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PAPER

Nanoindentation study of short-range ordering

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Abstract

Thermal ageing of nickel-base alloys can lead to the formation of brittle ordered phases, but the direct study of these phases is challenging. Nanoindentation is used in this study as an alternative technique to determine the extent of short-range ordering (SRO) in thermally aged Alloy 690 TT. Two methods are used for obtaining both qualitative (depth sensitivity) and quantitative (spatial stability) results, which are compared to data from metallography, microhardness and atomic force microscopy in order to discriminate between factors affecting the hardness. When intergranular precipitation and grain size become dominant factors with increasing indentation loads, nanoindentation at low loads enables to distinct within-grain hardness increase related to SRO.

1. Introduction

Alloy 690 TT (Ni-30Cr-10Fe) is a material of choice in the primary circuit of pressurized water reactors (PWR) due to its high primary water stress corrosion cracking (PWSCC) resistance [1]. It is known, however, that high levels of cold work (typically, cold-rolled to a 20% reduction) significantly increase the PWSCC susceptibility of the alloy and can result in intergranular (IG) cracking [2–4]. Thermal ageing can also increase the PWSCC susceptibility to similar levels [5]. It is a critical issue as components in the primary circuit are exposed to relatively high temperatures throughout the expected, and potentially extended, service life of the plant. Thermal ageing of Alloy 690 TT triggers an ordering reaction under a critical temperature, depending mostly on the iron content of the alloy (about 420 °C for 9–10 wt% Fe) [5–7]. This reaction consists of the nucleation and growth of the intermetallic phase Ni2Cr, which results in lattice contraction, hardness increase and intergranular embrittlement. The extent of ordering can range from ordered clusters of a few atomic spacings (short-range ordering, SRO) to widespread ordered domains (long-range ordering, LRO) [8-12]. Most of the recent studies show that the PWSCC mechanisms in Alloy 690 relate to thermally activated grain boundary (GB) migration, Cr-rich oxide formation at the crack tip and Cr-depletion in the migrated zone ahead of the crack tip [13–16]. Further, the formation of LRO in a model Ni-30.7 Cr wt% alloy resulted in a crack growth rate of 1.2×10^{-7} mm s⁻¹, similar to that of Alloy 690 with 20% cold work. It was argued that LRO increases the crack tip strength and decreases the toughness of the alloy [17]. While LRO is not likely to occur in commercial alloys during the service life of PWRs, the formation of SRO is expected [18]. The direct study of SRO in Alloy 690 is, however, difficult. The composition of the Ni₂Cr phase is very close to that of the bulk alloy and the extent of ordered domains is small, which prevents the observation with transmission electron microscopy (TEM) of ordered super lattice reflections typical of LRO. A promising method for the direct study of SRO is the joint use of atom probe tomography (APT) and orientation imaging microscopy (OIM) [19, 20]. Such a method, however, is very demanding in terms of sample preparation and requires access to APT. Such a method is, in addition, not suitable to study large arrays of materials without prior knowledge of potential ordering levels. Therefore, the use of another technique to screen materials prior to APT would be advantageous. While the amplitude of hardness changes related to LRO can match the resolution of microhardness measurements, the low-amplitude hardness variations characteristic of SRO warrant the use of nanoindentation. Indeed, it was showed that nanoindentation hardness measurements of Alloy 690 with 9.18 wt% Fe correlated well with lattice



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Table 1. Chemical composition of Alloy 690 used in this study.

		-	-		-				
Element	Ni	Cr	Fe	Mn	Si	Р	Cu	С	S
wt%	62.6	28.7	9.18	0.21	0.12	0.08	0.0048	0.037	< 0.001

Table 2. Summary of the 7 conditions of Allov 690.

Condition	Code
Solution annealed +WQ	SA
SA + 17 h at 700 °C	TT
$TT+10000$ h at 350 $^{\circ}C$	TT350
$TT+10000$ h at 420 $^{\circ}C$	TT420
$\rm TT+10000~h$ at 475 $^{\rm o}\rm C$	TT475
$TT+10000$ h at 550 $^{\circ}C$	TT550
TT + 20% cold-worked by rolling	TTCW

parameter measurements, with a hardness and lattice contraction peak upon ageing at 420 °C for 10 000 h [6]. Still, aside from the limitations of the nanoindentation technique itself (effects of grain orientation, surface preparation and indentation size), a concern remained that other metallurgical factors potentially overlapped with SRO. The aim of this study is to evaluate the potential of nanoindentation to assess the presence of ordering in Alloy 690 TT prior to a direct study using combined APT-OIM techniques.

2. Materials

The Alloy 690 material originated from an INCO commercial melt with 9.18 wt% Fe (see the chemical composition of the alloy in table 1). The material was first solution annealed and water quenched (SA). It was then (thermally) heat treated at 700 °C/10 23 K for 17 h (TT) before thermal ageing at 350 °C/6 23 K (TT350), 420 °C /693 K (TT420), 475 °C/7 48 K (TT475) and 550 °C/8 23 K (TT550) for 10 000 h. Another condition was added for comparison purposes: Alloy 690 TT with 20% cold work (TTCW), known for its higher PWSCC susceptibility. The resulting conditions are showed in table 2.

3. Experimental methods

3.1. Sample preparation

Samples were ground with Struers SiC grinding papers up to 4000 grit and polished with 3 μ m and 1 μ m Struers DiaPro diamond solutions. A first batch of specimens was finished using a Buehler MasterMet with colloidal silica alkaline suspension for 16 to 20 h to remove the last deformation layers resulting from grinding. Another batch of specimens was finished by hand polishing with 0.5 μ m and 0.25 μ m Struers SiC solutions and a final 0.05 μ m Al₂O₃ solution. The last stage of sample preparation was purposely different in order to assess the reproducibility of the results.

3.2. Electron microscopy

IG carbide precipitation was characterized by scanning electron microscopy (SEM) on a Zeiss Ultra 55. A series of 10 SEM images centred on GBs was taken for each condition for a total area of 115.5 μ m². The number and area of precipitates was then assessed using ImageJ particle analysis after removal of TiN particles. Grain sizes were calculated from electron backscatter diffraction (EBSD) maps using a step size of 0.06 μ m and a threshold of 100 pixels per grain. EBSD was also used to make sure that all specimens were free from noticeable residual surface deformation.

3.3. Hardness measurements

As illustrated in figure 1, the increasing indentation size with increasing applied load resulted in an interaction with potentially different microstructural features. Four hardness measurement approaches (load-controlled at 9.8 N and 1.5 mN, and depth-controlled at 100 nm and 1000 nm) were compared in order to discriminate between the factors influencing the hardness and separate the effect of SRO. On the first batch of specimens, Vickers hardness testing with a 1 kg load (9.8 N) and 10 s dwell time was performed to characterize the microhardness. Instrumented hardness testing was performed with a CSM Instruments Nanoindentation tester





Table 3. Parameters of nanoindentation measurements.

Fauinment	CSM Inst NHT	MTS-G200					
Experiment name	Hardness at 1.5 mN	Hardness at 100 nm	Hardness at 1000 nm				
Method	Standard loading	Continuous stiffness measurement					
Control	Load [mN]	Displacement [nm]					
Peak value	1.5	1500					
Dwell time [s]	10	10					
Ramping time [s]	20	30					
Harmonic frequency [Hz]	N/A	20					
Harm. displacement [nm]		2					
Surface finish [μ m]	0.06	0.05					

(NHT) using matrices of 20 \times 20 nanoindentations with a 1.5 mN load and a 5 μ m step size. Matrices of indentations were placed as to cover several grains. Vickers-like hardness values, noted HV_{IT}, were calculated using the Oliver and Pharr method [21]. Phase angle maps were obtained using atomic force microscopy (AFM) on a Veeco Dimension 3100 AFM system with an XY closed-loop scanner using TappingMode™. Analysis of the data was done using Gwyddion, a modular program for scanning probe microscopy data visualization. On the second batch of specimens, instrumented nanoindentation measurements were performed using a MTS-G200 nanoindenter with a continuous stiffness measurement (CSM) method at a harmonic frequency of 20 Hz to record continuously the hardness as the indenter tip penetrated into the specimen surface. Hardness values at a depth of penetration of 100 nm and 1000 nm were then compared. The parameters of both nanoindentation methods are showed in table 3. The different surface nanoindentation methods were purposely chosen in order to verify the reliability of the measurements. Figures 2 and 3 give an illustration of the type of results obtained from the different experiments. Figures 2 (a)-(d) show the hardness maps generated with data from matrices of nanoindentation at 1.5 mN for Alloy 690 SA, TT, T420 and TT550, respectively. The hardness data in each condition was consistent throughout the matrices, without effects of tip contamination or grain orientation on the results. In addition, AFM mapping over grain boundaries showed that the phase angle data (related to the surface stiffness and hardness) was consistent from one grain to another, with a clear but localized influence zone of GB on both sides of it (see figure 2(e)). Figure 3 illustrates the hardness versus depth of penetration profiles obtained from the CSM nanoindentation measurements. The hardening mechanism in TT and TT420 was notably different from that in TT550 condition. From these profiles, hardness data at 100 and 1000 nm depths of penetration were extracted and compared.







Figure 5. Evolution of narchess with an increasing depth of penetration measured with CSM nanoindentation. Alloy 690 11 and TT420 have relatively similar behaviour, while TT550 is softer at low depth of penetration (small interaction volume) and harder at higher depth of penetration (bigger interaction volume). The hardness profile of Alloy 690 with 20% cold work is showed for comparison.

4. Results

Figure 4 gives the summary of the results from microstructural characterization and hardness measurements. Vickers hardness testing results at 9.8 N correlate well with the grain size measurements from EBSD (see figure 4(a)) as the average indentation size at 9.8 N was larger than the average grain size of the material (see figure 1). However, CSM nanoindentation measurements at a depth of penetration of 1000 nm (about 68 mN for Alloy 690 TT) show a very good correlation with SEM observation of IG carbides/bulk surface ratio, with the exception of TT420, which was harder than expected considering the moderate amount and size of IG carbides. Lastly, CSM nanoindentation measurements at a depth of penetration of 100 nm (about 1.6 mN for Alloy 690 TT) and nanoindentation measurements at a depth of penetration of 100 nm (about 1.6 mN for Alloy 690 TT) and nanoindentation measurements at a depth of penetration of 100 nm (about 1.6 mN for Alloy 690 TT) and nanoindentation measurements at a depth of penetration of 100 nm (about 1.6 mN for Alloy 690 TT) and nanoindentation measurements at a depth of penetration of 100 nm (about 1.6 mN for Alloy 690 TT) and nanoindentation measurements at a depth of penetration of 100 nm (about 1.6 mN for Alloy 690 TT) and nanoindentation matrices with 1.5 mN gave very similar results (see figure 4(c)) with hardness levels increasing with increasing ageing temperature up to the expected critical ordering temperature (420 °C) and then decreasing with a further increase in temperature. This also correlates with the higher hardness of TT420 in the measurements at a depth of penetration of 1000 nm. Notably, hardness level upon ageing at 420 °C is in average higher than that of Alloy 690 with 20% cold work.

The large scatter in the results for the cold-worked material is due to the inhomogeneous microstructure and residual deformation. These results are in good agreement with the previous lattice parameter measurements,



testing at 9.8 N showing a clear correlation with the average grain size in all conditions, (b) CSM nanoindentation testing at 1000 nm (about 68 mN in Alloy 690 TT) showing a clear correlation with the amount and size of IG carbide precipitation, except in the case of TT420 which shows a higher than expected hardness, and (c) comparison of CSM nanoindentation testing at 100 nm penetration depth (about 1.6 mN in Alloy 690 TT) with nanoindentation mapping at 1.5 mN. The two methods give consistent results, showing hardness increase with increasing ageing temperature up to 420 °C, followed by a hardness decrease when increasing further the ageing temperature. It correlates well with the expected critical ordering temperature at 420 °C for Alloy 690 with 9–10 wt% Fe.

[6] with higher hardness correlating with larger lattice contraction. Figure 3 illustrates the transition in workhardening mechanisms from 100 to 1000 nm as TT550 changes from being softer than all other conditions at small depths of penetration to being harder than the other non-cold-worked conditions at higher depths of penetration, which can only be related to its higher IG carbide coverage. A similar behaviour was observed with TT475 condition. In comparison with them, TT350 was harder at low depths of penetration and softer at higher depths of penetration due to its lower IG carbide coverage. As seen in figure 2, the nanoindentation results cover relatively large areas (95 × 95 μ m) and multiple grains, while the effect of grain orientation on the hardness value is limited to the close vicinity of the grain boundary (see figure 2(e)).

5. Discussion

It is expected from the literature that the critical ordering temperature of Alloy 690 with 9–10 wt% Fe is about 420 °C, with the start of the disordering reaction at higher temperatures and full disordering at 550 °C [5]. Hardness measurements using nanoindentation were considered as a potential technique to assess the ordering level. However, hardness is not an intrinsic property of a material and depends on the deformation mechanisms occurring in the material volume of contact under a hardness indenter. For a given indenter geometry, a higher applied load on the indenter results in a bigger area of contact (see figure 1). As such, increasing the indentation load is a way to account for inhomogeneity in the microstructure and to increase the reproducibility of hardness measurements. However, it also means that smaller defects controlling the deformation mechanisms cannot be readily distinguished from each other. At lower applied loads, the contact area can become small enough that

only a small amount of defects control the deformation mechanisms. One consequence is the increase in the apparent hardness at low penetration depths, or indenter size effect (see figure 3). However, the identification of factors affecting the indenter/microstructure interaction becomes possible. By progressively increasing the applied load on sample and, thus, the interaction volume between the indenter and the specimen, the hardening mechanisms change:

- 1. First related to grain interiors (see figures 1 and 2(a)–(d) for a load of 1.5 mN or a depth of penetration of 100 nm.
- 2. Then to the surrounding intergranular precipitation and grain boundaries (see figure 4(b)) for a load of about 60–70 mN and a depth of penetration of 1000 nm.
- 3. Then to the grain size of the materials (see figures 1 and 4(a)) for a 9800 mN load and a contact diameter of about 80 μ m.

Therefore, by decreasing the indentation load, it is possible to distinct the effect of ordering on the hardness (see figure 4(c)) with results correlating well with the literature [5–11]. Measurements made using a 1.5 mN applied load or at a penetration depth of 100 nm are consistent and give similar results, despite changes in the surface preparation, different nanoindentation instruments and the use of different measurement methods. In addition, the reproducibility of the results was confirmed over multiple grains, taking into account the effect of grain boundaries and grain orientation (see figure 2), and showing the transition from within-grain deformation mechanisms to mechanisms affected by grain boundaries and intergranular carbides when increasing the depth of penetration and size of indentation (see figure 3). Therefore, it was possible to distinct low amplitude hardness variations related to changes in short-range ordering level using nanoindentation.

6. Conclusions

Visible microstructural changes induced by thermal ageing on Alloy 690 TT were compared to hardness measurements at different scales in order to distinguish between influencing factors and to isolate the effect of SRO on hardness. The main conclusions based on the study are summarized as follows:

- 1. A clear link was observed between grain size and hardness at high applied load (9800 mN), and between intergranular carbide density and hardness at intermediate loads (about 68 mN), with the exception of Alloy 690 TT aged at 420 °C showing a higher hardness than expected.
- 2. The influence of SRO was clearly evidenced by hardness testing at low loads (about 1.5 mN), with a good reproducibility of the results and good correlation with the literature and previous lattice parameter measurements.

The nanoindentation method proved itself valuable in the study of SRO, making possible the identification of low-amplitude hardness variations related to lattice contraction within grains, and taking into account the influence of intergranular carbides and grain boundaries. It can be considered as a powerful screening method for the assessment of ordering level before further characterization of the most promising specimens e.g. with APT-OIM techniques.

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