Transmission Electron Microscopy in the Heat Affected Zone of an AISI 304 Austenitic Stainless Steel Welded with the Application of a Magnetic Field of Low Intensity

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A transmission electron microscopy (TEM) study was carried out of the heat affected zone (HAZ) of an AISI 304 austenitic stainless steel gas metal arc weld with a magnetic field of 14.7 mT. Thin foils for TEM observation were prepared from the as-received 304 stainless steel and the HAZ of samples welded with and without magnetic field. M2C1 carbides were observed in conventional bright field (BF) and high resolution (HR) confirmed their presence in the as-received stainless steel. Elemental line scans performed in the base metal showed that the austenite/M2C1 interface was Cr-depleted in the austenite side. The results revealed that welding with magnetic field modified the distribution of Cr within the carbides and healed the Cr-depleted zones. This evidence accounts for the enhanced corrosion behaviour previously reported by the authors and strengthens the proposed mechanism where the interaction between the external magnetic field and the magnetic field generated by the direct current of the welding process promotes diffusion of Cr in short distances, healing thus Cr depletion.

Keywords: sensitization, austenitic stainless steel, gas metal arc welding, magnetic field

1. Introduction

Most of the Austenitic stainless steels (ASS) were developed for nuclear applications due to its excellent corrosion resistance, however, problems arose as they are prone to suffer sensitization when exposed to temperatures between 450 to 800°C.1,2) Sensitization in ASS refers to chromium depletion in the vicinity of the grain boundaries as a result of the precipitation of Cr rich carbides, becoming the stainless steels susceptible to localized corrosion attack3) and leading to premature failures in components.4) The precipitation of secondary Cr-rich phases such as chi (χ) and sigma (σ) can contribute to transgranular attack.5) The presence of pre-existent Cr-rich carbides or its precipitation and growth in the austenitic matrix can be due to fabrication processes such as cold working or welding. Owing to its technological relevance, the deterioration of the passive film in ASS and its impact on corrosion behaviour has been for a long time a major concern. Obviously, research efforts have been directed toward developing methods to overcome this relentless problem.6) For example approaches such as reduction in the content of carbon delays the onset for the precipitation of carbides,7) alloying with elements such as Ti that forms carbides thermodynamically more stables than chromium carbides,8) laser surface remelting9) and grain boundary engineering10) have been used through the years. The application of magnetic fields during welding was implemented to generate an electromagnetic stirring in order to disturb the dynamics of the weld pool and modify the mode of solidification and thereby the final microstructure of the weld metal.11,12) Recently13,14) the authors focused on the effect, in the HAZ, of the application of an external magnetic field of low intensity during welding an AISI 304 ASS. It was found that the corrosion resistance to localized attack in this zone exhibited improved corrosion behaviour, in terms of the degree of sensitization (DOS), in a chloride containing solution than samples of welds plainly welded. This study seeks to clarify the healing effect of Cr depleted zones in samples taken from the HAZ in pre-sensitized AISI 304 stainless steel welded under the effect of a magnetic field of low intensity by using transmission electron microscopy (TEM).

2. Experimental Procedure

A commercial AISI 304 austenitic stainless steel, 6 mm thick, in the as-received condition with the chemical composition shown in Table 1 was gas metal arc welded with an ER 309L filler wire (1.2 mm in diameter). The plates were machined to form a single V joint and welded at 3.6 mm/s by feeding the filler wire at 180 mm/s and using Ar as shielding gas with a flow of 30 L/min. Direct current-electrode positive (DC-EP) was used with 27 V and 240 A of voltage and current, respectively. Plates were welded with and without the application of an external magnetic field. In the former case, an external magnetic field of 14.7 mT was applied axial to the welding torch with the setup shown in Fig. 1.

For TEM characterization thin foils were cut from the as-received AISI 304 stainless steel and a specific site from the HAZ of the welded joints. Details about the selection of this site are given in13,14) and it corresponds to a zone prone to suffer sensitization in the HAZ. The samples were thinned down to 40 μm with emery paper and prepared for TEM

Table 1 Chemical composition of AISI-304 stainless steel (mass%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0.058</td>
<td>1.512</td>
<td>0.024</td>
<td>0.008</td>
<td>0.352</td>
<td>18.56</td>
<td>8.0</td>
</tr>
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observation by electropolishing using an electrolyte of 10% perchloric acid and 90% ethanol, at −20°C and 20 V in a Tenupol twin-jet polisher. A Tecnai F20 TEM operating at 200 kV and equipped with an energy dispersive X-ray (EDX) analyzer was used in this study.

3. Results

In the as-received base metal pre-existent carbides were found partitioning the austenitic matrix as observed in the conventional bright field image shown in Fig. 2(a). The particles exhibited a needle shape, typically between 20 to 30 nm in width and several micrometers in length. The TEM-EDX analysis in Fig. 2(b) shows that the carbide is mainly formed by Fe, Ni, C and Cr. In the bright zone labelled as HR in Fig. 2(a), the carbide was observed in high resolution (HR) TEM. Figure 3(a) represents a HRTEM image of the interface between the carbide and the γ matrix. Figure 3(b) shows a Fast Fourier Transform (FFT) between the carbide and the austenite, where double diffraction was observed; it was confirmed that the carbides are of the type M7C3.15) In this case, M represents a mixed structure of Fe, Cr and Ni. The interplanar spacing 0.209 nm, shown in the filtered image in Fig. 3(c), corresponds to the (422) plane. The M7C3 carbides have a hexagonal crystalline structure and correspond to the P31c space group, which was described initially as trigonal with a hexagonal Bravais lattice.16) TEM studies had proved that the crystal structure of M7C3 contains different orthorhombic unit cells.17) However, the evidence found in this study matches with the hexagonal structure.

Figures 4(a) and 4(b) show carbides in the HAZ of samples welded without and with magnetic field. These images were captured in scanning transmission electron microscopy (STEM) mode employing a high angle annular dark field (HAADF) detector. The difference in contrast...
between the carbide and the matrix is due the average atom number of Ni which strongly contributes to the Z-contrast. Concentration profiles for Ni and Cr across the γ/M_2C_3 interface were measured along the lines indicated in the images and they are shown in Figs. 4(c) and 4(d). It can be observed in Fig. 4(c), for the sample welded without magnetic field, that the chromium concentration within the M_2C_3 carbide is higher than the austenitic matrix whereas the concentration of nickel is reduced. In the M_2C_3/γ interface the Cr profile exhibits a depleted region with two deep peaks. Such site represents a potential site for localized corrosion in ASS. Conversely, the plot in Fig. 4(d) revealed that the Cr and Ni profiles for the sample welded with magnetic field showed a homogeneous distribution within the particle and without Cr depletion at the M_2C_3/γ interface. These differences were consistent within the specimens analyzed. Thus, the evidence shows that Cr is redistributed when welding is performed with the application of an external magnetic field of low intensity.

4. Discussion

The electromagnetic interaction (EMI) of low intensity occurs when two perpendicular magnetic fields simultaneously act on a solid material. In the particular case of this study, this interaction is induced during welding when the zone adjacent to the fusion line experiences cooling from a peak temperature of ~1230°C. In a paramagnetic material such as the 304 ASS, the EMI causes a perturbation on the vibration mode of the atoms in the crystalline lattice due to the Lorentz force exerted on the charge carriers. In this instance, two cases need to be considered; the first is the intrinsic magnetic field generated by the DC of the welding process and the second is the external magnetic field induced with the coil around the parent plates.

Let's consider the effect of the Lorentz force or electromagnetic force in the first case. Figure 5 shows the coordinates system for the analysis. The electromagnetic force, \( F_{EM} \), given by eq. (1) according to Fig. 5, is function of the moving charge, \( q \), the potential, \( E \), the velocity of the moving charge, \( v \), and the magnetic field, \( B_\| \),

\[
F_{EM} = q[B_i v_z + (E - B_j v_y) k]
\]

Making eq. (1) equal to the second law of Newton

\[
m[a_x + a_y + a_z] = q[B_i v_z + (E - B_j v_y) k].
\]

In the end and for the sake of briefness, the helical path followed by the electrons under the effect of the magnetic field induced by the welding DC (γ–z plane) is given by eqs. (3) and (4), where \( w \) is the angular frequency.

\[
y(t) = \frac{1}{w} E [wt - \sin(wt)]
\]

\[
z(t) = \frac{1}{w} E [1 - \cos(wt)]
\]

Consideration of the perturbation of the moving charge due to the external magnetic field with reference to Fig. 5, in a similar fashion to the first case, yields equations analogous to (3) and (4) that describe the helical path in the x–y plane in Fig. 5.

Thus, welding with DC induces a magnetic field which interacts with the external magnetic field applied, this EMI stirs the weld pool but also, it causes vibration of the atoms in the parent material. This effect enhances the diffusion of Cr in very short distances healing the Cr depleted M_2C_3/γ interfaces providing thus a better corrosion resistance in the HAZ as observed previously by the authors. Nucleation of new carbides and growth of those previously formed will depend on the availability of carbon. Studies on carbon diffusion in iron under the effect of a relatively large magnetic field (6 T), as compared to this study, revealed that whereas both a uniform and a “positive” magnetic field gradient reduce the diffusion coefficient, a “negative” magnetic field gradient promotes the diffusion of carbon in γ-iron. Different results were, however, reported by Wang et al. in annealed γ-Fe samples at 1000°C under a magnetic field of 12 T. These authors found that the diffusion of C is slightly enhanced when the magnetic field is applied perpendicular to the interface of the diffusion couple whereas it is lacking when the magnetic field is applied parallel to the interface. This behaviour was explained with the model of Zhang et al., where the atoms experience attraction (contraction of the lattice) along the direction of the magnetic field and repulsion (expansion of the lattice) in the normal plane.

The experimental evidence suggests that the EMI between the intrinsic magnetic field generated by the welding DC and the external magnetic field produced a “negative” magnetic field gradient. Analyzing the configuration of the experimental set up used in this study; in the transverse direction of the parents plates, the intensity of the magnetic field increases from the center of the joint toward the coil whereas the gradient in the longitudinal direction is because the welding torch is being displaced at constant speed. Thus, diffusion is not expected to be favoured solely in an specific plane, it will occur in all directions as dictated by the chemical potentials. Regarding the model of Zhang et al., the interaction described by the helical paths in Fig. 5 may be incorporated into this model as shown in Fig. 6. In this scenario, vibration of the iron atoms is exacerbated by the fact that two perpendicular magnetic moments are acting on them giving rise to a resultant magnetic moment. This type of interaction yields expansion and contraction of the crystalline lattice enabling diffusion without restrictive directions. Thus, the enhanced diffusivity of interstitial C atoms by the EMI leads
to homogenization and suppression of carbon segregations so that nucleation and further growth of pre-existent carbides are prevented.

5. Conclusions

The microstructural effects of the application of a magnetic field of low intensity in the HAZ of AISI 304 stainless steel have been investigated. The M\textsubscript{7}C\textsubscript{3} observed in the as-received AISI 304 stainless steel revealed Cr depleted zones in the M\textsubscript{7}C\textsubscript{3}/\gamma interface after GMA welding. After welding with the presence of an external magnetic field of low intensity, chemical composition profiles showed that Cr within the carbides exhibited a homogeneous distribution and the zones with reduced Cr content dissapeared. This evidence suggests that the EMI generated during welding with an external magnetic field of low intensity promotes the diffusion of Cr in short distances healing sensitized zones.

Acknowledgements

The authors acknowledge the financial support given by CONACyT and the CIC of the UMSNH.

REFERENCES