deformation. For e.g. the stress necessary to cause 1% creep in 10,000 h is 7 MPa for HK grade casting but is 14 MPa for the microalloyed alloy. Such property enhancements in heat resistant grades offers process benefits to users of heat resistant grades to extend their equipment and component lifetime and thereby increase the reliability. Another approach is to use superior alloy metallurgy to realize higher operational temperatures and thereby a better throughput. As is with corrosion resistant castings for aqueous corrosion applications, a closer interaction between the end user and foundry is desirable to realize benefits for all stakeholders.

Table 7: Creep resistance of heat resistant alloys [9,20].

ACI Designation	Temperature (°C)	900 °C	1000 °C	1100 °C
	Stress (MPa)	$\sigma_{1\%}$	$\sigma_{1\%}$	$\sigma_{1\%}$
	Time (h)	10,000 h	10,000 h	10,000 h
HD		4	1	-
HH		13	6	-
HK		17	7	2.5
HP		20	8	-
HP + Nb		22	9	3
HP + Nb (MA)		29	14	4

CONCLUSION

There exist numerous cast superaustenitics, Ni-Cr-Mo castings which can be used for aqueous corrosion resistance applications in the paper and pulp industry. Superaustenitic castings derive their mechanical strength by a combination of interstitial and substitutional solid solution strengthening. The ability to alloy with nitrogen enhances both the mechanical property as well as the corrosion resistance. The corrosion resistance is also improved by the presence of more than 6% Mo in most of the grades. Cast Ni-Cr-Mo castings offer even superior corrosion resistance than superaustenitic grades. They derive their strength by solid solution strengthening and their corrosion resistance due to the sufficient amount of Cr and Mo. They represent the ultimate in terms of corrosion resistant material amongst the stainless steels and related alloys. High carbon containing Ni-Cr-Fe castings for elevated temperature applications derive their mechanical strength via a combination of solid solution strengthening as well as precipitation hardening. Precipitation hardening is caused by formation of secondary carbides at service temperature. Numerous cast grades are available and effective use of micro alloying elements in these grades can lead to superior creep resistance. Cast high nickel-containing alloys for wet corrosion resistance as well as heat resistant applications need good understanding of solidification, heat treatment, chemical composition control as well as foundry experience. Innovation drive foundries have the capability to tailor make solutions for end users based on their historical knowledge and openness to work together. A closer cooperation at an early stage of a project between the end user and foundry can avoid numerous pitfalls which are normally associated with procurement of such high alloy, capital intensive and long lead time critical items.

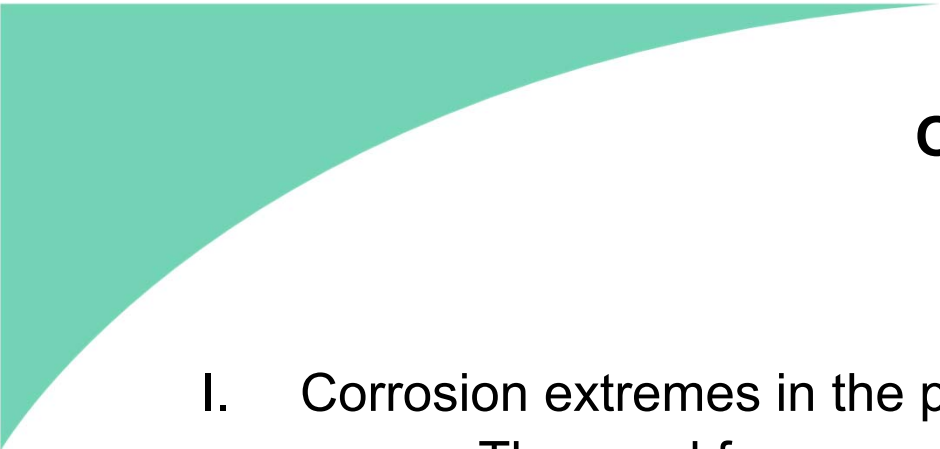
REFERENCES

1. M. Liljas, R. Pettersson, L. Wegrelius, R. Davison, "UNS S31254-A bleach plant success story", Paper No. 10083, CORROSION 2010.
2. J.J. Perdomo, "Rotary Lime Kiln Materials Issues and repairs", Paper No. 07212, CORROSION 2007.
3. J. Martin and M. Haggith (Eds.), "The state of the global paper industry 2018" Environmental Paper Network
4. Nickel Institute, Stainless steels and special alloys for pulp, paper and biomass conversion, 2nd Edition, 2017.
5. V.G. Gavriljuk, H. Berns, High Nitrogen Steels, Structure, Properties, Manufacture, Applications, Springer Verlag Berlin, 1999 ISBN 3-540-66411-4.
6. J. Anburaj, A. Chandrasekar, B. Anandavel, R. Narayanan, S.S. Mohamed Nazirudeen; „A study on melting practice of high nitrogen superaustenitic stainless steels using conventional induction melting technique”, Indian Foundry Journal, 2012, vol. 58, pp. 31-37.
7. ASTM A743/A743M Standard Specification for Castings, Iron-Chromium, Iron-Chromium-Nickel, Corrosion Resistant, for general applications.
8. DIN EN 10283 Corrosion resistant steel castings.
9. www.schmidt-clemens.de
10. www.fondinox.it
11. Phillips, Nathaniel Steven Lee, "Phase transformations in cast superaustenitic stainless steel"(2006). Retrospective Theses and Dissertations. 844. <https://lib.dr.iastate.edu/rtd/844>
12. J.N. DuPont, J.D. Farren, "Influence of Heat Treatment Time and Temperature on the Microstructure and Corrosion Resistance of Cast Superaustenitic Stainless Steels", Corrosion, 2011, vol.67, pp.055002:1-11.
13. Z.G. Song, E.X. Pu, "Precipitated phases of superaustenitic stainless steel 654 SMO", Journal of Iron and Steel, International. 2017, vol. 24, pp.743-749.
14. R. Kirchheiner, G-W. Overbeck, "Development of high performance cast alloys Alloy 31 and Alloy 9 for the chemical process industry", Paper No. 07187, CORROSION 2007.

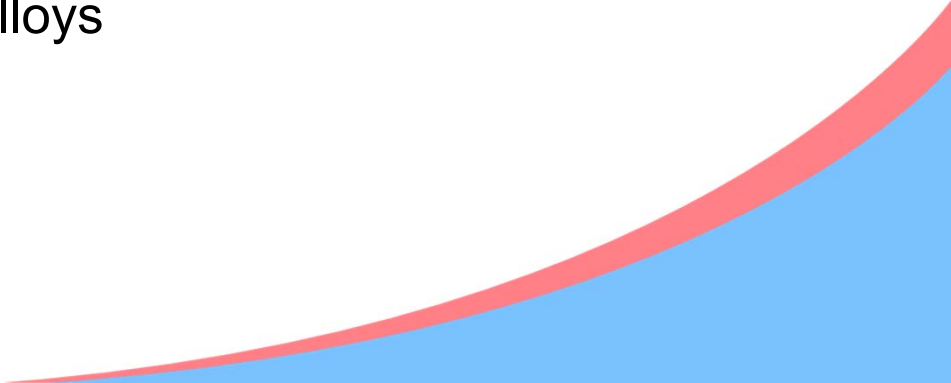
15. ASTM A494/A494M Standard Specification for Castings, Nickel and nickel alloy.
J R Davies (Ed.), *Cast Corrosion Resistant Nickel Alloys: ASM Specialty Handbook: Nickel, Cobalt and their alloys*: ASM International, 2000, ISBN: 978-0-87170-685-0.
16. S. Venkataraman, D. Jakobi, "A study on the microstructure, mechanical properties and corrosion resistance of centrifugally cast heavy wall thickness low carbon 46Ni-35Cr-9Mo alloy. Paper No. 9349, CORROSION 2017.
17. H. Asteman, D. Jakobi, "A new cast alloy with high strength and excellent corrosion resistance-an alternative to the conventional Ni-base alloys". Paper No. 5760, CORROSION 2015.
18. G Y Lai, *High Temperature Corrosion and Materials Applications*, 2007,ASM International, ISBN 978-0871708533
19. ASTM A297 Standard Specification for Steel Castings, Iron-Chromium and Iron-Chromium-Nickel, Heat Resistant, for General Application.
20. DIN EN 10295 Heat resistant steel castings.

Cast high nickel containing austenitic alloys for paper and pulp industry

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OUTLINE

- I. Corrosion extremes in the paper industry
 - The need for corrosion resistant metallic materials
 - II. Cast alloys for wet corrosion applications
 - Superaustenitics
 - Ni-Cr-Mo alloys
 - III. Cast corrosion resistant alloys for high temperature applications
 - Ni-Cr-Fe/Fe-Ni-Cr/Cr-Ni-Fe alloys
 - IV. Summary
- 

CORROSION EXTREMES IN THE PAPER INDUSTRY

Significant material selection challenge

- Spectrum of corrosive environments

Bleaching stage in pulp manufacture

- Operational T : 70-90 °C, pH : 2.5 -3.5
- Oxidizing acidic stage (D-stage) followed by alkaline, caustic extraction(E-stage)

Conversion of lime mud to lime by calcination

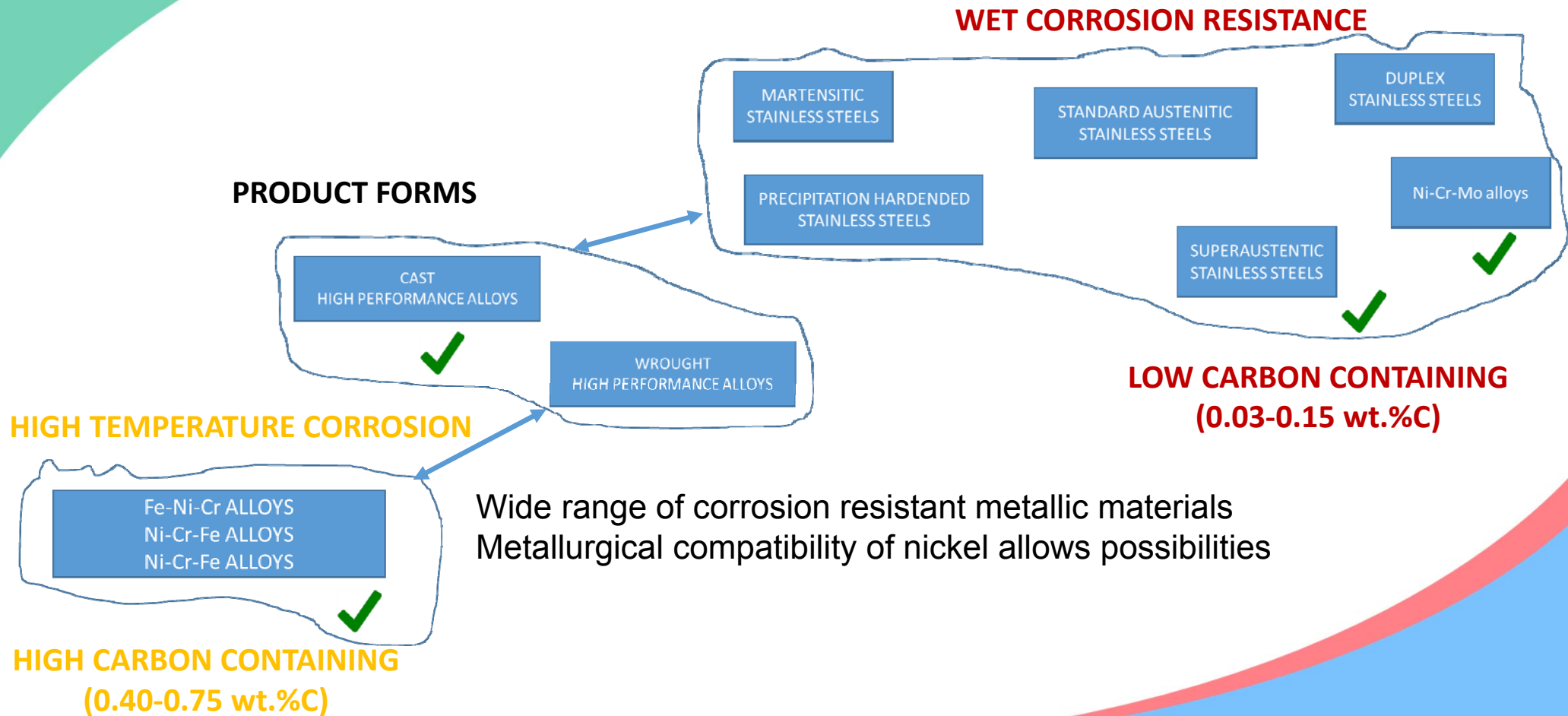
- Hot end of kilns experiencing temperatures of about 1150 -1250 °C

Paper and pulp industry is a highly capital and energy intensive one

- Stronger demand to be more environmental friendly
- Resources optimization (raw materials, water, energy)
- Reliable operation necessary for overall economic health

Corrosion resistant materials application offer engineering solutions

CORROSION EXTREMES IN THE PAPER INDUSTRY



CORROSION EXTREMES IN THE PAPER INDUSTRY

Castings – Opportunities and Challenges

Process offers the simplest form of converting a liquid metal into a solid shape

Offers design and compositional freedom

Necessitates good understanding of metallurgy and associated process variables

- Solidification
- Microstructure development
- Heat treatment

High alloy castings offer increasing complexity to high amount of alloying

- *Too many cooks spoil the broth*
 - *Depends on who is the chief cook (foundry)*

Calls for early stage involvement of end user and foundry

CAST ALLOYS FOR WET CORROSION APPLICATIONS

Superaustenitic stainless steels

Group of Fe-based alloys

Higher Cr, Ni, Mo and N than standard austenitic

Austenitic microstructure

Element	Stabilizes	Impact
Cr	Ferrite	• Promotes passive film formation • Corrosion resistance in oxidizing media
Ni	Austenite	• Stabilizes austenite • Increases corrosion resistance in reducing media • Increases SCC resistance
Mo	Ferrite	• Increases Localized corrosion resistance • Increases corrosion resistance in dilute HCl and H₂SO₄
C	Austenite	• Limited to lowest practical levels since • Carbides decrease corrosion resistance by depleting matrix
N	Austenite	• Increases localized corrosion resistance
Cu	Austenite	• Increase corrosion resistance in reducing acid like H₂SO₄ and H₃PO₄
Mn	Austenite	• Increases solubility of nitrogen

Superaustenitic stainless steels

Single values denote maximum, balance is Fe
 654SMO: Outokumpu
 Märker® MARESIST® G 4565 S: Schmidt + Clemens
 AGI: Alloy Casting Institute

CAST ALLOYS FOR WET CORROSION APPLICATIONS

Superaustenitic stainless steels

ACI Designation Generic Designation	CAST STANDARDS		WROUGHT STANDARDS	
	ASTM	DIN EN	ASTM	DIN EN
Alloy 24	-	-	S34565	1.4565
Alloy 28	-	-	N08028	1.4563
Alloy 31	-	-	N08031	1.4562
654 SMO	-	-	S32654	1.4652
904L	-	-	N08904	1.4539
254SMO/CK3MCuN	J93254	1.4557	S31254	1.4547
CK35MN	-	-	-	-
AL-6XN/CN3MN	J94651	~ 1.4588	N08367	-
1.4458	-	1.4458	-	-
1.4584	-	1.4584	-	-
1.4416	-	1.4416	-	-
1.4587	-	1.4587	-	-
Alloy 926		1.4588	N08926	1.4529
Märker® MARESIST® G 4565 S	-	-	S34565	1.4565
254 SMO, 654 SMO : Outokumpu				
AL-6XN : ATI				
Märker® MARESIST® G 4565 S: Schmidt + Clemens				

7 of them covered by international standards

- ASTM, EN

6 of them directly adopted by foundries

- Based on wrought composition

1 standalone cast alloy

CAST ALLOYS FOR WET CORROSION APPLICATIONS

Superaustenitic stainless steels

As- cast microstructure is not 100 % austenitic

- Formation of first solid changes composition of remaining liquid
- Segregation essentially due to Mo
- Formation of undesirable phases in interdendritic region
- Slow cooling results in formation of carbides too

Need for solution annealing heat treatment + water quenching

- Homogenize the austenite
- Dissolution of undesirable phases (sigma, carbides)

Proper understanding of influence of chemistry and phase formation

CAST ALLOYS FOR WET CORROSION APPLICATIONS

Superaustenitic stainless steels

	ACI Designation Generic Designation	0.2% Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	Impact energy (J)	PREN (%Cr +3.3Mo+16N)	
						min.	max.
Marginal ←	1.4584	185	450	30	60	32	41
	904L	200	460	25	70	32	41
	1.4416	185	450	30	60	36	42
	Alloy 28	200	460	30	70	36	41
	1.4587	220	480	30	60	40	47
1 st generation ←	1.4588	210	480	30	60	40	48
	Alloy 24	340	600	35	140	42	52
	CK3MCuN	260	550	35	120	42	47
	Alloy 926	260	550	35	120	42	48
	CN3MN	260	550	35	120	43	49
2 nd generation ←	G 4565 S	325	600-750	35	100	43	51
	1.4557	260	500	35	50	43	48
	CK35MN	280	570	35		45	52
	Alloy 31	285	450-650	40	120	48	55
	654 SMO	340	620	35	120	53	59

PREN ≥ 40 = Superaustenitic stainless

Mechanical properties derived by solid solution strengthening

Higher Mo and N lead to enhancement in mechanical properties

CAST ALLOYS FOR WET CORROSION APPLICATIONS

Superaustenitic stainless steels

Increased general corrosion resistance due to presence of Mo in passive film

For oxidizing environment, a grade with more Cr gives better performance

For reducing media, grades with higher Cr, Ni, Mo and Cu are superior

Pitting resistance increased with higher Cr, Mo and N

Critical pitting temperature (CPT) as per ASTM G48

CK3MCuN is at 50 °C

G 4565 S is 80 °C

Cast 654 SMO > 80 °C

SCC resistance + caustic cracking resistance > standard austenitic



CAST ALLOYS FOR WET CORROSION APPLICATIONS

Ni-Cr-Mo alloys

Highest corrosion resistance amongst stainless steels and related alloys

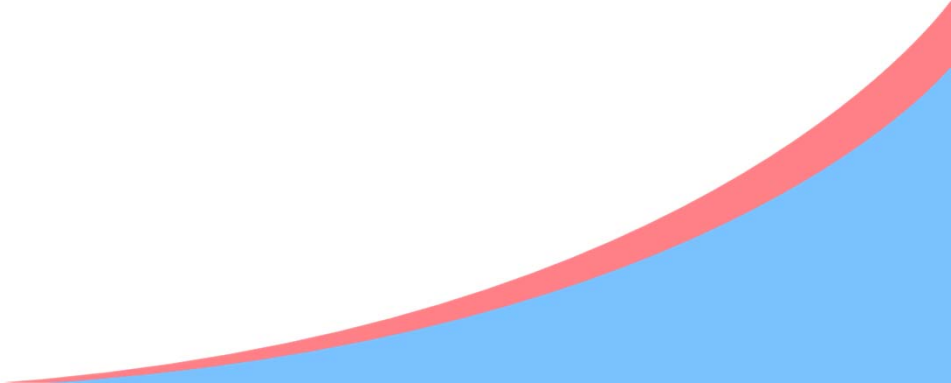
- Pitting
- Crevice
- SCC

Covered by ASTM standards

- Developed as cast equivalents of wrought Ni-Cr-Mo alloys

Proprietary grades also available

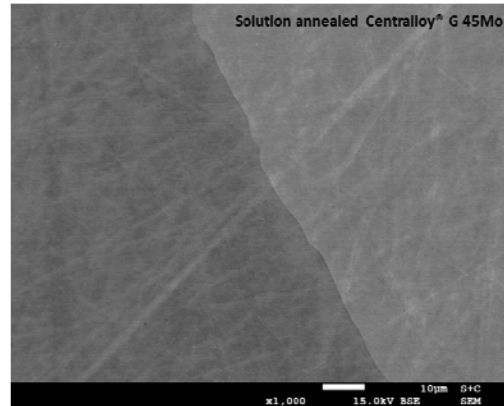
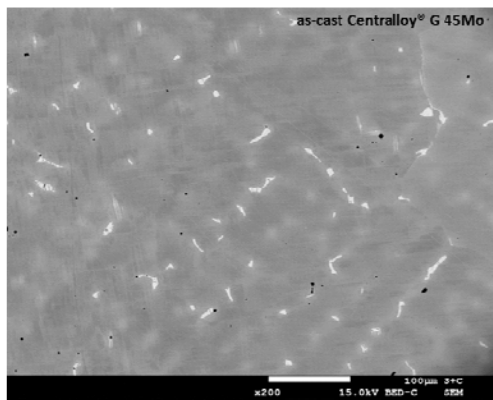
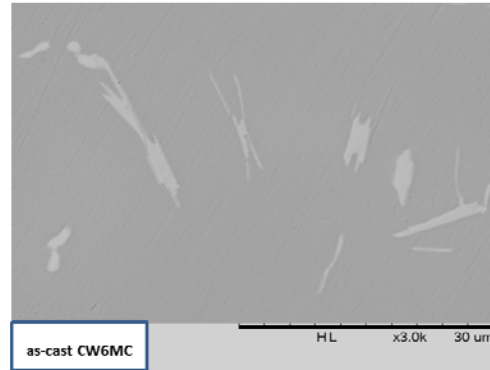
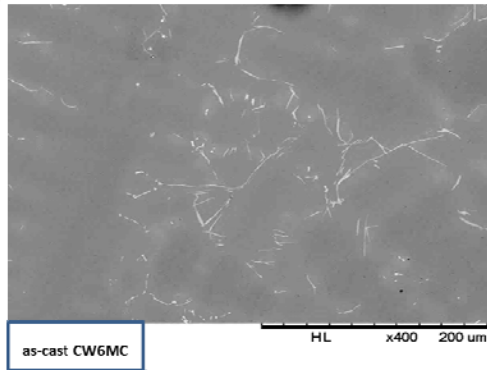
Used for the most severe service conditions



Cast Nickel based alloys used for wet corrosion environments									
ACI Designation (UNS)	Wrought Grade Generic Designation (UNS)	Cr	Mo	Fe	Cu	C	Si	Mn	Others
CW6MC (N26625)	Alloy 625 (N06625)	20.00-23.00	8.00-10.00	5.00	-	0.06	1.00	1.00	3.15-4.50 Nb
CX2MW (N26022)	Alloy C-22 (N06022)	20.00-22.50	12.50-14.50	2.00	-	0.02	0.80	1.00	2.50-3.50 W 0.35 V
Centralloy® G 45Mo	-	34.00-36.00	9.00-10.00	5.00-9.00	1.00-3.00	0.015	0.20	0.40	0.24 N 1.50 W 1.50 Ta
CW2M (N26455)	Alloy C-4 (N06455)	15.00-17.50	15.00-17.50	2.00	-	0.02	0.80	1.00	1.00 W
Euzonit® G 60	-	18.00-21.00	15.00-16.50	1.00	-	0.02	0.50	1.00	-
CW12MW (N30002)	Alloy C-276 (N10276)	15.50-17.50	16.00-18.00	4.50-7.50	-	0.12	1.00	1.00	3.75-5.25 W 0.20-0.40 V
CX2M (N26059)	Alloy 59 (N06059)	22.00-24.00	15.00-16.50	1.50	-	0.02	0.50	1.00	-
CW6M (N30107)	Alloy C	17.00-20.00	17.00-20.00	3.00	-	0.07	1.00	1.00	-
Single values denote maximum, balance is Ni Centralloy® and EUZONIT: Schmidt + Clemens									

CAST ALLOYS FOR WET CORROSION APPLICATIONS

Ni-Cr-Mo alloys



CW6MC

As-cast structure

Not 100% austenitic

Post solution annealing + water quench

CW6MC = γ + Intermetallic

Centralloy® G 45Mo

Standalone cast alloy

As-cast structure

γ + Cr,Mo-rich intermetallic

Post solution annealing + water quench

G45MO = γ

CAST ALLOYS FOR WET CORROSION APPLICATIONS

Ni-Cr-Mo alloys

ACI Designation (UNS)	0.2% Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	PREN (%Cr+3.3Mo+16N)	
				min.	max.
CW6MC (N26625)	275	485	25	46	56
CX2MW (N26022)	310	550	30	61	70
Centralloy® G 45Mo	350	550	35	64	69
CW2M (N26455)	275	495	25	65	75
EuzonIt G 60	265	550	35	68	75
CW12MW (N30002)	275	495	4	68	77
CX2M (N26059)	270	495	40	72	78
CW6M (N30107)	275	495	25	73	86

Mechanical properties are derived by solid solution strengthening

- Cr, Mo, W and Nb – substitutional elements
- Interstitial strengthening by N difficult in high Ni-containing alloys

Centralloy® G 45Mo

- Standalone cast alloy and bridge between superaustenite and Ni-Cr-Mo

Superior mechanical property with similar corrosion resistance

CAST ALLOYS FOR HIGH TEMPERATURE APPLICATIONS

Fe-Ni-Cr/Cr-Ni-Fe/Ni-Cr-Fe alloys

Material property requirements are oxidation resistance and mechanical properties

Mechanical properties at high temperature

Creep resistance

Ductility at high temperatures

Austenite is stronger than ferrite at elevated temperatures

Element	Impact
Cr	• Oxidation resistance by formation of chromia scale • Aids in formation of chromium carbides
Ni	• Stabilizes austenite • Increases Oxidation resistance, carburization resistance • Increases thermal fatigue resistance
C	• Formation of carbides necessary for creep strength
Si	• Increase oxidation resistance • Increases melt fluidity
Nb,Ti,Zr	• Aid in formation of carbides which enhance creep resistance further

CAST ALLOYS FOR HIGH TEMPERATURE APPLICATIONS

Fe-Ni-Cr/Cr-Ni-Fe/Ni-Cr-Fe alloys

Solidification mode is austenitic

Formation of primary carbides due to sufficient carbide formers and carbon

Supersaturation of austenite by carbon due to non-equilibrium cooling process of casting

Supersaturated carbon aid in precipitation of secondary carbides in the matrix during service

Cast alloys have an edge over wrought alloys for high temperature service

- Coarser grain size favorable for creep
- Higher carbon compositions easier to cast than work

Fe-Ni-Cr/Cr-Ni-Fe/Ni-Cr-Fe alloys

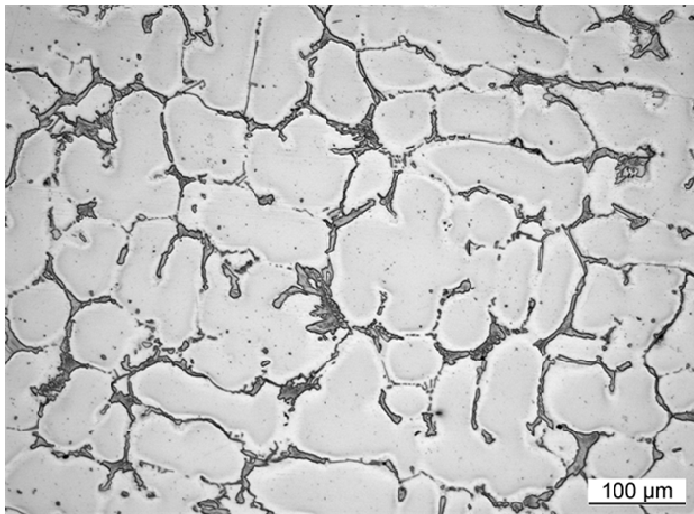
Cast high nickel alloys used for high temperature applications in the paper and pulp industry								
ACI Designation	UNS (W. Nr.)	Cr	Ni	C	Mn	Si	Mo	Other
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HE	J93403	26.00-30.00	08.00-11.00	0.20-0.50	2.00	2.00	0.50	-
HF	J92603	19.00-23.00	09.00-11.00	0.20-0.40	2.00	2.00	0.50	-
HH	J93503	24.00-28.00	11.00-14.00	0.20-0.50	2.00	2.00	0.50	-
HI	J94003	26.00-30.00	14.00-18.00	0.20-0.50	2.00	2.00	0.50	-
HK	J94224	24.00-28.00	18.00-22.00	0.20-0.60	2.00	2.00	0.50	-
HL	J94604	28.00-32.00	18.00-22.00	0.20-0.60	2.00	2.00	0.50	-
HN	J94213	19.00-23.00	23.00-27.00	0.20-0.50	2.00	2.00	0.50	-
HP	J95705	24.00-28.00	33.00-37.00	0.35-0.75	2.00	2.00	0.50	-
HP + Nb	(1.4852)	24.00-27.00	33.00-35.00	0.30-0.50	2.00	1.00-2.50	0.50	0.80-1.80 Nb
HP + Nb (MA)	Centralloy® G 4852 MICRO	24.00-27.00	33.00-35.00	0.30-0.50	2.00	1.00-2.50	0.50	0.80-1.80 Nb Ti, Zr
Single values denote maximum, balance is Fe Centralloy® G 4852 MICRO: Schmidt + Clemens								

CAST ALLOYS FOR HIGH TEMPERATURE APPLICATIONS

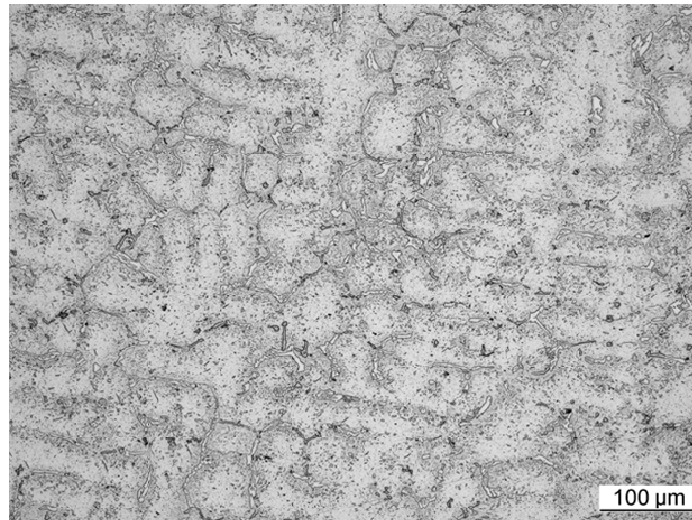
Fe-Ni-Cr/Cr-Ni-Fe/Ni-Cr-Fe alloys

As cast state has interdendritic carbides [$\gamma + M_7C_3 + M(C,N)$]

Formation of fine, homogenously distributed secondary carbides during service
[$M_{23}C_6$ + Secondary $M(C,N)$]



as-cast HP + Nb (MA)



ex-service HP + Nb (MA)

CAST ALLOYS FOR HIGH TEMPERATURE APPLICATIONS

Fe-Ni-Cr/Cr-Ni-Fe/Ni-Cr-Fe alloys

Most important properties are creep resistance and oxidation resistance

Chromia-scales offer surface protection to T of up to 1150 °C

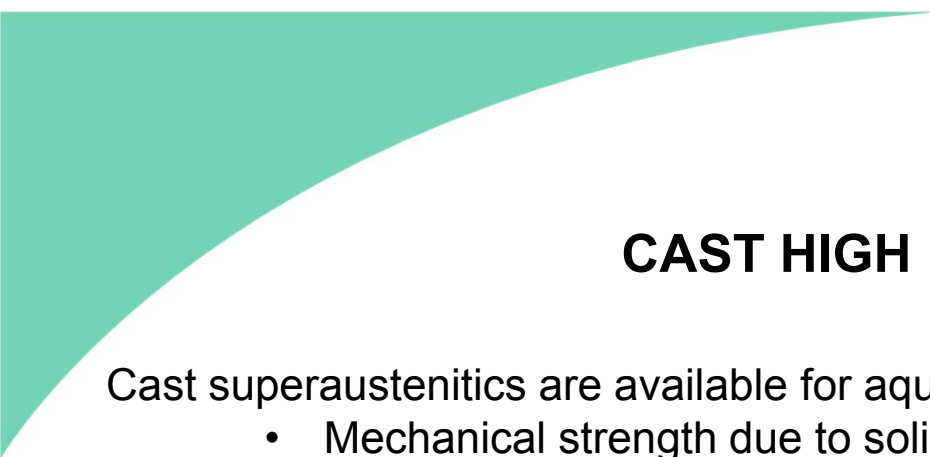
Alumina scale offer surface protection to T of up to 1250 °C

ACI Designation	Temperature (°C)	900 °C	1000 °C	1100 °C
	Stress (MPa)	$\sigma_{1\%}$	$\sigma_{1\%}$	$\sigma_{1\%}$
	Time (h)	10,000 h	10,000 h	10,000 h
HD		4	1	-
HH		13	6	-
HK		17	7	2.5
HP		20	8	-
HP + Nb		22	9	3
HP + Nb (MA)		29	14	4

14 MPa for HP+Nb (MA)

7 MPa for HK grade

Increased creep resistance due to Ti, Nb and Zr



SUMMARY

CAST HIGH PERFORMANCE ALLOYS

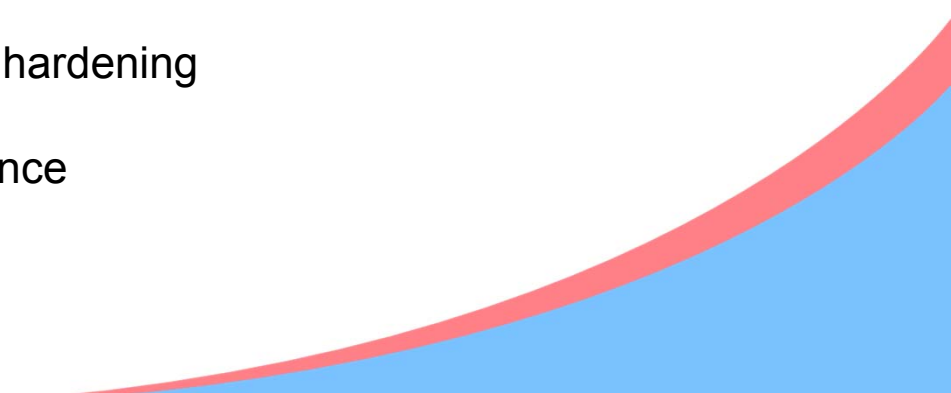
Cast superaustenitics are available for aqueous corrosion resistance applications

- Mechanical strength due to solid solution strengthening
- Corrosion resistance due to > 6% Mo as well as nitrogen

Cast Ni-Cr-Mo alloys represent the ultimate in corrosion resistance

- Mechanical properties due to solid solution strengthening
- Corrosion resistance due to high Cr + Mo as well as other alloying elements

Cast Ni-Cr-Fe castings for high temperature service

- Solid solution strengthening + precipitation hardening
 - Oxidation resistance by chromia scale
 - Secondary carbides enhance creep resistance
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THANK YOU VERY MUCH



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