The Improvement of Corrosion Resistance of Sensitized Alloy 82 Welds Using Laser Surface Melting

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The corrosion resistance of sensitized Alloy 82 welds is improved by laser surface melting (LSM) with a continuous CO2 laser beam. The effects of the LSM treatment on the segregation of impurities in the matrix and the precipitation of carbides at the grain boundaries are systematically explored. The observed results show that the LSM process results in the formation of a rapidly solidified surface layer with a thickness of approximately 160–180 μm. In addition, the corrosion test results show that the LSM treatment improves the resistance of the weld to both intergranular corrosion (IGC) and pitting corrosion. The improved corrosion resistance can be attributed to a higher proportion of low-angle boundaries (2–15°) in the solidified microstructure, the elimination of Cr-carbide precipitates in the matrix, and the suppression of Cr-depletion zones at the grain boundaries. Overall, the results confirm the effectiveness of LSM treatment for the in-situ repair and corrosion resistance restoration of Alloy 82 welds.

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Keywords: Alloy 82 weld, laser surface melting (LSM), intergranular corrosion (IGC), pitting corrosion

1. Introduction

Alloy 182/82 is widely used in the nuclear power industry for the preparation of dissimilar metal welds (DMWs) consisting of austenitic stainless steel (SS) and low alloy steel. However, these welds commonly suffer intergranular corrosion (IGC), interdendritic stress corrosion cracking (IDSCC), intergranular stress corrosion cracking (IGSCC) and primary water stress corrosion cracking (PWSCC) following sensitization effect due to the precipitation of Cr-rich carbides during the welding process. To ensure the safety of the power plant, it is therefore necessary to develop effective methods for improving the corrosion resistance of the DMWs.

Corroded components in the coolant water systems of boiling water reactors (BWRs) are generally repaired by depositing Alloy 52/52M weld overlays (WOLs) on the affected area. It has been shown that WOLs mitigate IGSCC by inducing a compressive stress within the welded material and forming a corrosion-resistance layer on the treated surface. However, while WOLs provide an effective means of mitigating the effects of IGSCC and PWSCC, they have several important disadvantages, including a long working time and the risk of hot cracking defects due to a high dilution of the base metal.

Accordingly, the use of laser surface melting (LSM) to improve the corrosion resistance properties of alloy welds has attracted growing interest in recent years. LSM is a high energy density process with a low heating effect, and therefore promotes a localized re-melting and solidification of the weld surface without affecting the mechanical properties of the other regions. Many studies have examined the effectiveness of LSM in improving the IGC/IGSCC resistance of sensitized austenitic SS and Alloy 600. In general, the results have shown that the rapid solidification rate in LSM suppresses the precipitation of Cr-rich carbides at the grain boundaries, and thereby reduces the number of potential sites for IGC/IGSCC initiation.

Several studies have shown that LSM also has the ability to improve the stress corrosion cracking (SCC) resistance of Alloy 182. While several new weld metals, e.g., Alloy 52/52M, with a higher corrosion resistance than Alloy 182/82 have been introduced in recent years, the corrosion resistance of Alloy 182/82 welds continues to be a major concern since many old nuclear power plants are expected to remain in operation for sixty years or more. Furthermore, Alloy 82, with only a moderate corrosion resistance, is still widely used in the construction of new nuclear power plants. The effectiveness of LSM in improving the corrosion resistance of Alloy 182 is well documented in the literature. However, the application of LSM to sensitized Alloy 82 welds has yet to be reported. Accordingly, the present study investigates the grain boundary character distribution (GBCD), elemental composition, degree of sensitization (DOS) and IGC resistance properties of Alloy 82 overlay welds prepared using a manual gas tungsten arc welding (GTAW) process.

2. Experimental Procedures

The experimental trials were performed using 316L SS plates with dimensions of 80 mm × 50 mm × 6 mm as the base metal. Alloy 82 was purchased from Tientai Electrode Co., Ltd. in the form of wire with a diameter of 2.4 mm, and was deposited on the 316L SS plates using a manual GTAW process. Overlay welds with a thickness of 4 mm were prepared in a three-pass process. The welding current, welding voltage and travel speed were set in the ranges of 120–130 A, 14–15 V and 1.9–2.4 mm/min, respectively. The chemical compositions of the weld metal and overlay weld are shown in Table 1. It is noted that both compositions are within specification requirements (AWS A5.14.
ERNiCr-3).

The as-welded (AW) plates were sensitized (SEN) at 650 °C for 24 hours using heating/cooling rates of 100 °C/hour. The SEN plates were polished with 600-grit SiC abrasive paper in order to roughen the surface and increase the absorption of the laser beam energy. LSM treatment was then performed using a continuous CO2 laser beam with an output power of 4.8 kW, a scanning speed of 0.8 m/min and a laser spot size of 10 mm. To prevent oxidization, the LSM process was performed in He shielding gas with a flow rate of 20 l/min. Moreover, the weld beads produced in each pass were offset by a distance of 5 mm from one another in order to increase the size of the treatment area8,11). Figure 1 presents schematic illustrations of the GTAW and LSM processes.

Test coupons with dimensions of 10 mm × 10 mm (length × width) were cut from the AW, SEN and SEN+LSM plates using an electrical discharge machining wire cutter. The microstructures of the vertical cross-sectional surfaces were examined by optical microscopy (OM). The horizontal surfaces were characterized via electron back-scattered diffraction (EBSD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Prior to observation, the specimens were etched in a solution of 88% phosphoric acid (H₃PO₄) under a potential of 3 V for 30 s. The precipitates and segregation distribution of the alloying elements were analyzed by energy dispersive spectroscopy (EDS) and electron probe microanalysis (EPMA), respectively. Thin foil specimens for TEM observations were prepared using a double-jet thinner with 10% perchloric acid at −10 °C and an agitation voltage of 20 V.

The corrosion resistance properties of the various specimens were evaluated by means of double-loop electrochemical potentiodynamic reactivation (DL-EPR) tests and potentiostatic corrosion tests. The tests were performed at room temperature in a 0.05 M H₂SO₄ solution containing 0.003 M CH₃CSNH₂. The scanning rate was set as 0.5 mV/s in every case. CH₃CSNH₂ was deliberately chosen as the activator for the tests since previous studies have shown that the addition of potassium thiocyanate (KSCN) to H₂SO₄ solution may corrode the matrix to such an extent that the DOS of the alloy cannot be reliably determined13–15). For each specimen, the DOS was evaluated as the ratio of the maximum anodic current in the reverse scanning curve to that in the forward scanning curve (i.e., DOS = Ir/Ia). Following the corrosion tests, the surface morphologies of the various specimens were examined microscopically in order to identify the intrinsic corrosion mechanism.

### Table 1: Chemical compositions of filler metal and overlay weld (mass%).

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Mn</th>
<th>Fe</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>Co</th>
<th>Ti</th>
<th>Cr</th>
<th>Nb+Ta</th>
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<tr>
<td>Specification</td>
<td>Max</td>
<td>2.5</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>18.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Requirements</td>
<td>0.10</td>
<td>3.5</td>
<td>7.0</td>
<td>0.03</td>
<td>0.015</td>
<td>0.50</td>
<td>0.50</td>
<td>57.0</td>
<td>0.12</td>
<td>0.75</td>
<td>22.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Filler Metal</td>
<td>0.035</td>
<td>3.0</td>
<td>1.30</td>
<td>0.003</td>
<td>0.001</td>
<td>0.08</td>
<td>0.01</td>
<td>72.50</td>
<td>0.04</td>
<td>0.36</td>
<td>20.04</td>
<td>2.41</td>
</tr>
<tr>
<td>Overlay Weld*</td>
<td>0.04</td>
<td>2.82</td>
<td>1.86</td>
<td>0.004</td>
<td>0.002</td>
<td>0.04</td>
<td>0.01</td>
<td>71.52</td>
<td>0.05</td>
<td>0.34</td>
<td>20.46</td>
<td>2.69</td>
</tr>
</tbody>
</table>

*measured using optical emission spectrometer.

### 3. Results and Discussion

#### 3.1 Microstructural observations

Figure 2(a) presents cross-sectional micrographs of the various Alloy 82 overlay welds. For all of the welds, the subgrain structure is primarily dendritic with interdendritic...
constituents. The dendrites are formed as a result of constitutional supercooling and grow in the direction of the heat flow path (i.e., perpendicular to the substrate surface). As a result, the dendritic structures are all parallel to one another and have the same crystallographic orientation within each grain.

As shown in Fig. 2(c), the microstructure of the SEN+LSM specimen contains two distinct zones, namely a laser-melted zone (LMZ) with a thickness of approximately 160–180 μm and an unaffected zone. Moreover, Fig. 2(f) shows that the rapid solidification rate in LSM results in the formation of a thin upper layer of fine cellular dendrite with a thickness of around 18–20 μm and a thicker lower layer of columnar dendrite with a dendritic spacing of approximately 3–4 μm.

Figure 3(a) presents a TEM micrograph of the AW specimen. A small number of fine precipitates are observed dispersed along the grain boundary. For the SEN specimen, the grain boundaries contain a large number of precipitates with a near-continuous distribution (see Fig. 3(b)). However, following LSM treatment, the number of precipitates is significantly reduced (see Fig. 3(c)). In other words, it appears that the LSM treatment prompts the dissolution of the grain boundary precipitates into the matrix and leads to the formation of a homogeneous surface layer with only a small number of fine precipitates as a result.

The SEM image of the AW specimen (Fig. 4(a)) shows the presence of a small number of block-like particles with a size of several microns. (Note that similar particles were also observed in the SEN and SEN+LSM specimens.) The EDS analyses show that these particles are either rich in Nb and Ti with traces of C and N (see Fig. 4(b)), or rich in Nb with traces of C and Ti (see Fig. 4(c)). Previous studies have indicated that these particles are either a mixture of NbC and TiC/TiN, or complex carbide/nitride precipitates (Ti, Nb) (C, N). Nb and Ti both have a higher affinity for C than Cr. It is thus inferred that the precipitation of these blocky particles during the overlay welding process is beneficial in suppressing the formation of Cr-depletion zones. It is further speculated that the absence of Cr-rich precipitates in the as-welded matrix contributes to an improved IGC resistance. It is noted that similar inferences have been reported for Alloy 6917,18).

Sennour et al.19) showed that Alloy 82 welds with a high carbon content (19 mass% Cr, 0.034 mass% C) are more likely to form Cr-carbides during sensitization at 600 °C for 7 hours than welds with a low carbon content. In the present study, the overlay welds were prepared using Alloy 82 filler metal with a high C content of 0.035 mass%. Consequently, the formation of Cr-depletion zones near the grain boundaries of the SEN sample (see Fig. 6(b)) can be attributed most probably to the precipitation of Cr-carbides in the matrix.

During the LSM process, the temperature of the melted pool exceeds the liquidus point of Alloy 82 (1400°C) and is high enough to decompose the carbides. Due to the concentration difference between the Cr-carbides and the matrix, the Cr atoms diffuse into the matrix while in the liquid state.
Consequently, both the Cr-carbides and the Cr-depletion zones are eliminated in the LSM specimen.

3.2 Grain boundary characteristics

Figure 5(a) shows the inverse pole figure (IPF) maps of the AW, SEN and SEN+LSM weldments. Note that NiCrFe austenitic phase data were used for phase construction in every case. Note also that the maps show the upper surface of the overlay weld, and beam scanning was performed in the horizontal direction i.e., perpendicular to the welding direction (see the legend of Fig. 5). The results show that all of the overlay welds have an austenitic matrix. During weld metal solidification, the dendrites within each grain tend to grow in the easy-growth direction, i.e., <100> in austenitic materials\(^{20}\). Hence, the grains in the AW sample are oriented predominantly in the <001> direction. In Fig. 5(a), the intensity of the red color in the contour plot of the AW sample corresponds to a value around 5 times higher than that of the random background. For the SEN sample, the intensity of the red color is reduced to around 2 times that of the random background. However, it is still seen that the (100) pole is strongly aligned. Since no evidence of recrystallization during the sensitization process is available in the present study, it is presumed that the difference in the crystal orientations of the AW and SEN samples, respectively, can be attributed to the non-uniformity of the microstructure as a result of the multi-pass welding process. For the SEN+LSM sample, the red regions in the pole figure have an intensity only 1.5 times higher than that of the random background. In other words, the LSM process transforms the microstructure of the sensitized Alloy 82 weld from an isotropic structure to an anisotropic structure.

The grain boundary maps in Fig. 5(b) show that the majority (74.6\%) of the subgrain boundaries in the SEN+LSM sample have an intensity only 1.5 times higher than that of the random background. In other words, the LSM process transforms the microstructure of the sensitized Alloy 82 weld from an isotropic structure to an anisotropic structure.

![EBSD results for overlay welds: (a) IPF maps; (b) grain boundary maps.](image-url)
sample have a low orientation angle of around 2–15°. By contrast, most of the grain boundaries in the SEN sample have a higher orientation angle in the range of 15°–62.8°. The detailed analysis results presented in Table 2 show that the fraction of high-angle boundaries (>15°) in the AW and SEN specimens is equal to 67.9% and 60.1%, respectively. By contrast, in the SEN+LSM specimen, the fraction of high-angle boundaries is equal to just 25.4%. Moreover, the densities of the high-angle boundaries in the AW and SEN specimens are around 212.4 cm/cm² and 255.6 cm/cm², respectively, whereas that of the high-angle boundaries in the SEN+LSM specimen is slightly lower (210.1 cm/cm²).

Previous studies have reported that segregates and precipitates are more likely to form along high-angle boundaries than low-angle boundaries. The EBSD results thus indicate that around 60.1% and 255.6 cm² of the grain boundaries in the SEN specimen may be decorated with segregates and/or precipitates. This inference is consistent with the SEM image presented in Fig. 3(b), which shows a near-continuous dispersion of precipitates along the grain boundaries in the sensitized specimen.

Figures 6 and 7 present the EPMA results for the elemental compositions of the SEN and SEN+LSM specimens, respectively. Figure 6(a) shows the presence of some blocky particles (white spots) in the interdendritic regions of the SEN specimen. The EPMA results (Figs. 6(b)–(e)) reveal that these particles are enriched in C, Nb and Ti. Hence, it is inferred that C, Nb and Ti elements are rejected into the interdendritic liquid during the solidification stage of the welding process. The SEM image presented in Fig. 6(f) shows that the particles exert a grain boundary pinning effect. This observation is consistent with the findings of Lipold et al. that Alloy 82 welds, with a high Nb content, form NbC carbides at the end of solidification, which not only pin the migrated grain boundaries, but also produce tortuous high-angle boundaries, and thus prompt the formation of segregates and precipitates. In the absence of these NbC carbides, the pinning effect is removed, and hence the grains have a relatively straight boundary, as shown in Fig. 7(f) for the SEN+LSM sample. The C mapping results in Fig. 6(c) confirm the precipitation of C-rich particles along the grain boundaries of the SEN weld. By contrast, the Cr mapping results (Fig. 6(b)) show a distinct Cr depletion along the grain boundaries. As mentioned above, the lack of Cr at the grain boundaries can be attributed most probably to the precipitation of Cr-carbides in the matrix during sensitization.

The SEM image presented in Fig. 7(a) shows that the LSM process prompts a refinement of the blocky particles in the interdendritic region. Furthermore, as shown in Figs. 7(b) and 7(c), no C-enrichment zones or Cr-depletion zones are formed at the grain boundaries. In other words, the EPMA results confirm that the Cr-carbides in the SEN specimen are completely melted/dissolved during the LSM treatment due to the high-energy laser beam and are not re-precipitated during the subsequent cooling process due to the rapid cooling rate. It is noted that these results are consistent with the findings of Lim et al. for Alloy 600, in which Cr-carbides were also not observed at the grain boundaries in the LMZ following LSM treatment. However, a small number of Cr-carbides were found at some of the high-angle grain boundaries in a LSM Alloy 600 sample sensitized at 600°C for 24 hours. Notably, the IGC morphology of the sensitized LSM sample was found to be exactly correlated with the distribution of these grain boundary Cr-carbides. Therefore, based on the findings of Lim et al. and the microstructural observations and GBCD analysis results obtained in the present study, it can be expected that the SEN+LSM specimen should have a high resistance to IGC.

The detailed analysis results presented in Table 2 show that the fraction of high-angle boundaries (>15°) in the AW and SEN specimens is equal to 67.9% and 60.1%, respectively. By contrast, in the SEN+LSM specimen, the fraction of high-angle boundaries is equal to just 25.4%. Moreover, the densities of the high-angle boundaries in the AW and SEN specimens are around 212.4 cm/cm² and 255.6 cm/cm², respectively, whereas that of the high-angle boundaries in the SEN+LSM specimen is slightly lower (210.1 cm/cm²).

Fig. 6 EPMA investigation results for SEN specimen: (a) SEM image; (b)–(e) Cr, C, Nb and Ti element mappings, respectively; (f) SEM image of tortuous grain boundary.

<table>
<thead>
<tr>
<th>Rotation angle</th>
<th>AW</th>
<th>SEN</th>
<th>SEN+LSM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>Max.</td>
<td>Length</td>
<td>Fraction (%)</td>
</tr>
<tr>
<td>2°</td>
<td>5°</td>
<td>1.34</td>
<td>13.3</td>
</tr>
<tr>
<td>5°</td>
<td>15°</td>
<td>1.89</td>
<td>18.8</td>
</tr>
<tr>
<td>15°</td>
<td>62.8°</td>
<td>6.83</td>
<td>67.9</td>
</tr>
</tbody>
</table>
3.3 Corrosion properties

Figure 8 shows the DL-EPR curves of the AW, SEN and SEN+LSM specimens. It is seen that the AW specimen experiences no anodic dissolution during the reactivation scan. In other words, the DOS value is equal to zero, and both the grain boundary regions and the interior of the grains remain passivated. However, for the SEN specimen, a high anodic current density is produced during reactivation. The DOS is equal to approximately 31%; indicating that the weld has a high degree of sensitization24). For the SEN+LSM specimen, the passive current is almost the same as that for the AW specimen, and the DOS value is again equal to zero. Overall, the DL-EPR results confirm that the LSM treatment effectively improves the corrosion resistance of the sensitized Alloy 82 weld.

Figure 9 presents optical micrographs of the three specimens following the DL-EPR tests. The SEN specimen shows signs of extensive IGC and pitting corrosion (Fig. 9(b)). By contrast, the AW and SEN+LSM specimens exhibit only slight corrosion. Therefore, it can be inferred that the high anodic reactivation current density of the SEN specimen observed in Fig. 8 stems from IGC and pitting corrosion. To confirm this inference, potentiostatic corrosion tests were conducted for each specimen for two hours using the respective peak potentials shown in Fig. 8. After testing, the specimen surfaces were examined via OM (see Fig. 10). For the SEN specimen (Fig. 10(b)), pitting holes were formed along the grain boundaries with a size larger than those produced in the DL-EPR test due to the long testing period. In other words, the results confirm that the sensitization process suppresses passivation and promotes the formation of pitting holes. As the corrosion process continues,
these holes interconnect and result in rapid IGC and crack growth\textsuperscript{25). However, after LSM treatment, the sample regains its passivation properties, and has a similar corrosion resistance to the AW specimen, as shown in Figs. 10(a) and 10(c).

In summary, the results obtained in this study suggest that the AW specimen has a low DOS due to its high Cr content and the presence of Nb-Ti carbides, which suppress the formation of Cr-depletion zones. By contrast, the SEN specimen has a high DOS due to the near-continuous precipitation of Cr-carbides along the high-angle grain boundaries, which lead to the formation of Cr-depletion zones\textsuperscript{26,27). Finally, the SEN+LSM specimen has a low DOS due to the elimination of these microstructural inhomogeneities and sensitized microstructures (e.g., Cr-depletion zones) at the grain boundaries. The severe pitting corrosion of the SEN specimen in the potentiostatic test can be attributed to both interdendritic corrosion (IDC) and corrosion around the precipitates, and stems mainly from Cr depletion and galvanic corrosion in the interdendritic regions. It is noted that similar results were reported for Alloy 182 by Peng \textit{et al.}\textsuperscript{28) The EBSD analysis results suggest that the improved resistance of the SEN+LSM specimen stems mainly from a reduction in the fraction and density of high-angle grain boundaries compared to that in the AW and SEN samples.

4. Conclusion

LSM treatment has been performed to restore the intergranular corrosion resistance of sensitized Alloy 82 overlay welds containing 20.04 mass\% Cr and 0.035 mass\% C. The experimental results support the following main conclusions:

1. Approximately 67.9\% and 212.4 cm\textsuperscript{2}/cm\textsuperscript{2} of the grain boundaries in the as-welded (AW) Alloy 82 sample are high-angle boundaries ($\beta > 15^\circ$). These boundaries induce the precipitation of Cr-carbides during sensitization (SEN) at 650°C for 24 hours, and therefore prompt the formation of Cr-depletion zones close to the grain boundaries. The Cr-depletion zones lead in turn to extensive IGC and pitting corrosion, and induce a high DOS value of approximately 31\% in DL-EPR tests performed in 0.05 M H\textsubscript{2}SO\textsubscript{4} solution with 0.003 M CH\textsubscript{3}CSNH\textsubscript{2}.

2. The pitting corrosion observed in the SEN sample is associated with both IDC and corrosion around the precipitates in the weld as a result of Cr depletion and subsequent galvanic corrosion in the interdendritic regions.

3. Around 74.6\% and 541.4 cm\textsuperscript{2}/cm\textsuperscript{2} of the grain boundaries in the SEN+LSM specimen are low-angle boundaries (2–15°). Consequently, the formation of Cr-carbides is suppressed. Moreover, the microstructure of the LMZ in the SEN+LSM sample consists of fine cellular/columnar subgrains with a high resistance to IGC. The superior IGC resistance of the SEN+LSM specimen can be attributed mainly to the absence of Cr-carbide precipitates in the matrix and Cr-depletion zones along the grain boundaries due to the high heat input and rapid cooling rate associated with the LSM process.

REFERENCES

1336

H.-T. Lee and T.-C. Liu