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Atom probe characterization of copper solubility in the Midland weld after neutron irradiation and thermal annealing

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Abstract

An atom probe field ion microscopy characterization has been performed to determine the copper matrix concentration in a submerged arc beltline weld of the Midland Unit 1 pressurized water reactor after 4 conditions: unirradiated, unirradiated and annealed for 168 h at 454°C, neutron-irradiated in a test reactor to a fluence of 1.1×10^{23} n m^{-2} ($E > 1$ MeV) at a temperature of 288°C, and neutron-irradiated and annealed for 168 h at 454°C. Atom probe analysis of the unirradiated material revealed a substantial depletion of the copper in the matrix to 0.119 ± 0.007 at% Cu from the bulk value of between 0.18 and 0.28 at% Cu. Annealing the unirradiated material produced intragranular copper-enriched precipitates and reduced the matrix copper level by ~25% to 0.088 ± 0.012 at% Cu. Neutron irradiation also produced copper-enriched precipitates and reduced the matrix copper level by almost 50% over the stress relieved material to 0.058 ± 0.008 at% Cu. Annealing the neutron-irradiated material reduced the matrix copper level further to 0.050 ± 0.010 at% Cu. These results indicate that the annealing treatment coarsens the copper-enriched precipitates produced during neutron irradiation with a slight decrease in the matrix copper content. © 1997 Elsevier Science B.V.

1. Introduction

Atom probe field ion microscopy has clearly demonstrated that one of the main sources of embrittlement of the pressure vessel steel during service in a nuclear reactor is the formation of a high number density of ultrafine intragranular copper-enriched precipitates [1–12]. If this embrittlement can be controlled or eliminated, it should be possible to extend the service life of a nuclear reactor. Several studies have demonstrated that the embrittlement may be dramatically reduced or even eliminated by annealing the pressure vessel at a low temperature (343 to 454°C) (e.g. [13–18]). It should be noted that these temperatures are also in the range in which phosphorus segregation to grain boundaries, i.e., temper embrittlement, is dramatically enhanced [19,20] and therefore this approach should be avoided in high phosphorus steels.

The annealing treatment is designed to reduce the number of intragranular precipitates. There are two primary mechanisms by which the number of precipitates could be reduced: (1) by dissolution of the precipitates into the matrix with a concomitant increase in the matrix copper level, or (2) by a coarsening mechanism with little or no increase or possibly a decrease in the matrix copper content. These two mechanisms are shown schematically in Fig. 1. However, it is difficult to accurately predict which of these two mechanisms is operating since it depends on the precise state of the system after neutron irradiation at low temperature. Neutron irradiation may accelerate low temperature phase transformations due to the presence of extra vacancies in the matrix resulting from the cascades that are formed by the interaction of the neutron with the crystal lattice. This process affects the free energy of the system and hence may alter the position of the phase fields [21]. In addition, the equilibrium copper

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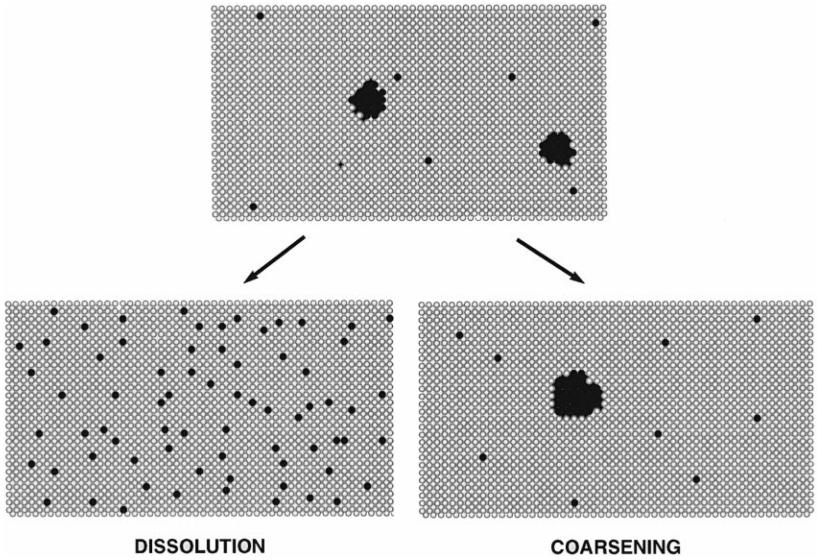

Fig. 1. Schematic diagram of two possible mechanisms for the reduction of embrittlement of a neutron irradiated pressure vessel steel by (a) dissolving the copper-enriched precipitates into the matrix and (b) coarsening the copper-enriched precipitates.

solubility in these steels is not well characterized at these low temperatures due to the slow kinetics. These two mechanisms will have a significant difference on the rate and severity of re-embrittlement during subsequent service in the nuclear reactor. The re-embrittlement should be approximately the same as for the original material in the first case, whereas a significantly lower level of re-embrittlement would be expected in the second case since the matrix copper level is significantly lower. It should be noted that this argument assumes that everything else is the same and that no other mechanisms are triggered by the annealing treatment.

An atom probe field ion microscopy characterization has been performed in order to distinguish between these two mechanisms. In principle, the atom probe is capable of measuring all three primary parameters involved with this mechanism: size and number density of the precipitates and the matrix composition. However due to the small size ($\sim$ 1–5 nm) and relatively low number density ($\sim 10^{21}$ m^3) of the copper-enriched precipitates, the magnitude of the error associated with the measurement of size and number density with the atom probe is large. In contrast, the measurement of the matrix composition may be accomplished with high precision and is performed by collecting a sufficient number of atoms from the matrix while avoiding other microstructural features such as precipitates. Therefore, this atom probe characterization has focused on measuring the matrix copper concentrations.

2. Experimental

The material used from this study was taken from a 200 mm thick section of the beltline submerged arc weld (designated a Babcock and Wilcock WF-70 weld) of the Midland Unit 1 pressurized water reactor. This weld was fabricated with the use of copper-coated welding wires and Linde 80 flux and is known to be a low upper shelf (LUS) energy, high copper weld. The chemical composition and mechanical properties of this weld have been extensively studied and the results have been reported in detail elsewhere [22]. Bulk chemical analysis revealed that the copper content of this weld varied from 0.18 to 0.28 at% Cu [22]. A summary of the compositions for the five different positions studied across the weld (section 1–13) as measured by chemical analysis are given in Table 1. All materials used in this study were subjected to a standard post-weld heat treatment at a temperature of 607 ± 14°C for 22.5 h prior to subsequent irradiation or annealing treatments. The weld was examined in four conditions: unirradiated, unirradiated and annealed for 168 h at 454°C,

Table 1
Bulk chemical composition of the weld as a function of distance though weld

Material		Cu	Ni	Mn	Cr	Mo	Si	C	P
1	wt%	0.24	0.58	1.60	0.11	0.40	0.58	0.07	0.015
	at%	0.21	0.55	1.62	0.12	0.23	1.15	0.34	0.027
2	wt%	0.21	0.61	1.45	0.14	0.42	0.65	0.11	0.018
	at%	0.18	0.58	1.46	0.15	0.24	1.28	0.51	0.032
3	wt%	0.22	0.63	1.49	0.14	0.43	0.57	0.11	0.016
	at%	0.19	0.59	1.50	0.15	0.25	1.12	0.51	0.029
4	wt%	0.25	0.60	1.60	0.11	0.41	0.65	0.07	0.018
	at%	0.22	0.57	1.61	0.12	0.24	1.28	0.35	0.032
5	wt%	0.32	0.60	1.61	0.11	0.41	0.67	0.08	0.022
	at%	0.28	0.57	1.62	0.12	0.24	1.32	0.36	0.039

Table 2
Composition of the matrix in unirradiated weld as a function of distance though weld as determined in the atom probe (at%), balance is iron

Material	Cu	Ni	Mn	Cr	Mo	Si
1	0.09 ± 0.01	0.53 ± 0.02	1.34 ± 0.04	0.11 ± 0.01	0.14 ± 0.01	0.96 ± 0.03
2	0.11 ± 0.01	0.55 ± 0.03	1.34 ± 0.05	0.07 ± 0.01	0.22 ± 0.02	1.54 ± 0.05
3	0.10 ± 0.02	0.68 ± 0.04	1.66 ± 0.07	0.07 ± 0.01	0.14 ± 0.02	1.30 ± 0.06
4	0.06 ± 0.02	0.39 ± 0.05	1.02 ± 0.08	0.12 ± 0.03	0.21 ± 0.03	1.52 ± 0.09
5	0.14 ± 0.01	0.51 ± 0.02	1.22 ± 0.03	0.14 ± 0.01	0.14 ± 0.01	1.16 ± 0.04

neutron-irradiated in the University of Michigan Ford test reactor to a fluence of 1.1×10^{23} n m^{-2} ($E > 1$ MeV) at a temperature of 288°C, and neutron-irradiated and annealed for 168 h at 454°C. Previous characterization of this weld by Sokolov et al. [23] indicated a shift in the Charpy transition temperature of $\Delta T_{41J} = 103$°C for the neutron irradiated material and $\Delta T_{41J} = 24$°C for the irradiated and annealed material. These values represent a recovery of ~ 76%. No data are currently available for the annealed unirradiated weld; however, data from the same annealing treatment on similar welds have not revealed any substantial shift in the Charpy transition temperature. The shift in fracture toughness transition temperature was $\Delta T_0 = 92$°C for the neutron irradiated material and $\Delta T_0 = 13$°C for the irradiated and annealed material.

Atom probe characterization of these four conditions was performed in the ORNL energy-compensated atom probe [24]. This instrument features high mass resolution ($\Delta m/m = 1/2500$) and a low minimum detection level (~ 50 appm in this study). Field ion images were recorded with neon as the image gas. Atom probe analyses were performed with a specimen temperature of 50 K and a pulse fraction of 20%. These conditions have been shown previously to eliminate the possibility of preferential evaporation and retention of atoms during field evaporation in this type of material. Most concentrations quoted in this paper were calculated from $X = \sum N_i / N$ where N_i is the total number of atoms of the solute of interest and N is the total number of ions collected from all analyses of the same material [25]. Most error bars quoted in this paper are based on counting statistics and are given by $\sigma = \sqrt{(X(1-X)/N)}$ [25].

3. Results and discussion

Atom probe analysis of the unirradiated material revealed a substantial depletion of the copper in the matrix to 0.119 ± 0.007 at% Cu (1190 appm). This value is the average copper content of all the atom probe analyses taken at five different locations. However, a significant variation in the copper content ranging from 0.06 to 0.14 at% Cu was found with position in the weld as shown in Table 2. This position to position variation is also evident in the individual measurements from a single location and is therefore occurring on a highly local scale. For example, the simple average and standard deviation of the individual atom probe measurements from different specimens in location 1 of the weld was 0.091 ± 0.030 at% Cu compared to an ensemble average and standard deviation based on the total number of atoms of each element collected of 0.085 ± 0.010 at% Cu. Similar variations were found in the atom probe analyses at the other locations. This point to point variation in composition was consistent with the variation found in the chemical analyses and indicated that the copper level varies both at the microscopic and macroscopic scales. It is therefore not appropriate to compare the compositions determined at the same location in the chem-

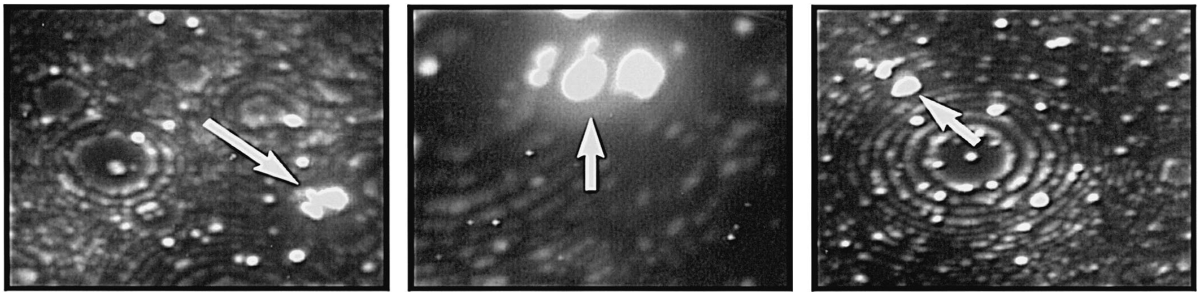

Fig. 2. Field ion micrographs of ultrafine (< 1 nm diameter) spherical refractory precipitates in unirradiated weld.

Table 3
Composition of the matrix after annealing, irradiation, and irradiation and annealing treatments as determined in the atom probe (at%), balance is iron

Material	Cu	Ni	Mn	Cr	Mo	Si
Unirradiated (average of all data)	0.119 ± 0.007	0.51 ± 0.02	1.46 ± 0.02	0.09 ± 0.01	0.18 ± 0.01	1.33 ± 0.02
Unirradiated and annealed at 168 h at 454°C	0.088 ± 0.012	0.52 ± 0.03	1.15 ± 0.04	0.05 ± 0.01	0.20 ± 0.02	0.85 ± 0.04
Irradiated 1.1×10^{23} m^{-2} ($E > 1$ MeV)	0.058 ± 0.008	0.49 ± 0.02	1.03 ± 0.03	0.08 ± 0.01	0.20 ± 0.02	1.64 ± 0.04
Irradiated and annealed at 168 h at 454°C	0.050 ± 0.010	0.48 ± 0.03	1.06 ± 0.05	0.06 ± 0.01	0.17 ± 0.02	1.54 ± 0.06

ical analyses with the atom probe analyses due to the macroscopic and microscopic variation in the copper concentration.

A relatively high number density of brightly imaging, roughly spherical refractory precipitates approximately 1 nm in diameter were also observed in the field ion images of all the materials examined, as shown in Fig. 2. Atom probe analysis revealed that these precipitates contained molybdenum, carbon and nitrogen and therefore correspond to a molybdenum carbonitride precipitate. Similar precipitates have been observed previously in A302B and A533B steels [2,7,8].

Annealing the unirradiated material for 168 h at 454°C produced some intragranular copper-enriched precipitates and reduced the matrix copper level by approximately 25% to 0.088 ± 0.012 at% Cu, as shown in Table 3. This decrease is shown on the phase diagram in Fig. 3. These trends are in agreement with thermodynamic predictions based on the Thermocalc program. However, the measured value was slightly higher than the predictions of 0.072 and 0.047 at% Cu for a ternary Fe–Cu–Ni alloy from the Kaufman and the Scientific Group Thermodata Europe (SGTE) databases, respectively. This small difference may be due to the annealing time of 168 h not being sufficient to attain equilibrium, the effects of the other elements in the system slightly altering the copper solubility, or inaccuracies in extracting or extrapolating information from the database information at this low temperature as indicated by the difference between the two databases. No significant change was found in the nickel, chromium and molybdenum levels over the unirradiated material but small decreases in silicon and manganese levels were observed.

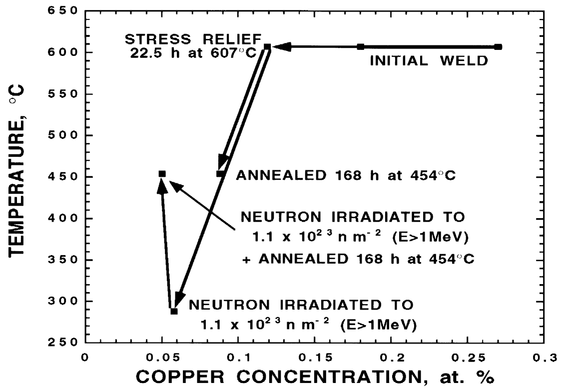

Fig. 3. Diagram showing the reductions in copper content of the matrix as a function of the different treatments.

This annealing treatment produces a decrease in the solid solution hardening from the copper in the matrix and an increase in the precipitation hardening from the copper-enriched precipitates. This low temperature annealing treatment should be beneficial in reducing the neutron irradiation induced embrittlement of new pressure vessels in low phosphorus steels since it reduces the copper content of the matrix.

Neutron irradiation to a fluence of 1.1×10^{23} n m^{-2} ($E > 1$ MeV) at a temperature of 288°C also produced some copper-enriched precipitates and reduced the matrix copper level by almost 50% to 0.058 ± 0.008 at% Cu over the stress relieved material, as shown in Table 3. This value is similar to that found in previous atom probe studies of other pressure vessel steels [7,8,11]. No significant change was found in the nickel, chromium and molybdenum levels over the unirradiated material but a small increase in silicon and a decrease in the manganese levels were observed.

Annealing the neutron-irradiated materials reduced the matrix copper level further to 0.050 ± 0.010 at% Cu, as shown in Table 3. No significant changes from the neutron-irradiated material were observed in the concentrations of the other alloying elements. In addition, some ultrafine intragranular copper-enriched precipitates were observed in this material, as shown in Fig. 4. These values and trends are in good agreement to previous results from a Babcock and Wilcox weld [12]. Therefore, annealing neutron-irradiated pressure vessel steel welds appears to reduce embrittlement by coarsening the copper-enriched precipitates with a decrease in the matrix copper content. Since this level is significantly lower than that measured in the unirradiated and annealed material (0.088 at% Cu), it appears that further reduction in the copper level in the matrix could be achieved by adopting a longer annealing time at 454°C. Applying this heat treatment to new vessels would provide an improved safety margin to neutron embrittlement. In addition, this level is slightly lower than that in the neutron irradiated material and therefore indicates that the copper solubility at the service temperature of 288°C should be lower than 0.050 at% Cu since the

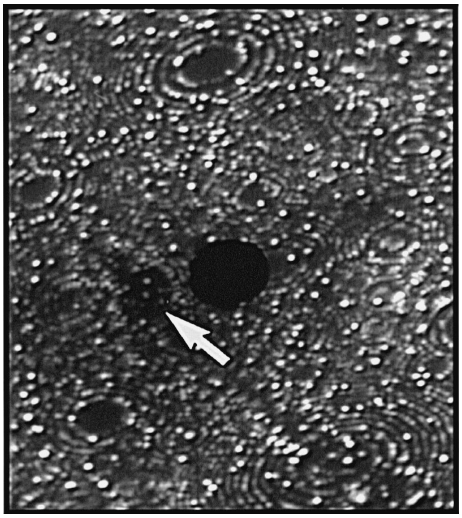

Fig. 4. Field ion micrograph of a copper-enriched precipitate in the matrix of the weld that was irradiated to a fluence of 1.1×10^{23} n m^{-2} $(E > 1$ MeV$)$ at a temperature of 288°C and then annealed for 168 h at 454°C.

solubility should decrease with decreasing temperature. Therefore, some re-embrittlement should occur on re-irradiation due to the formation of additional copper-enriched precipitates and possibly some additional coarsening of the existing copper-enriched precipitates thereby making them more effective at pinning dislocations. Since the copper level is a factor of ~ 2.4 less than that in the matrix after the stress relief, these results predict that the amount of re-irradiation embrittlement should be significantly less than during the initial neutron irradiation. This reduced level of re-embrittlement has been observed in other Linde 80 welds [18].

4. Conclusions

This atom probe study has demonstrated that the copper in solution in the matrix of an unirradiated pressure vessel steel weld decreases with annealing for 168 h at 454°C and also after neutron irradiation to a fluence of 1.1×10^{23} n m^{-2} $(E > 1$ MeV$)$ at a temperature of 288°C. An additional decrease in copper level was measured by annealing the neutron irradiated material for 168 h at 454°C. Annealing neutron-irradiated pressure vessel steel welds appears to reduce embrittlement by coarsening the copper-enriched precipitates with a decrease in the matrix copper content.

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