Effect of Grain Size on Degree of Sensitization of Chrome-Manganese Stainless Steel

Ravindra V. TAIWADE, Rohan SHUKLA, Himanshu VASHISHTHA, Avinash V. INGLE and Ravin K. DAYAL

1) Department of Metallurgical and Materials Engineering, Visvesvaraya National Institute of Technology, Nagpur, 440 010 India. 2) School of Mechanical and Building Sciences, VIT University, Chennai, 600 048 India.

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The use of chrome-manganese stainless steels (Cr–Mn SSs) of 200-series grade has tremendously increased in past few years in various applications like construction, home accessories, office appliances, light poles etc. Their mechanical properties, weldability and corrosion/oxidation resistance provide the best all-round performance stainless steels at relatively low cost. Therefore, they serve as an appropriate alternative to 300-series stainless steels now days. Similar to 300-series steels, Cr–Mn SSs are also submitted to various fabrication practices like welding, hot rolling, cold working, solution annealing or stress relieving processes. This leads to change in their grain size due to higher operating temperature during service. The grain size has a major influence on the intergranular corrosion (IGC) developed due to sensitization phenomena. Several investigations have been made on the influence of grain size on IGC behaviour of 300-series stainless steels, but this information about Cr–Mn SS is scanty till now. Therefore, in this paper an attempt has been made to evaluate the effect of grain growth on degree of sensitization (DOS) of Cr–Mn SS and finally concluded that the DOS decreases with increase in grain size.

KEY WORDS: grain size; chrome-manganese stainless steel (Cr–Mn SS); as-received (AR); solution annealing (SA); degree of sensitization (DOS).

1. Introduction

Austenitic stainless steels (ASSs) stands for three fourth of global stainless steel (SS) production due to various important and superior properties like ductility, drawability, strength, toughness, wear resistance, inter-granular corrosion resistance etc. The total worldwide production of stainless steels exceeded 24 million tons in 2005, and ASSs occupied approximately 70% of it. The ASSs are primarily divided into two basic categories called as 300-series and 200-series stainless steels. The 300-series (mainly 304 and 316 SS) are the most popular grades of ASS. In 300-series, various alloying elements like nickel (Ni), manganese (Mn), nitrogen (N), copper (Cu) and carbon (C) are used to promote austenitic structure when added to iron-chromium (Fe–Cr) alloy system. Nickel contributes as a major constituent in order to stabilize the austenite structure and improves formability, weldability, toughness and corrosion resistance in aggressive environment. But, due to high cost and inadequate supply of Ni in India, the local producers approached to a new grade of stainless steel that is 200-series in applications such as constructions, home accessories, office appliances, light poles, out-door installations etc. 200-series SS are also referred as "chrome-manganese stainless steel (Cr–Mn SS) consisting Mn as an austenitic stabilizer which replaces the major constituent Ni." Therefore, future will place greater demands on 200-series alloys in replacement of 300-series as an economical substitute.Similar to 300-series steels, Cr–Mn stainless steels are also subjected to various fabrication processes like welding, hot rolling, cold working, solution annealing or stress relieving and during these practices a very high temperature exposure leads to change in grain size. This alteration in grain size has a major influence on the intergranular corrosion (IGC) due to sensitization. In sensitization phenomena, the steel is subjected to slow heating or cooling in the temperature range of 723–1 123 K which extracts chromium from the grains and forms chromium carbide (Cr23C6) at grain boundaries, leaving a Cr-depleted zone extending adjacent to either side of grain boundaries. Taiwade et al. recently published electrochemical data on sensitization behaviour of Cr–Mn ASS. They also compared IGC behaviour and corrosion resistance of Cr–Mn steel with AISI 304 SS systematically. Several investigations have been made by many researchers on the effect of grain size on the IGC of 300-series. Beltran et al. performed studies on AISI 304 SS with three different grain sizes viz. 15, 40 and 150 μm (by straining). They concluded that when the samples were heat treated from a lower aging temperature (898 K) to a higher aging temperature (1 048 K), the sensitization/desensitization process occurs very rapidly for grain sizes ranging from 150 to 15 μm. Yu et al. have studied the effect of solution annealing treatment and sensitization on IGC...
behaviour of 316 SS and based on electrochemical potentiodynamic reactivation (EPR) results they concluded that degree of sensitization (DOS) decreased as solution annealing temperature and time increased. Li et al.\(^{23}\) have evaluated the effect of grain growth on chromium carbide precipitation and IGC of 316L SS using electrochemical tests. They showed that chromium carbide precipitations were much delayed in larger grains. However, the influence of grain size on DOS of Cr–Mn SS has not been carried out yet; therefore this present research work serves as the motivation for the current investigation. The work delivers the qualitative and quantitative information about the measurement of grains by microscopy/intercept method and its outcome on DOS was studied with the help electrochemical tests.

2. Materials and Methods

The Cr–Mn stainless steel was obtained in the form of a sheet (in hot rolled and mill annealed condition) from local producer. The typical chemical composition determined by optical emission spectrometer is given in Table 1.

Total twenty square shaped samples of dimension 10 mm × 10 mm × 3 mm (thickness) were obtained using wire-cut electrical discharge machine. Out of twenty, two samples which are not subjected to any thermal treatments, referred to as-received (AR). The remaining (eighteen samples) were solution annealed (SA) in Si–C muffle furnace (Lenton make) at three different temperatures viz. 1 323 K, 1 373 K, 1 423 K for 1 h, 2 h, 3 h each followed by water quenching (WQ). Two sets of solution annealed samples (nine each) were used in this investigation. One set was used to perform grain size measurement and the other for sensitization. In IGC studies the samples were thermally aged (TA) in muffle furnace at a temperature of 973 K for 1 h followed by air cooling (AC). The systematic procedure for preparation of sample for tests like ASTM standard A-262 Practice A and double loop electrochemical Potentiodynamic reactivation (DLEPR) test is described as follows:

A brass stud of 20 mm length and 8 mm diameter with M3 internal treads was fixed to one of the flat unexposed surface of sample using silver paste (for electrical conductivity). The entire assembly was then mounted in cold setting resin leaving threaded portion of brass stud for electric connection. The open surface area (100 mm²) of this mounting resin leaving threaded portion of brass stud for electric connection. The open surface area (100 mm²) of this mounted sample was polished on emery papers (180, 240, 400, 600 and 800 grit), and then immediately on velvet cloth smeared with 0.75 μm alumina (Al₂O₃) slurry. The samples were ultrasonically cleaned in distilled water prior to each test.

Following relationship was used to find out grain size of AR sample, namely step, ditch or dual structures. The microstructures with partially ditched grain boundaries represent dual structures while one or more grains completely surrounded by ditches are termed as ditch structures.\(^{11,17,24,25}\)

Degree of sensitization (DOS) was obtained using DLEPR test. Solution containing of 0.5 M H₂SO₄ + 0.01 M NH₄SCN (at room temperature, 27°C) was used to perform DLEPR test. It was carried out using a Potentiostat (Solartron-1285), in conventional three-electrode electrochemical cell, with platinum gauge grid as counter electrode, saturated calomel electrode (SCE) as the reference electrode and sample as the working electrode. Before exposing the sample, the test solution was de-aerated by purging dry (oxygen free) argon gas for 1 hour. All the DLEPR experiments were initiated after attaining nearly steady-state open circuit potential (about 30 min). The tests were performed at a scan rate of 6 V/h (1.667 mV/s) and having a potential range from −500 mV (SCE) to +300 mV (SCE). This gives us the forward scan. The scanning direction was then reversed, and the potential was reduced to −500 mV for obtaining a backward scan. The %DOS was then computed as the ratio of (Ia/Ir) × 100\(^{26,27}\) where, Ia and Ir are the activation and reactivation peak current density measured during forward and reverse scans respectively. In order to determine average grain size of AR and SA samples, Heyn’s Intercept Method was used. The procedure of measurement of grain size is explained as follows.

The number of grains intercepted by a line of fixed length. The grains touched by the end of the line are counted as half grains. Counts are made on at least three fields to assure a reasonable accuracy. The length of the line in millimetre (mm) divided by the average number of grains intercepted by that line gives the average intercept length.\(^{28,29}\) Following relationship was used to find out grain size of given samples.

\[
\text{Average grain size at } 100x \text{ (in microns)} = \frac{\text{Total length of line at } 100x}{\text{Number of grain intercepted by the line}} \quad \ldots \quad (2.1)
\]

The width of depleted region of few sensitized samples was measured using electron probe micro analyzer (EPMA). The EPMA line scans across the grain boundary was obtained in conjunction with SEM using JEOL 8600M Electron Probe Micro analyzer.\(^{11,30}\) The scan was performed for a set of 30 data points and unit data point corresponds to 1 nm. The EPMA data was processed using “ORIGIN PRO 8” software.

3. Results & Discussion

3.1. Influence of Solution Annealing Temperature on Grain Size

Figure 1(a) shows a micrograph of as-received (AR) Cr–Mn SS sample and Figs. 1(b)–1(j) show the microstructures of samples solutionized at 1 323 K, 1 373 K, 1 423 K for 1 h,
2 h, 3 h each respectively. All the solutionized samples were clearly showing the step structure without any attack of carbides. The average grain size of all samples (AR/SA) was measured by linear intercept method (as per Eq. (2.1)). The grain size for these samples was found to vary and shown qualitatively in micrographs of Figs. 1(a)–1(j) and quantitatively offered in Table 2. A very fine and uniform grain structure was observed for AR sample and the average grain size was measured to be 39 μm. The grain size for sample solutionized at 1 323 K for 1 h, 2 h and 3 h was found to be 62, 71 and 80 μm and on increasing the temperature, subsequent grain growth was observed. The largest grain size was measured up to 135 μm for sample solutionized at 1 423 K for 3 h. Yu et al.19) have also investigated the effect of various solution annealing conditions on the grain growth. The mentioned solution annealing conditions are similar to our research work. The results derived are in good agreement with the current studies. Thus it is confirmed that the grain size increased with increase in solution annealing temperature and duration. The grain coarsening at various elevated temperature occurred because these solutionizing conditions help in dissolving carbides and providing sufficient energy for grains to grow. This behaviour can also evident qualitatively in the micrographs of Figs. 1(b)–1(j).

### 3.2. Influence of Grain Size on Sensitization Behaviour

In order to see the effect of grain size on sensitization
behaviour, above mentioned solution annealed samples with varying grain sizes were thermally aged (TA) at 973 K for 1 h. The results obtained from practice A test are shown in Figs. 2(a)–2(j). Micrograph of AR sample is shown in Fig. 2(a) indicating austenite structure with few partial attacked grains (dark black lines) and categorized as dual structure. Thermal ageing treatment results in the formation of chromium carbide (Cr₂₃C₆) precipitates along the grain boundaries and generating ditch structure. Figures 2(b)–2(c) shows thick Cr depleted region with small grain size i.e. 62 and 71 μm, the effect is then continuously decreases for the grain size of 80 to 111 μm (Figs. 2(d)–2(h)). Further for the coarser grains (118 to 135 μm) the substantial reduction in Cr depleted region was observed which is shown in Figs. 2(i)–2(j). Thin Cr depleted regions qualified to drop in sensitization effect. Therefore, we can say that as the grain size increases, sensitization tendency decreases.

3.3. Influence of Grain Size on Degree of Sensitization (DOS)

Figure 3(a) shows the DLEPR curve for AR sample and considered as a reference curve. The DLEPR curves for solution annealed samples (aged at constant temperature of 973 K for 1 hour) are shown in Figs. 3(b)–3(j). The DOS data obtained from DLEPR curves for various grain sizes is presented in Table 3. Figure 3(b) shows the highest DOS value of 29.95% with smallest grain size (62 μm) and the value decreases to 16.55% for largest grain size (135 μm). The mechanism related to the effect of grain size on IGC is explained by various researchers. In this mechanism the fundamentals of complete sensitization is considered. The relationship exists between the grain size and the time to attain the state of complete sensitization is explained as follows.

\[ t_{\text{max}} = \left( \frac{d}{d_0} \right)^{2/3} t_{\text{max},0} \] ........................(3.1)

Where, \( t_{\text{max}} \) and \( t_{\text{max},0} \) are the times required to reach the state of complete sensitization. And \( d, d_0 \) are the grain sizes. \(^{19,32}\)

![Fig. 2. Optical micrographs acquired (at 200x) of AR and SA samples thermally aged (TA) at 973 K for 1 h after oxalic acid etch test.](image-url)
The chromium concentration at the grain boundaries at any sensitization time during the sensitization stage is related to $t_{\text{max}}$ and is defined as:

$$c = c_0 \exp \left(-kt/t_{\text{max}}\right) \quad \text{(3.2)}$$

Where, $t$ is the sensitization time, $c$ is the chromium concentration at the grain boundaries at any sensitization time, $c_0$ is the initial concentration of chromium and $k$ is a constant.\(^{19,33}\)

From these two equations, it can be assumed that if $t$ is shorter than $t_{\text{max}}$ and is kept the same for the different grain size samples, the chromium concentration at the grain boundaries of a large grain size sample will be higher than that of a small grain. This means that the precipitation of a large grain sample will be less than that of a small grain. As a result, the DOS of a large grain sample will be lower than that of a small grain. It means that as the grain size increases, the chromium in the matrix have to travel a very long distance to reach towards the grain boundaries to form chromium carbide. Therefore, this inverse co-relationship between the grain size and DOS endorsed in minimizing the effect of sensitization and intergranular corrosion. This is also evident from micrographs of Figs. 2(i)–2(j) which clarifies that when the samples solutionized at 1423 K for 2 h and 3 h, a very large area of grain matrix (or reduced Cr depleted zone) which is available to produce protective passive film of Cr$_2$O$_3$ on the surface and helps in improving the corrosion resistance of the steel.

![DLEPR Curves for AR and SA+TA samples.](image)

**Table 3.** DOS data obtained from DLEPR curves.

| S.N. | Sample History                      | %DOS |
|------|------------------------------------|------|
| 1    | As Received                        | 02.91|
| 2    | 1323 K-1 h-WQ+973 K-1 h-AC         | 29.95|
| 3    | 1323 K-2 h-WQ+973 K-1 h-AC         | 27.99|
| 4    | 1323 K-3 h-WQ+973 K-1 h-AC         | 23.07|
| 5    | 1373 K-1 h-WQ+973 K-1 h-AC         | 22.59|
| 6    | 1373 K-2 h-WQ+973 K-1 h-AC         | 19.36|
| 7    | 1373 K-3 h-WQ+973 K-1 h-AC         | 18.82|
| 8    | 1423 K-1 h-WQ+973 K-1 h-AC         | 18.25|
| 9    | 1423 K-2 h-WQ+973 K-1 h-AC         | 17.84|
| 10   | 1423 K-3 h-WQ+973 K-1 h-AC         | 16.55|
thermal cycle of 1 h ageing at 973 K gives high DOS for all solution annealed samples, whereas %DOS subsequently decreases with increase in ageing time. The lowest %DOS values of 18.25, 17.48 and 16.55 were observed for samples which were solution annealed at 1 423 K for 1 h, 2 h and 3 h respectively with larger grain sizes (111, 118 and 135 μm). This shows the influence of grain size on desensitization kinetics of Cr–Mn SS steel. Because during solution annealing, coarser grains attributed to desensitization which refers to replacement of Cr in the Cr-depleted zone resulting in homogenization. It was also found that for shorter duration of annealing resulted in fine grain size which offers more sites for attacking grain boundaries and developing thicker depleted regions and hence more susceptible to IGC.

The width of Cr-depleted zone was further confirmed with the help of EPMA line scan. Figure 5 shows the schematic including grain matrix, grain boundaries, Cr-carbide precipitation and width of the Cr-depleted region. The EPMA line scan of solution annealed samples aged at 973 K for 1 h is shown in Fig. 6. The line p-p’ indicates the section along the grain boundary where the EPMA scan was performed. The EPMA scan was conducted on three different solutionized samples (1 323 K, 1 373 K and 1 423 K aged at 3 h) sensitized at 973 K and their grain sizes were 80, 88 and 135 μm respectively. The minimum chromium concentration for these samples was found to be 7.25, 8 and 8.20 wt% and the corresponding width of Cr-depleted region was measured to be 11.5, 9.75 and 9 nm respectively. This reduction in width attributed to increase in grain size and decrease in DOS.

4. Conclusions

(1) Influence of solution annealing temperature on grain size was evaluated qualitatively using ASTM standard A 262 practice-A test.

(2) Effect of grain size on DOS was evaluated quantitatively using DLEPR test.

(3) The inverse co-relationship between the grain size and DOS was established and it endorsed in minimizing the effect of sensitization and intergranular corrosion.

(4) EPMA line scan confirms that the reduction in width of Cr-depleted region attributed to increase in grain size and decrease in DOS.

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REFERENCES

1) A. J. Sedriks: Corrosion of Stainless Steels, 2nd ed., J. Wiley & Sons, New York, (1996), 13.

2) T. Oshima, Y. Habara and K. Kuroda: ISIJ Int., 47 (2007), No. 3, 359.

3) N. Parvathavarthini: Corrosion of Austenitic Stainless Steels, Mechanism, Mitigation and Monitoring, ed. by H. S. Khatak and Baldev Raj, Woodhead Publishing House, Cambridge, England, (2002), 117.

4) J. C. Lippold and D. J. Kotecki: Welding Metallurgy and Weldability of Stainless Steels, John Wiley & Sons Inc., UK, (2005), 141.

5) A. S. Lima, A. M. Nascimento, H. F. G. Abreu and P. De Lima-Neto: J. Mater. Sci., 40 (2005), 139.

6) R. V. Taiwade, S. J. Patre and A. P. Patil: Trans. Indian Inst. Met., 64 (2011), No. 6, 513.
7) C. P. Cutler, G. E. Coates and D. C. Jenkinson: 6th Eur. Stainless Steel Conf., Sci. & Market, The Swedish Steel Producers’ Association, Stockholm, Sweden, (2008), 421.
8) “New 200-series” Steels, An Opportunity or A Threat to the Image of Stainless Steel, ISSF, Brussels, Belgium, (2005).
9) 200-Series Stainless Steel – CrMn Grades, ASSDA Technical Bulletin, 1st ed., ASSDA, Australia, (2006).
10) R. L. Plaut, C. Herrera, D. M. Escriba, P. R. Rios and A. F. Padilha: Mater. Rev., 10 (2007), No. 4, 453.
11) R. V. Taiwade, A. P. Patil, R. D. Ghugal, S. J. Patre and R. K. Dayal: ISIJ Int., 53 (2013), No. 1, 102.
12) D. S. Bergstrom and C. A. Bötti: Stainless Steel World 2005, KCI Publishing, The Netherland, (2005), 5119.
13) R. S. Parmar: Welding Engineering and Technology, 1st ed., Khanna Publication, New Delhi, India, (2004), 543.
14) N. Parvathamvarthini and R. K. Dayal: J. Nucl. Mater., 305 (2002), 269.
15) A. Yae Kina, V. M. Souza, S. S. M. Tavares, J. M. Pardal and J. A. Souza: Mater. Charact., 59 (2008), 651.
16) R. K. Dayal, N. Parvathamvarthini and B. Raj: Int. Mater. Rev., 50 (2005), 129.
17) R. V. Taiwade, A. P. Patil, S. J. Patre and R. K. Dayal: ISIJ Int., 52 (2012), No. 10, 1879.
18) A. Di Schino and J. M. Kenny: J. Mater. Sci. Lett., 21 (2002), 1631.
19) X. Yu, S. Chen and L. Wang: J. Serb. Chem. Soc., 74 (2009), No. 11, 1293.
20) R. Sousa, J. Filho, A. Tanaka, A. Oliveira and W. Ferreira: J. Mater. Sci., 41 (2006) 2381.
21) R. Beltran, J. G. Maldonado, L. E. Murr and W. W. Fisher: Acta Mater., 45 (1997), 4351.
22) X. Yu, S. Chen, Y. Liu and F. Ren: Corros. Sci., 52 (2010), 1939.
23) S.-X. Li, Y.-N. He, S.-R. Yu and P.-Y. Zhang: Corros. Sci., 66 (2013), 211.
24) Recommended Practices for Detecting Susceptibility to Intergranular Corrosion in Stainless Steels: A-262-02, ASTM Annual Book, 3.02, ASTM Publications, Philadelphia, PA, (2002).
25) A. P. Majidi and M. A. Streicher: Corrosion, 40 (1984), 584.
26) D. N. Wasnik and I. Samajdar: Acta Mater., 50 (2002), 4587.
27) R. Singh, S. Ghosh Chowdhury and I. Chattoraj: Metall. Mater. Trans. A, 39 (2008), 2504.
28) J. Hilliard: Metal Prog., 85 (1964).
29) H. Abrams: Metallography, 4 (1971), 59.
30) R. V. Taiwade, A. P. Patil, S. J. Patre and R. K. Dayal: JMEPEG, 22 (2013), 1716.
31) R. Singh, S. G. Chowdhury, B. Ravikumar, S. K. Das, P. K. Dey and I. Chattoraj: Scr. Mater., 57 (2007), 185.
32) Y. F. Yin and R. G. Faulkner: Corros. Sci., 49 (2007), 2177.
33) H. Sahlaoui, H. Sidhom and J. Philibert: Acta Mater., 50 (2002), 1383.