JOURNAL OF MATERIALS SCIENCE **39** (2004) 2257– 2261

Development of an electrochemical reactivation test procedure for detecting microstructural heterogeneity in Ni-Cr-Mo-W alloy welds

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Alloy-22 (UNS N06022), a Ni-Cr-Mo-W based alloy shows excellent corrosion resistance in both oxidizing and reducing environments and is a candidate material for fabrication of outer wall of nuclear waste containers [1–3]. This alloy is considered, as readily weldable [3–6]. In solution-annealed condition, wrought Alloy-22 reveals a single-phase austenite structure without any grain boundary secondary phase precipitates [1, 2]. Topologically close packed (TCP) phases such as μ, σ, and P, which are stable at higher temperatures, were observed to be retained at room temperature as terminal solidification constituents during solidification of weld metal [6]. As the chemical composition of these TCP phases is rich in Mo and W, presence of these phases could result in localized depletion of alloying elements in the matrix and make the alloy more susceptible to corrosive attack. Moreover, the weld microstructure revealed segregation of Mo and W at the interdendritic regions [3, 4]. Multipass welding and post weld heat treatment could increase the quantity of secondary phase precipitation. As the corrosion and toughness properties are affected by the presence of TCP phases and segregation of alloying elements [3], it is important to quantify these microstructural changes in comparison with that of solution annealed condition. A rapid nondestructive testing technique such as electrochemical potentiokinetic reactivation (EPR) test could be an appropriate tool for such microstructural evaluation, especially *in-situ* service conditions. EPR test has been successfully applied for quantifying the degree of sensitization in austenitic and duplex stainless steels [7, 8]. There is no standard EPR test procedure available for detecting intergranular corrosion susceptibility of Ni-Cr-Mo alloys. Recently the present authors reported a test procedure to detect Cr depletion in thermally aged Alloy-22 wrought materials using an electrolyte of 1 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN [9]. However, this test solution could not reactivate the weld metal, as the Cr profile was not affected by the solidification structure and the TCP phases [4]. In this short communication, development of a testing procedure, which could detect the presence of Mo and W depleted regions in Alloy-22 welds, is reported.

38 mm thick Alloy-22 (UNS N06022) plates (chemical composition 0.002% C, 0.14% Mn, 0.009% P, 0.001% S, 0.04% Si, 59.2% Ni, 20.62% Cr, 13.91% Mo, 0.01% Co, 0.01% Cu, 2.68% W, 2.8% Fe and 0.171% V) with double V edge preparation were butt welded with similar composition filler material, Class ERNiCrMo-10, using multi-pass gas tungsten arc welding (GTAW) process. 12.5 mm size cubic specimens were cut from the welded material for electrochemical evaluation tests. The weld specimens were given following three different thermal aging treatments viz., 1. Aged at 760 °C for 1 h, 2. 760 °C for 140 h and 3. 700 °C for 24 h. For comparison, as-welded specimens and as received (mill annealed) wrought specimens were also investigated. The specimens were mounted on epoxy resin exposing only the top surface, which contained a single weld bead in longitudinal direction. An insulated copper wire with a glass shield was soldered at the backside of each of the specimens for electrical connection. The weld metal surface was metallographically polished with a series of emery papers down to 600 grit. The specimen surface did not include heat affected wrought material and the exposed area was 1.5 cm^2.

Double loop electrochemical potentiokinetic reactivation tests were carried out using the following electrolyte solutions:

a) 0.5 M H_2SO_4 + 1 M HCl + 0.01 M KSCN
b) 1 M HCl
c) 2 M HCl + 0.01 M KSCN
d) 1 N HNO_3 + 2 M HCl + 0.01 M KSCN
e) 1 M H_2SO_4 + 2 M HCl + 0.01 M KSCN
f) 2 M HCl + 0.01 M $Fe_2(SO_4)_3$ + 0.01 M KSCN

A conventional three-electrode system was used in a five-necked 1-liter flask with specimen test electrode and two Pt auxiliary (counter) electrodes (Ingold electrodes, Boston, MA) on opposing sides of the working electrode, for more uniform current distribution. A silver/silver chloride (SSC) electrode in saturated KCl solution was used as the reference electrode with a solution bridge and Luggin probe. For each test, the solution electrolyte was de-aerated for one hour prior to specimen immersion with a pure-nitrogen purge, which continued throughout the test. Cyclic polarization was carried out using a potentiostat (Gamry Instruments Inc., Warminister, PA, USA) by scanning the potential from the open circuit corrosion potential to +400 mV (SSC) and reversing the potential back to the initial corrosion potential at a scan rate of 0.5 mV/s. The peak current recorded during forward scan was denoted as

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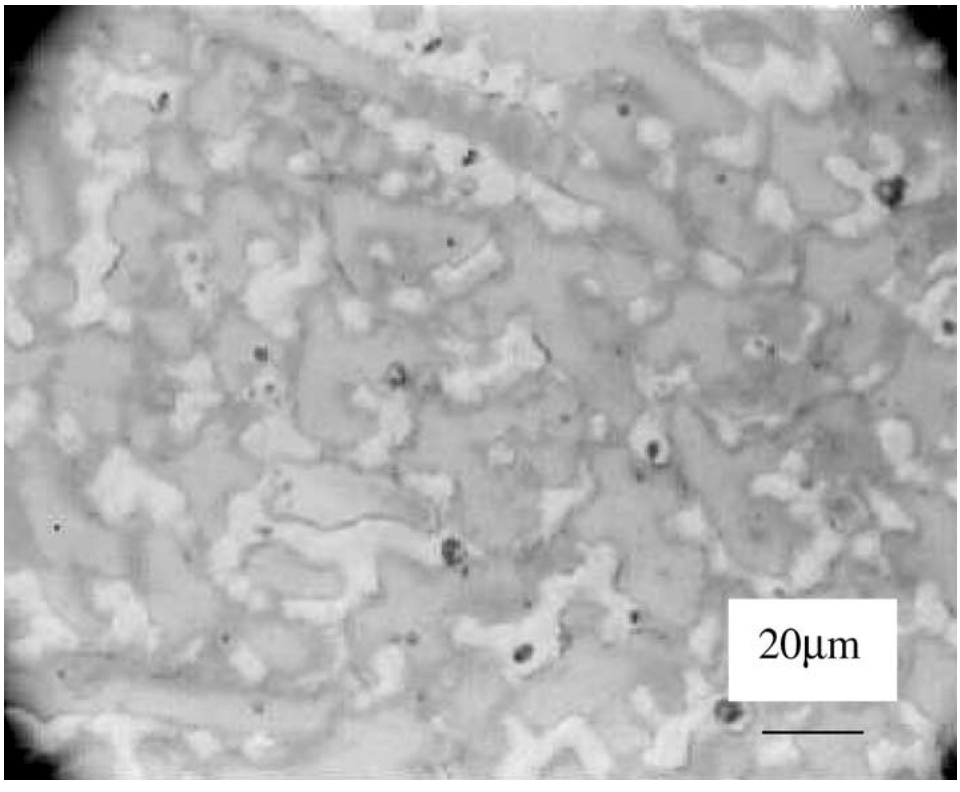

Figure 1 As weld microstructure of Alloy-22.

I_a and the peak current during reverse scan (if any, depending on the alloy element depleted condition) was denoted as I_r. The ratio, I_r/I_a indicated the degree of sensitization [8]. Tests were carried out at 30 and 60 °C.

Fig. 1 shows the as-welded microstructure revealing the dendritic structure after electrochemical etching of the specimen at 1.2 V for 60 s in 1 N sulfuric acid solution. Retention of TCP phase during weld metal solidification is not seen. Fig. 2 shows the microstructure of aged weld metal at 760 °C for 1 h. The interdendritic regions were found to be attacked more, indicating possible secondary phase formation at the Mo segregated areas. The microstructure of the weld metal aged at 760 °C for 140 h revealed grain boundary precipitates along with interdendritic precipitates, as shown in Fig. 3.

Double loop EPR tests carried out at 30 °C in all of the above test solutions did not show either activation or

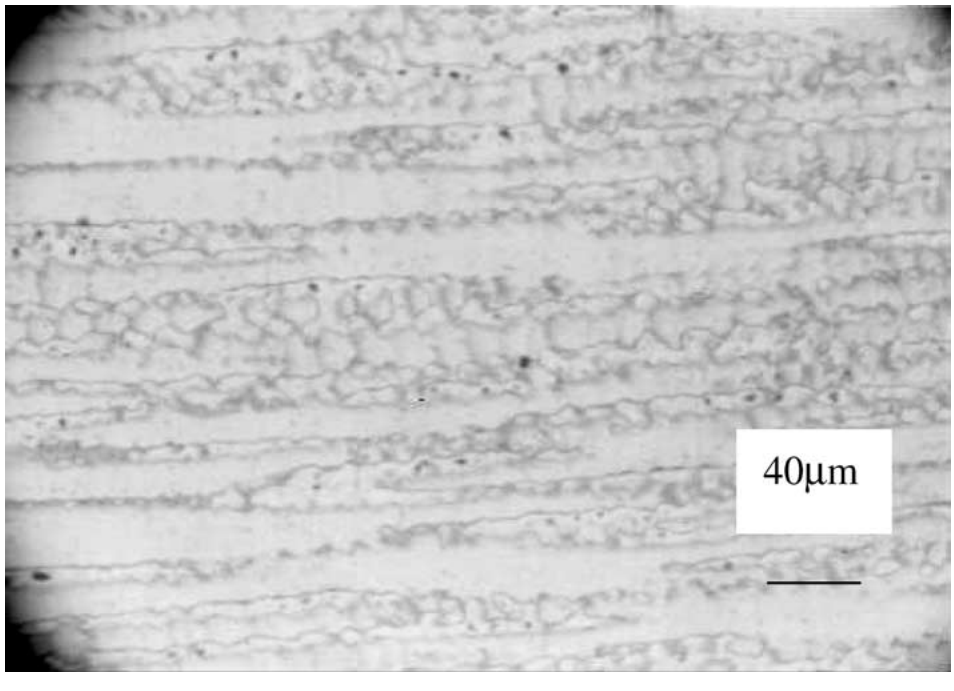

Figure 2 Microstructure of Alloy-22 weld-aged at 760 °C for 1 h.

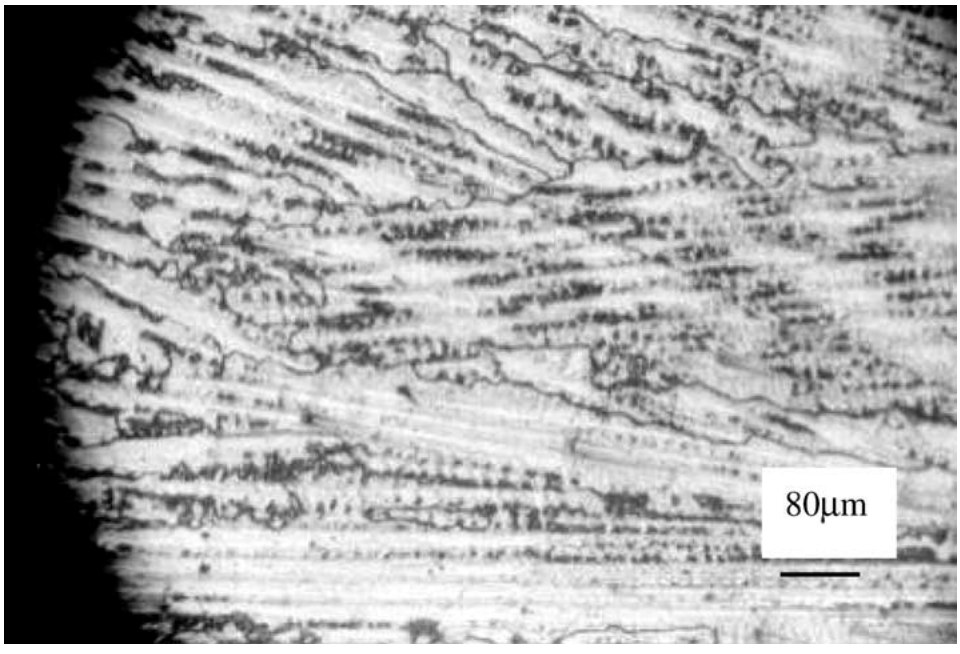

Figure 3 Microstructure of Alloy-22 weld-aged at 760 °C for 140 h.

reactivation peak current for any of the specimens. The specimens showed passivity during forward potential sweep without revealing a critical current peak prior to passivation. The reverse potential sweep after reaching the potential of 400 mV (SSC) also did not show reactivation peak at 30 °C. Even though the hydrochloric acid solution is considered to attack Mo depleted regions near TCP phases, absence of reactivation current peaks indicated the corrosion resistance of the material at lower temperature. Therefore, EPR tests were carried out at a slightly elevated temperature, 60 °C in 2 M HCl + 0.01 M KSCN solution, which is high enough to make the alloy elements depleted regions susceptible to corrosive attack and at the same time not too high a temperature for convenient handling during *in-situ* testing at service conditions.

Fig. 4 shows typical results of double loop EPR tests in 2 M HCl + 0.01 M KSCN solution at 60 °C. Table I summarizes the peak current ratios (I_r/I_a) of EPR tests which is a good indication of degree of depletion of Mo and W in weld specimens of Alloy-22. Minimum three experimental runs were carried out for each aged

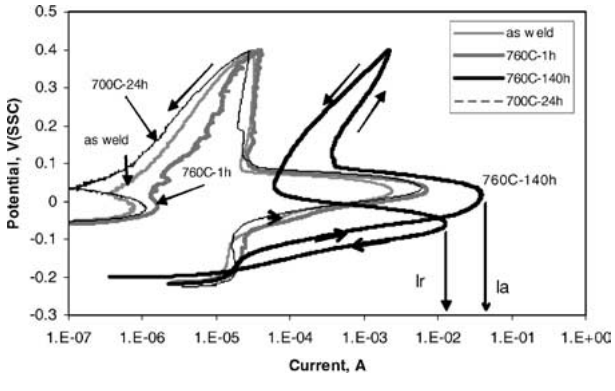

Figure 4 Double loop EPR test results of Alloy-22 weld specimens in 2 M HCl + 0.01 M KSCN solution at 60 °C.

TABLE I Reactivation current to activation current ratios of weld specimens during double loop EPR tests in 2 M HCl + 0.01 M KSCN solution at 60 °C

Aged condition	Minimum I_r/I_a	Maximum I_r/I_a	Average I_r/I_a
Mill annealed wrought	NP	NP	NP
As-welded	3.4×10^{-4}	5.43×10^{-4}	4.27×10^{-4}
700 °C for 24 h	2×10^{-4}	3.98×10^{-4}	2.94×10^{-4}
760 °C for 1 h	1.97×10^{-4}	2.47×10^{-4}	2.28×10^{-4}
760 °C for 140 h	0.227	0.322	0.29

condition of the specimens. The Table I gives minimum, maximum and average values of the ratios of the peak currents among the test runs.

The weld specimens aged at 760 °C for 140 h showed very high ratios of reactivation to activation current as compared to other aged specimens. When comparing the current ratios, it could be observed that as-welded specimens showed relatively higher values than the values of the specimens aged at 700 °C for 24 h and 760 °C for 1 h. However, if the current peaks during forward and reverse sweeps are considered independently for different aged weld specimens, it could be observed that the current peaks increased with aging conditions, as seen in Fig. 4. The current peak during forward sweep (I_a), which is also denoted as critical current for passivation, is an indication of the ability of the material to passivate. For example, the critical current density for passivation of 304 SS in 1 N H_2SO_4 was observed to be two orders higher than that of Alloy-22 [10]. The critical current was observed to increase with the aggressiveness of the environment. Therefore, the increase in critical current for passivation clearly indicates the loss in corrosion resistance of the material with aging.

In this present study, as-welded specimens showed lower peak currents during both forward and reverse

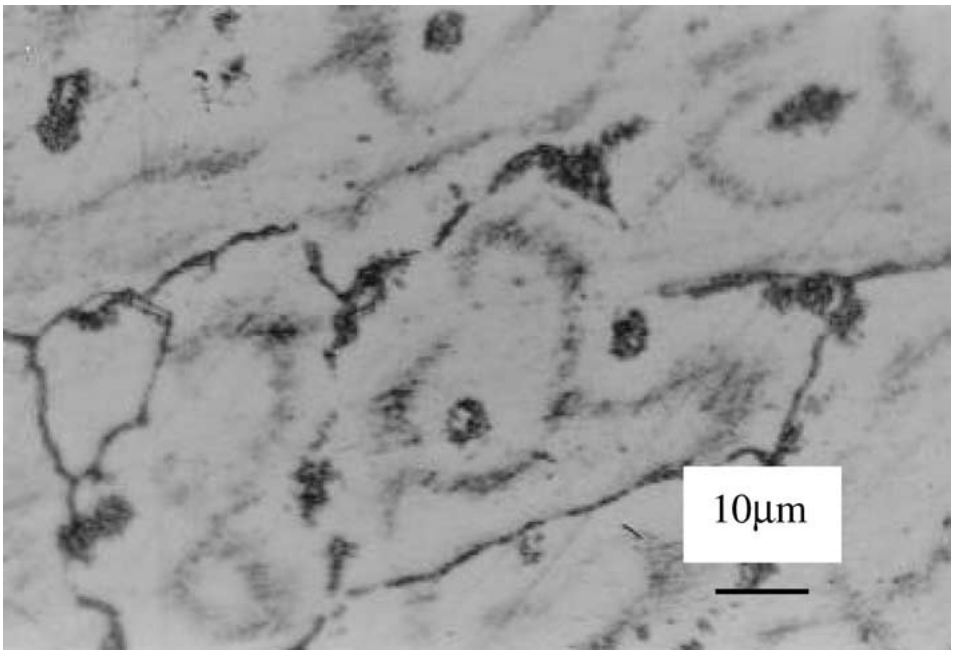

Figure 5 Microstructure of Alloy-22 weld-aged at 760 °C for 140 h etched at potential corresponding to reactivation current peak in 2 M HCl + 0.01 M KSCN at 60 °C.

sweeps than the aged weld specimens, even though the current ratio was higher. The observation of reactivation current peak for as-welded specimen is an indication of presence of Mo and W depleted regions. The depletion of these elements could occur at the dendrite cores and near TCP phases. Summers *et al*. [3] reported 2.7 vol% of TCP phases in as-welded condition. The volume of TCP phases increased to about 5% when aged at 760 °C for 1 h or 700 °C for 20 h and to about 30% after aging for 100 h at 760 °C. The reactivation current behavior could be directly correlated to the formation of TCP phases and associated Mo depletion, as the current during reverse sweep increased only marginally during initial stage of aging at 760 °C and increased substantially after prolonged aging which followed the volume fraction of TCP phases present in the material. Fig. 5 shows the microstructure of the weld metal aged at 760 °C for 140 h after etching at reactivation potential in 2 M HCl + 0.01 M KSCN at 60 °C. It shows attack near TCP phases rather than on the dendritic core region. The areas near grain boundaries and the interdendritic regions were preferentially attacked where depletion of Mo and W due to precipitation of TCP phases could be expected. The dendritic core regions were not attacked, indicating that Mo and W depletion at the dendritic core during solidification [4] did not result in reactivation current peak. The EPR results indicate that aging of Alloy-22 welds at 700–760 °C possibly causes a deeply depleted zone of alloying elements in the vicinity of intermetallic precipitates such as μ phase which is enriched in Mo with a possible composition of Ni_7Mo_6 or Ni_3Mo_2 [11, 12]. In this investigation formation of such TCP phases are not found to affect the Cr profile as no reactivation peaks were observed during EPR tests in 1 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN solution. This solution was observed to detect the Cr depletion profiles in aged wrought Alloy-22 [9] and duplex stainless steel [8]. A flat Cr profile for as-welded condition was reported by Cieslak *et al*. [4].

Overall, comparison of the values of current peaks during forward and reverse sweeps of electrochemical potentiokinetic testing of Alloy-22 weld materials in 2 M HCl + 0.01 M KSCN solution at 60 °C could be used for evaluating the phase stability of the materials.

Acknowledgments

This work was sponsored by the Office of Civil Radioactive Waste Management of the U.S. Department of Energy under the cooperative agreement with the University and Community College System of Nevada. The authors are grateful to Dr. Gerald Gordon, Dr. Frank Wong, and Dr. Raul Rebak for their interest and support.

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Received 12 June
and accepted 26 September 2003