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Cluster formation in in-service thermally aged pressurizer welds

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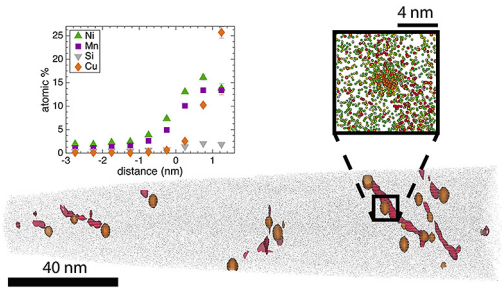
HIGHLIGHTS

- Clustering during in-service thermal aging of a pressurizer weld is studied.
- Atom probe tomography reveals Cu-rich clusters on dislocations and boundaries.
- The clusters contribute to the hardness increase of the material.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermal aging of reactor pressure vessel steel welds at elevated temperatures may affect the ductile-to-brittle transition temperature. In this study, unique weld material from a pressurizer, with a composition similar to that of the reactor pressure vessel, that has been in operation for 28 years at 345 °C is examined. Despite the relatively low temperature, the weld becomes hardened during operation. This is attributed to nanometre sized Cu-rich clusters, mainly located at Mo- and C-enriched dislocation lines and on boundaries. The welds have been characterized using atom probe tomography, and the characteristics of the precipitates/clusters is related to the hardness increase, giving the best agreement for the Russell-Brown model.

1. Introduction

The pressurizer is a component of the primary coolant circuit in a pressurized water reactor (PWR) with the purpose of regulating the pressure and temperature within the primary circuit (which includes the reactor pressure vessel, RPV). Hence, the structural integrity of the pressurizer is of great importance. The vessel of the pressurizer is generally made from low alloy ferritic/bainitic type steels, i.e. identical to that of a RPV. Studies of irradiated (for instance [1–6]) and thermally aged [7,8] RPV steels report finding nanometre-sized Cu-rich clusters within the microstructure, containing various amounts of Ni, Mn, and Si. The clusters are known to affect the mechanical properties by increasing the yield strength and the ductile-to-brittle transition temperature, i.e. having an embrittling effect.

The Swedish nuclear reactors Ringhals R3 and R4 are known to have RPVs containing low Cu (0.04–0.08 at.%) and high Ni

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(1.50–1.58 at.%) and Mn (1.37–1.48 at.%) [9]. This in turn affects the radiation induced clusters, forming with low Cu content [10–12]. Still, pure thermal aging of the same material has not been much studied. Also, most studies on thermal aging of RPV materials have been performed using elevated temperatures and short aging times in order to simulate the same diffusion distances of the elements. This type of accelerated testing might, however, have limited validity, as solubilities and phase equilibria are different at lower temperatures. In this paper, the material studied has been thermally aged at 345 °C for 28 years (215,000 h) of operation as an actual pressurizer. The pressurizer was exchanged in conjunction with a major upgrade of the R4 reactor, including the replacement of steam generator tubes of Alloy 600 to Alloy 690. Atom probe tomography (APT) is used together with hardness measurements in order to characterise the effect of the thermal aging.

2. Materials and methods

The studied weld is a vertical submerged arc weld of the former R4 pressurizer, and it is compared with an archive reference material from the Forsmark nuclear power plant, manufactured using the exact same weld wire heat and according to the same specifications as the pressurizer welds.

For the APT analysis, a LEAP 3000X HR, with an energy compensating reflectron, from Imago Scientific Instruments was utilized. Both voltage and laser pulsing modes were used, in order to obtain the more accurate Si and P distribution (and more well defined clusters [13]) of voltage pulsing and to analyse large volumes using laser pulse mode. For voltage pulse mode, the specimen temperature was 50 K, and the pulse fraction 20%. For laser pulse mode, the temperature was 30 K and the laser pulse energy 0.3 nJ. In both cases the pulse frequency was 200 kHz and the target evaporation rate 0.2–0.5% (detected ions per pulse). The specimens were prepared using a two-step electropolishing method [14] with final millisecond pulsing in order to get rid of any surface oxides.

The APT data reconstruction was performed in IVAS™ 3.6 (Cameca). The reconstruction parameters were chosen in order that the plane distance of (002) or (011) planes should be equal to tabulated values (for the analyses when this was possible). For voltage pulsed runs the reconstruction parameters used were a *k*-factor of 5.3 and an evaporation field of 33 V/nm. For laser pulsed runs the corresponding values were 4.0 and 23 V/nm. The image compression factor was set to 1.65 for all reconstructions. The Cu cluster sizes were estimated based on the number of clustered atoms, and utilising the maximum separation method [1,15] with parameters $d_{max} = 0.40$ nm, $N_{min} = 20$ and order 1, and solute elements Cu, Ni and Mn. The peak overlap of $^{58}Ni^{++}$ and $^{58}Fe^{++}$ at m/n = 29 Da was ranged as Ni as the effect of increased cluster to matrix contrast by excluding the 29-peak was estimated to be insignificant for the relatively Cu-rich clusters. The use of Cu atoms only would give more well-defined clusters due to the low matrix Cu level, but would underestimate the size of the clusters due to their core-shell structure.

Table 1
Hardness measurements for the materials, including the standard deviations within the measurements.

Material	H_V10 [kg/mm^2]
Reference	203 ± 2
Pressurizer	235 ± 7

3. Results

The measured hardness of the pressurizer weld and the reference material are presented in Table 1. There is a clear increase in hardness due to the in-service aging of the pressurizer. The larger standard deviation in the measured hardness of the pressurizer than the reference material origins in the measurement; the hardness indents were made on a 10 cm line throughout the weld, whereas the indents in the reference material were made on a Charpy-specimen.

As the analysed materials are welds, some differences in the composition between analyses are expected when using APT, due to the inhomogeneity of the welds and the relatively small volume of an APT analysis. In Table 2, the measured average compositions of the reference material and the pressurizer weld are given. The composition is expected to be similar to that of the RPV of Ringhals R3 and R4, with high Ni and Mn contents and low Cu content [9]. Carbides are excluded from the analysis volumes when determining the composition, and hence the C content reported in Table 2 is lower than the nominal value.

In the thermally aged pressurizer material, Mo-enriched dislocation lines were found, decorated with Cu-rich clusters, see Figs. 1–3. The average distance between clusters along dislocation lines was 15 nm, with a distribution ranging from 7 to 35 nm. Larger distances might obviously be missed due to the limited extent of the APT analysis volumes. The clusters on the dislocation lines vary between 1 and 4 nm in diameter, with an average of 1.9 ± 0.3 nm. Hereby it was assumed that the clusters do not contain any Fe. In the analysis data, slightly less than 50% of the cluster content was Fe, with a decreasing concentration towards the centre of the clusters. It is therefore assumed that the measured Fe is mainly due to local magnification effects [16,17]. As seen in the proxigram of the clusters in Fig. 2, the Cu-rich core is surrounded by a shell of Ni, Mn and Si. The total number density of Cu-clusters in the pressurizer was found to be $0.16 \pm 0.05 \cdot 10^{23}$ m^{-3}. In the reference material, no Cu-rich clusters were observed.

The Mo-enriched dislocation lines are unevenly distributed within the volumes, see Fig. 1, where there are no dislocation lines in the first 300 nm of the reconstruction. In the same figure, the dislocations are located on a plane (arrowed). The average density of Mo-enriched dislocations is estimated to be $2.3 \pm 1.0 \cdot 10^{14}$ m^{-2}. The number of excess Mo atoms per dislocation length was found to vary from 5 to 30 atoms per nm (taking the detection efficiency of 37% into account), the number of C atoms also located on the dislocation lines varies within the same range; with no obvious correlation. In the voltage pulsed pressurizer analyses, P can also be distinguished on the dislocation lines (0.4–1.4 P atoms per nm). Dislocations are also found in the reference material, see Fig. 4 a.

Table 2
Compositions from APT analyses. Averages and the standard deviations between the analyses are given in at.%. In total four analyses are used for the reference composition and seven analyses for the pressurizer.

	Reference (at. %)	Pressurizer (at. %)
C	0.04 ± 0.01	0.04 ± 0.03
Mo	0.19 ± 0.02	0.19 ± 0.05
Si	0.31 ± 0.07	0.30 ± 0.02
P	0.01 ± 0.01	0.01 ± 0.01
V	0.0030 ± 0.0026	0.0012 ± 0.0007
Mn	1.35 ± 0.05	1.24 ± 0.12
Cr	0.03 ± 0.01	0.06 ± 0.01
Co	0.02 ± 0.01	0.02 ± 0.01
Cu	0.07 ± 0.02	0.10 ± 0.02
Ni	1.77 ± 0.33	1.68 ± 0.28
Fe	bal.	bal.