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ABSTRACT

The influence of heat treatment time and temperature on the microstructure and corrosion resistance of cast stainless steel alloys CN3MN (UNS J94651) and CK3MCuN (UNS J93254) were investigated with a combination of microscopy techniques and immersion corrosion testing. The as-cast alloys exhibited significant residual microsegregation of Mo across the dendritic substructure and the presence of sigma (σ) phase in the interdendritic regions. Complete dissolution of the sigma phase and homogenization of Mo occurred after a heat treatment of 1,205°C for 4 h for castings with an average dendrite spacing of 35 µm. A heat treatment of only 1,150°C for 1 h was sufficient to produce similar results in welds with a smaller dendrite spacing of 10 µm. The use of the 1,205°C/4-h treatment restored the corrosion resistance of the cast alloys to a level that is comparable to the wrought counterpart alloys when evaluated using the ASTM G48 Method A test. This improvement is attributed to homogenization of Mo and dissolution of the σ phase. Calculated curves are proposed to estimate the combination of time and temperature needed for effective heat treatment of castings with various dendrite spacings.

KEY WORDS: austenitic stainless steel, heat treating, homogenization, localized corrosion, microsegregation

INTRODUCTION

Superaustenitic stainless steel castings are used in a variety of environments where good corrosion resistance and toughness are required. Mo is a key alloying element that is added for improved resistance to crevice and pitting corrosion. Recent work has suggested that Mo, in combination with N, promotes selective dissolution of iron at the surface and leads to Cr enrichment beneath the passive film, thus increasing corrosion resistance. A nitride layer has also been detected at the film-metal interface along with a ferrous molybdate (FeMoO₄) layer in the outer regions of the passive film. These phases have been proposed to provide secondary kinetic barriers for further enhancement in corrosion performance. In wrought alloys, where the Mo is homogeneously distributed, the protective surface film that develops provides excellent pitting and crevice corrosion resistance. However, the stability of the protective film is adversely affected in regions of Mo depletion that is commonly observed in castings and welds.

Mo segregates to the liquid during solidification because of the relatively low solubility of Mo in austenite. The inability of Mo to diffuse down the concentration gradient as a result of the low diffusivity of Mo in austenite leaves the dendrite cores depleted in Mo. As a result, castings and welds are susceptible to preferential corrosive attack at the dendrite cores. The Mo enrichment in the liquid also leads to the formation of brittle interdendritic σ phase that has deleterious effects potentially can be eliminated with a post-casting heat treatment designed to homogenize the Mo and dissolve the interdendritic σ phase. However, the influence of heat treatment time and temperature on the homogenization and dissolution
behavior in these alloys has not yet been investigated. In addition, no reports are available that describe the influence of heat treatment on the resultant corrosion behavior. The objective of this research was to determine the influence of heat treatment time and temperature on the microstructure and concomitant corrosion resistance of cast superaustenitic stainless steel alloys CN3MN (UNS J94651)\(^{(1)}\) and CK3MCuN (UNS J93254). These alloys were selected because of their relatively high Mo concentrations and industrial experience that indicates significant differences in the corrosion performance of cast and counterpart wrought alloys. The results of this work are useful for designing industrial heat treatments that can be used to restore the corrosion resistance of cast alloys to a level similar to that of their wrought counterparts.

**EXPERIMENTAL PROCEDURES**

**Alloy Preparation**

Alloys CN3MN and CK3MCuN were cast into sand molds to produce samples that were approximately 25 by 25 by 3,050 mm in dimension. The compositions of the cast and counterpart wrought alloys are provided in Table 1. The numbers in parenthesis for the cast alloys are the allowable composition ranges according to ASTM A743.\(^6\) Alloys AL6XN\(^\text{†}\) (UNS N08367) and 254SMO\(^\text{†}\) (UNS S31254) are the counterpart wrought alloys for CN3MN and CK3MCuN, respectively. They were included in the experiment as a basis for comparison. Samples for heat treating were extracted from the original castings and machined into 19- by 19- by 6.3-mm specimens. The samples were heat-treated at 1,150°C and 1,205°C for 1, 2, and 4 h in a laboratory tube furnace. Flowing Ar was utilized during the heat treatment to prevent surface oxidation. Samples from the wrought alloys were machined to the same dimensions from plate. Attempts were made initially to include heat treatment temperatures of 1,260°C and 1,315°C. However, subsequent examination of samples exposed to these temperatures revealed a secondary intergranular phase associated with liquation, indicating these temperatures were above the solidus temperatures of the alloys. Therefore, these temperatures were not evaluated further.

**MICROSCOPY**

Samples for microstructural characterization were mounted in thermosetting epoxy and polished to a 0.05-µm finish using standard metallographic techniques. Electrolytic etching was accomplished using a 10% sodium cyanide (NaCN) solution at 3 V to 5 V for 5 s to 10 s. Microstructural evaluation was performed on all samples using standard light optical microscopy (LOM) techniques. Secondary-phase fraction measurements were conducted using a Reichert-Jung\(^\text{†}\) metallograph in combination with Leco\(^\text{†}\) image analysis software. A minimum of 10 fields were used to measure the area fraction of the secondary phase, and the area fraction was assumed to equal the volume fraction.

Phase identification was conducted using electron back-scatter diffraction (EBSD) and x-ray energy-dispersive spectroscopy (XEDS). The EBSD patterns and XEDS spectra were collected using an FEI\(^\text{†}\) scanning electron microscope (SEM) equipped with both back-scattered electron and EDS detectors. HKL Flamenco\(^\text{†}\) and HKL Spirit\(^\text{†}\) software packages were used to collect and interpret the EBSD and EDS raw data. A 20-kV accelerating voltage was used for both techniques and a 60° tilt was required for the EBSD measurements. The EBSD patterns were processed using a band detection technique to calculate band spacings and angles and identify matches to known standard patterns. The mean angular deviation (MAD) was used as an indication of agreement, with a MAD < 1° considered as confirmation for positive phase identification.\(^7\) Electron probe microanalysis (EPMA) was performed using a JEOL 733\(^\text{†}\) superprobe with integrated wavelength dispersive spectrometers (WDS). All measurements were made using a 20-kV accelerating voltage with a 35-nA beam current. The compositions

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\(^{(1)}\) UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

\(^{†}\) Trade name.
were measured using a ZAF data reduction technique that converts x-ray counts into weight percentages.\(^8\)

**CORROSION TESTING**

After heat treating, samples for corrosion testing according to ASTM G48 Method A\(^9\) were prepared to an 80-grit surface finish. The samples were weighed to the nearest 0.001 g and immersed in an acidified ferric chloride solution (6% FeCl\(_3\) by mass, 1% hydrochloric acid [HCl]) at 75°C for 72 h. After corrosion testing, the samples were scrubbed using a nylon brush, ultrasonically cleaned, and dried with ethanol (C\(_2\)H\(_6\)O) to remove any debris from the pits. Total weight loss was used as an indicator of corrosion resistance.

**RESULTS AND DISCUSSION**

**As-Cast Microstructures**

Figure 1 shows light optical photomicrographs of each alloy in the as-cast condition. Also shown are the microstructures of autogenous welds placed on each alloy (using the gas-tungsten arc process at 100 A, 9 V, and 3.0 mm/s travel speed). These welds were placed on the surface of each sample used for heat treating to assess the influence of dendrite spacing. The microstructure of each alloy consists of austenite dendrites with an interdendritic eutectic-type constituent. Figure 2 shows a SEM image and EDS spectra of the interdendritic region. The spectra were acquired from the primary austenite (Figure 2[b]), eutectic-type austenite (Figure 2[d]), and secondary interdendritic phase (Figure 2[c]). Note that the interdendritic phase is enriched in Mo and Cr relative to the austenite. Typical EBSD patterns from each phase are shown in Figure 3. The calculated patterns are also shown and confirm that the matrix is austenite (Figures 3[b] and [d]) while the secondary phase is \(\sigma\) (Figure 3[c]). These results are consistent with the EDS spectra, since \(\sigma\) is known to be rich in Mo and Cr.\(^4,10\) The \(\sigma\) phase was the only secondary phase observed for all heat treatment conditions. Figure 4 shows an EPMA trace acquired across several dendrites in the as-cast CK3MCuN alloy. The Mo concentration varies from about 4.5 wt% in the dendrite...
cores to about 9 wt% in the interdendritic regions. The Cr, Si, and Ni segregate in a similar direction (i.e., toward the liquid during solidification), while Fe segregates in the opposite direction. Results for alloy CN3MN showed essentially identical results.

Initial solidification of these alloys starts with primary $L \rightarrow \gamma$ austenite, which leads to Mo rejection into the liquid.\(^4\)\(^1\)\(^0\) The process continues until the $L \rightarrow \gamma + \sigma$ eutectic-type composition is reached in the liquid, at which point solidification terminates with the formation of an interdendritic $\gamma/\sigma$ constituent. The residual microsegregation is expected in these alloys and is attributed to the low diffusivity of Mo in $\gamma$.\(^4\)\(^1\)\(^0\) This also leads to extensive enrichment of Mo in the liquid, which accounts for formation of the interdendritic $\sigma$ phase. It has been shown that the extent of microsegregation and resultant secondary-phase formation is generally insensitive to the cooling rate for these alloys.\(^1\)\(^1\) Lower cooling rates during solidification provides more time for back-diffusion during solidification, which, in itself, would reduce the extent of residual segregation. However, this effect is offset by larger dendrite spacings that are produced with slower cooling rates, so that the extent of microsegregation generally is not affected by cooling rate (within the range of rates typical for casting and arc welding).

**Sigma Phase Dissolution Kinetics**

Figure 5 shows light optical photomicrographs of alloy CK3MCuN after heat treatment times of 1, 2,
and 4 h at 1,150°C. The sample heat-treated for 1 h also shows the weld. Note that dissolution is not complete within the casting at times up to 4 h at this temperature, but is complete in the weld after only 1 h. The dissolution observed in the weld indicates that 1,150°C is above the γ/σ solvus, but more time would be needed for dissolution in the casting because of the larger dendrite spacing (average dendrite spacing of 35 µm in the casting compared to 10 µm in the weld). Figure 6 shows results for the casting for a temperature of 1,205°C. At this temperature, significant dissolution occurs after the 2-h heat treatment, and dissolution is complete after 4 h (the features visible in Figure 6c are shrinkage porosity, not second-
ary phase). Identical results were observed for alloy CN3MN.

Figure 7 shows the variation in $\sigma$ phase content as a function of heat-treating time and temperature for each alloy. Also shown in each plot is the computed dissolution behavior of $\sigma$ phase as determined by the model proposed by Singh and Flemings.\textsuperscript{12}

\[
V_t = \left( V_0 + \frac{C_M - C_0}{C_\sigma} \right) \exp \left( -\frac{\pi^2 D t}{4 l_0^2} \right) - \frac{C_M - C_0}{C_\sigma}
\]

(1)

Singh and Flemings derived this expression for a binary alloy containing microsegregation and non-equilibrium eutectic. They used this expression to investigate dissolution kinetics in multicomponent Al alloys by treating the alloys as an Al-Cu binary system. This expression was adopted to the current work by treating the alloys as a $\gamma$-Mo binary system, since Mo is the primary element that segregates during solidification and leads to formation of the Mo-rich $\sigma$ phase while Ni, Cr, and Si do not segregate strongly (as shown in Figure 4). In this case, $V_t$ is the volume fraction of $\sigma$ after dissolution time $t$, $V_0$ is the initial volume fraction of $\sigma$, $C_M$ is the maximum solid solubility of Mo in $\gamma$, $C_0$ is the nominal Mo concentration, $C_\sigma$ is the Mo concentration of the $\sigma$ phase, $l_0$ is half the dendrite spacing, and $D$ is the diffusivity of Mo in $\gamma$. $V_0$ and $l_0$ were measured for each alloy using image analysis techniques. The value for $C_\sigma$ was calculated at 9 wt% Mo with Thermo-Calc\textsuperscript{1} software using the CALPHAD method with the Fe database.\textsuperscript{13} This value is in good agreement with the EPMA measurements that show the maximum concentration of Mo in the primary austenite was also $\sim$9 wt% Mo. The value for $C_\sigma$ was determined in a previous study as 25.9 wt% Mo using EPMA.\textsuperscript{4} Values of $D_{Mo}$ were calculated from the diffusivity data provided by Malik, et al.,\textsuperscript{14} in which $D_0 = 1.1 \times 10^{-4}$ m$^2$s$^{-1}$ and $Q = 275$ kJ mol$^{-1}$.

There is reasonable agreement between the calculated and measured $\sigma$ phase contents in Figure 7 considering the difficulty in measuring secondary phase fractions at these low values and that a binary dissolution model is applied to these multi-component alloys. The measurements and calculations each indicate that dissolution will not be complete at 1,150°C up to 4 h, while a 4-h to 5-h exposure at 1,205°C dissolves the $\sigma$ phase. The calculations also indicate that complete dissolution should occur in the weld at 1,150°C for 1 h due to the reduced dendrite spacing of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Light optical photomicrographs of alloy CK3MCuN after heat treatment times of (a) 1, (b) 2, and (c) 4 h at 1,150°C. The sample heat-treated for 1 h also shows the (d) weld.}
\end{figure}
10 µm, which is also consistent with the observations (Figure 5).

Homogenization Kinetics

Figure 8 shows typical EPMA Mo concentration profiles acquired on alloy CK3MCuN after heat treatment conditions of 1,150°C/4 h (Figure 8[a]) and 1,205°C/4 h (Figure 8[b]). Significant residual microsegregation persists after the 1,150°C/4-h treatment, whereas the residual segregation is essentially eliminated after the 1,205°C/4-h treatment. The EPMA data was used to determine the index of residual segregation of Mo for each heat treatment condition via:

\[
\delta_i = \frac{C_{M_i} - C_{m_i}}{C_0 - C_{m_i}}
\]

where \(C_{M_i}\) and \(C_{m_i}\) represent the maximum and minimum Mo concentrations after a given homogenization time, and \(C_0\) and \(C_{m}\) represent the maximum and minimum initial Mo concentrations, respectively. Complete homogeneity was confirmed using a homogeneity criteria, which determines whether the raw, uncorrected x-ray intensities collected for each element fall within the statistical limits of a homogenous sample. The homogeneity criteria is given as:

\[
\bar{N} - 3\sqrt{N_i} \leq N_i \leq \bar{N} + 3\sqrt{N}
\]

where \(N_i\) is the measured Mo x-ray intensity of a given measurement and \(\bar{N}\) is the average Mo x-ray intensity of all measurements. Heat treatment conditions in which all x-ray intensity measurements fell within the sample homogeneity criteria are statistically homogenous and assigned a \(\delta\) value of zero.

The variation in \(\delta\) for Mo with time and temperature is shown for each alloy in Figure 9 (EPMA measurements were not conducted on all heat treatment conditions). Note that ~40% to 70% of the residual segregation of Mo still persists after the 1,150°C/4-h treatment for the casting. By contrast, the weld is nearly completely homogenized (\(\delta \sim 0.1\)) after a 1,150°C/1-h treatment as a result of the finer dendrite spacing. Complete homogenization of the casting was only observed for the 1,205°C/4-h treatment. Also shown in Figure 9 is the calculated variation in \(\delta\) with time and temperature according to the simple homogenization model originally proposed by Kattamis and Flemings for a single-phase alloy:

\[
\delta_i = \exp \left[ -\frac{\pi^2D_t}{k_0} \right]
\]

where the values are as previously defined. The measured homogenization kinetics are significantly slower than those calculated using Equation (4). This is to be expected since Equation (4) assumes a single-phase alloy and therefore does not account for the influence of sigma phase on the required homogenization time. The presence of sigma phase is significant because it provides a source of Mo diffusion into the primary austenite as it dissolves, and this is not accounted for in the single-phase homogenization
FIGURE 7. Variation in sigma phase content as a function of heat-treating time and temperature for (a) CN3MN and (b) CK3MCuN.

FIGURE 8. Typical EPMA composition traces acquired on alloy CK3MCuN showing the distribution of Mo after heat treatment at (a) 1,150°C for 4 h and (b) 1,205°C for 4 h.

FIGURE 9. Variation in index of residual segregation ($\delta$) with time and temperature for each alloy.
model above. Therefore, complete homogenization is not attainable until the sigma phase is completely dissolved.

**Corrosion Resistance**

As previously described, the relatively poor corrosion resistance of castings and welds in these alloys has been attributed to Mo microsegregation. With this in mind, Figure 10 shows the variation in weight loss from the ASTM G48 test as a function of the index of residual segregation for the cast samples (welds were not corrosion tested in this program). Corrosion occurred by a combination of general corrosion and pitting. The measured weight loss for each counterpart wrought alloy is also shown for comparison. There is a clear correlation between the corrosion performance and index of residual segregation. In particular, the corrosion resistance in this test is comparable to that of the wrought alloys for a heat treatment of 1,205°C/4 h. Figure 11 shows corrosion results for all the heat treatment conditions. (EPMA measurements were not conducted on all the heat-treated samples, so δ values are not provided for all the heat treatment conditions in Figure 10.) The characterization results demonstrated that the 1,205°C/4-h treatment was effective at eliminating residual microsegregation and dissolving the secondary sigma phase. The improvement in corrosion resistance is attributed to these favorable microstructural changes.

These results are significant with regard to typically used industrial heat treatments. For example,
the pertinent specification for these alloys requires a minimum postcasting heat treatment of 1,150°C/1 h. However, the results shown here clearly demonstrate that, for the typical casting conditions and dendrite spacings evaluated in this work, this heat treatment will not promote significant homogenization or dissolution. Higher temperatures and longer times would be needed for significant improvement.

The required combination of time and temperature for complete dissolution will be affected by the cooling rate and resultant dendrite spacing. As described above, dissolution of the interdendritic σ phase requires longer times than homogenization of Mo within the dendrites. In addition, reasonable agreement was observed between the volume fraction of the σ phase measured experimentally and calculated with Equation (1). Therefore, the dissolution model in Equation (1) can be used to estimate the times and temperatures required for effective heat treatment as a function of cooling rate and resultant dendrite spacing. The variation in dendrite spacing (λ) with cooling rate (ε) for these alloys can be estimated by:

\[
\lambda = 80 \varepsilon^{-0.33}
\]  

where \( \lambda \) is measured in µm and \( \varepsilon \) is calculated in °C/s. Once \( \lambda \) is known by means of the cooling rate, the time and temperature required for dissolution can be estimated using Equation (1). Figure 12 illustrates the results of such calculations for each alloy. It is recognized that these results are only approximations that are subject to the accuracy and limitations of the dissolution model. Nevertheless, these curves are useful because they permit estimation of the required times and temperatures that are needed for dissolution as a function of the casting cooling rate, which is commonly determined using commercially available heat flow software.

**CONCLUSIONS**

The influence of heat treatment time and temperature on the microstructure and corrosion resistance of cast stainless steel alloys CN3MN and CK3MCuN were investigated with a combination of microscopy techniques and immersion corrosion testing. The following conclusions can be drawn from this work.

- In the as-cast condition, the alloys exhibit primary austenite dendrites with residual microsegregation of Mo and interdendritic σ phase. The formation of σ phase is attributed to liquid enrichment in Mo during solidification.
- Complete homogenization of Mo and dissolution of σ phase can be achieved in castings with an average dendrite spacing of 35 µm with a 1,205°C/4-h heat treatment.
- The 1,205°C/4-h heat treatment restored the corrosion resistance of each alloy to a level that is comparable to the wrought counterpart materials.
- Heat treatment curves are proposed that provide estimates of the times and temperatures required to restore the corrosion resistance of cast alloys with various dendrite spacings.

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