ELSEVIER

Materials Science and Engineering A270 (1999) 38–43

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Grain boundary segregation during heat treatment at 600°C in a model Alloy 600

M. Thuvander [a,b], M.K. Miller [a], K. Stiller [b,*]

[a] *Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6376, USA*
[b] *Department of Experimental Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

Received 12 September 1998; accepted 27 December 1998

Abstract

The carbon distribution in the vicinity of grain boundaries, in solution in the matrix, and in carbides has been studied by the atom probe at various stages of the intergranular carbide precipitation process in an austenitic nickel-base model alloy similar to commercial Alloy 600. The grain boundary precipitation evolved from small discrete carbides after 4 h at 600°C to a semi-continuous carbide film after 16 h, and finally to large discrete carbides after 213 h. Enrichments of carbon, boron, nitrogen and phosphorus were found at the grain boundaries in all ageing conditions. Large variations were observed between different grain boundaries and at different positions of an individual grain boundary in the same ageing condition. The highest carbon concentration was accompanied by chromium enrichment, indicating the nucleation of chromium-carbides. After ageing for 213 h, the amount of carbon segregation to the boundary was very low, which suggests that the driving force for carbon segregation is less than that for carbide precipitation. Phosphorus was only detected at the grain boundaries when the carbon concentration was low. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbides; Ni-base alloy; Grain boundary segregation

1. Introduction

The nickel-based superalloy Alloy 600 is frequently used for steam generator tubes in pressurised water reactors. The grain boundary chemistry is of particular interest, since the material is sometimes susceptible to intergranular stress corrosion cracking [1]. The cracking behaviour, in particular in high-purity water at temperatures of ~350°C, has been difficult to explain. Several mechanisms have been proposed that address the various critical microstructural features, e.g. the carbon matrix concentration and the presence of carbides and segregated elements at the grain boundaries.

Auger electron spectroscopy (AES) investigations have shown that boron and phosphorus segregate to grain boundaries in Alloy 600 [2]. However, due to experimental limitations, AES cannot be applied to study carbon segregation, especially when carbides are present at the grain boundary. Segregation in these materials has, to some extent, also been studied by atom probe field ion microscopy (APFIM) [3].

The evolution of the intergranular carbide precipitation at various temperatures has been studied by transmission electron microscopy (TEM) [4]. The precipitation starts with small discretely distributed carbides that develop into a semi-continuous carbide film. After prolonged heat treatment, the carbides coarsen and the resultant microstructure contains large, discretely distributed carbides. These three stages have been identified for temperatures ranging from 500 to 900°C. Naturally, the process is faster at higher temperature. In most cases, Cr_7C_3 is the dominant carbide [5], but in a few studies, $Cr_{23}C_6$ has been reported to be the most frequent [6].

In this study, the segregation and precipitation occurring in a model material, similar to Alloy 600, during heat treatment at 600°C has been investigated by APFIM. The changes in the amounts of carbon at the grain boundaries and in solution in the matrix have

* Contact author: Dr Krystyna Stiller, Experimental Physics, Chalmers, SE-412 96; Göteborg, Sweden. Tel.: +46 31 772 3320; fax: +46 31772 3224.

E-mail address: stiller@fy.chalmers.se (K. Stiller)

0921-5093/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S0921-5093(99)00236-1

Table 1
Bulk composition of the model Alloy 600 used in this investigation

	C	B	Cr	Fe	Ni	N	P	Al	Si	Mn	Mg
wt.%	0.022	<0.001	16.0	10.0	73.6	0.005	<0.003	0.052	0.08	0.05	0.031
at.%	0.10	<0.006	17.6	10.3	71.6	0.02	<0.006	0.11	0.16	0.05	0.07

been considered. In a previous study [7], the temperature dependence of segregation and precipitation, when heat-treated for 1 h, was investigated. It was found that after annealing for 1 h at 600°C, the average amount of carbon segregation corresponded to 10% of a close-packed layer of carbon.

2. Experimental

The investigated model alloy was produced by AB Sandvik Steel. The bulk composition is presented in Table 1. The material was solution annealed (SA) at 950°C for 10 min and subsequently heat-treated at 600°C for 1, 4, 16 and 213 h. The grain size of the material was approximately 20 μm.

The atom probe experiments were performed with the atom probes at Chalmers University and Oak Ridge National Laboratory (ORNL), as well as the energy-compensated optical position-sensitive atom probe (ECOPoSAP) at ORNL. The analyses were performed at ~60 K, with 20% pulse fraction. Neon was used as the imaging gas. Pulsed electropolishing and pre-selection in the TEM was applied to fabricate specimens for grain boundary analysis.

3. Results and discussion

TEM was used to confirm that the various heat treatments had produced the expected grain boundary carbide morphology. The result was in relatively good agreement with earlier investigations [4,8], even though the precipitation process was somewhat slower, presumably due to a lower carbon content. After heat treatment for 1 h at 600°C, grain boundary carbides could not be discerned. As the treatment proceeded for 4 h, small (10 nm) discrete carbides formed, Fig. 1(a). The amount of carbide phase then continued to increase, and after 16 h a semi-continuous carbide film was present at the grain boundaries, Fig. 1(b). Coarsening took place and after 213 h, large (50 nm) discretely distributed carbides decorated the grain boundaries, Fig. 1(c).

The gradual depletion of carbon in the matrix was followed by analysis in both the conventional and three-dimensional atom probes. Median values of the carbon concentration are presented in Table 2. As expected, the concentration decreases with time, but large variations were found between different analyses of the same material. This indicates that the matrix was far from homogeneous after the relatively short solution anneal, as also found in [7].

Precipitate-free segments of grain boundaries were investigated by APFIM in the SA material and after heat treatment for 1, 4 and 213 h at 600°C. In the material heat-treated for 16 h, it was not possible to find precipitate-free grain boundary segments. Also, the carbide film in this material made electropolishing more difficult. In the field ion images, the grain boundaries appeared dark, Fig. 2(a), and therefore no information about the amount of segregating elements present at the boundaries could be deduced from the images. Field ion images of darkly imaging grain boundary carbides in the material heat treated for 4 and 213 h are presented in Fig. 2(b and c), respectively. Unfortunately, the analyses of the carbides were too limited to give the accurate composition, but they appeared to be consistent with Cr_7C_3 from the measured composition.

A total of 11 grain boundaries were successfully investigated in the conventional atom probe, with five boundaries in the material heat treated for 1 h, and two boundaries in each of the other materials (SA, 4 and 213 h). The boundaries could be analysed between one and five times, by repositioning the probe aperture relative to the boundary, thereby improving the statistics of the measurements. Carbon, boron, nitrogen and phosphorus were found to segregate to the grain

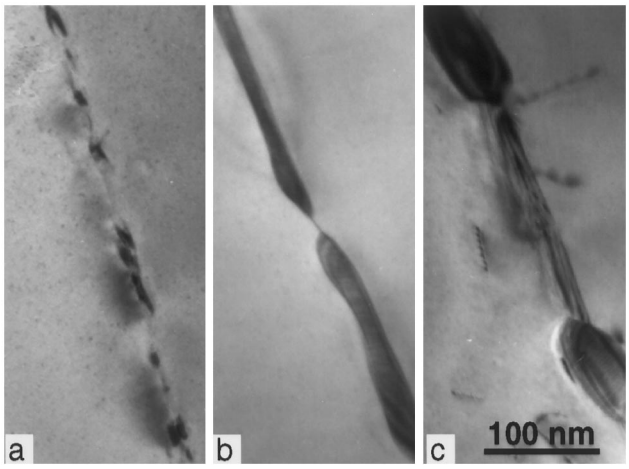

Fig. 1. TEM images of the material after heat treatment at 600°C for (a) 4 h, (b) 16 h and (c) 213 h.

Table 2
Median values of carbon matrix concentration

	SA	1 h	4 h	16 h	213 h
at.ppm	868 ± 267	732 ± 180	818 ± 170	520 ± 32	309 ± 21

boundaries. Because of the overlap between nitrogen and silicon, it cannot be determined which of those elements segregate from the AP analyses alone. However, the presence of intergranular carbo-nitrides after heat treatment for 1 h at 700°C suggests that nitrogen segregates in this material [7]. Additionally, AES has shown that silicon does not segregate in Alloy 600 [9].

The average amount of segregation of carbon, boron, phosphorus and nitrogen is presented in Fig. 3, in terms of the Gibbsian interfacial excess (number of segregated atoms nm^{-2} of the grain boundary), which can be calculated directly from an AP analysis [10]. The results indicate a significant variation of the carbon segregation with heat treatment, whereas the boron and nitrogen segregation appears to be relatively constant. Some carbon was present at the grain boundaries already after SA (0.7 nm^{-2}). Subsequent heat treatment at 600°C initially caused an increase in the amount of carbon (3.4 nm^{-2} after 1 h), but eventually the precipitation of chromium-rich carbides resulted in a decrease of segregated carbon to 1.4 nm^{-2} after 4 h and to 0.1 nm^{-2} after 213 h. The concentration of phosphorus was low in all analyses, but a clear increase was observed after the longest time, in accordance with the relatively slow phosphorus diffusion.

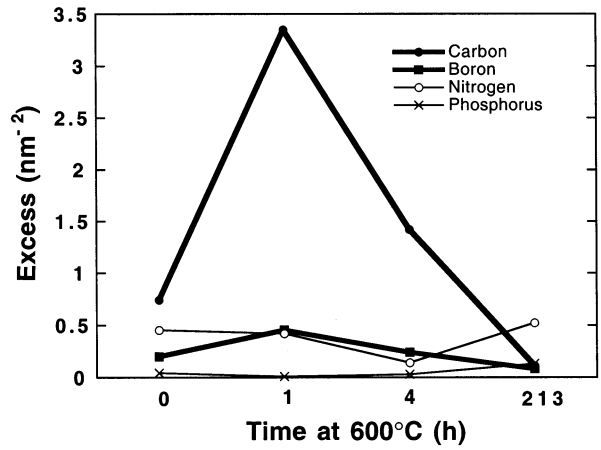

Fig. 3. Average amount of grain boundary segregation as a function of ageing time at 600°C, expressed in terms of the Gibbsian interfacial excess.

The average values of Gibbsian interfacial excess only partly reflect the evolution of the grain boundary microstructure, since large variations were found between different grain boundaries and sometimes even at different positions of an individual grain boundary, i.e. only a few nanometers apart. The four sets of histograms in Fig. 4 show the result of each analysis. The variations of carbon were correlated with variations in the local chromium concentration. In the SA material, the chromium concentration at the boundary was close to the bulk value, except for the second analysis of specimen no. 1, where the high carbon value (3.4 nm^{-2}) was accompanied by a local increase of the chromium concentration to 20 at.% Cr (all concentrations are given in at.%).

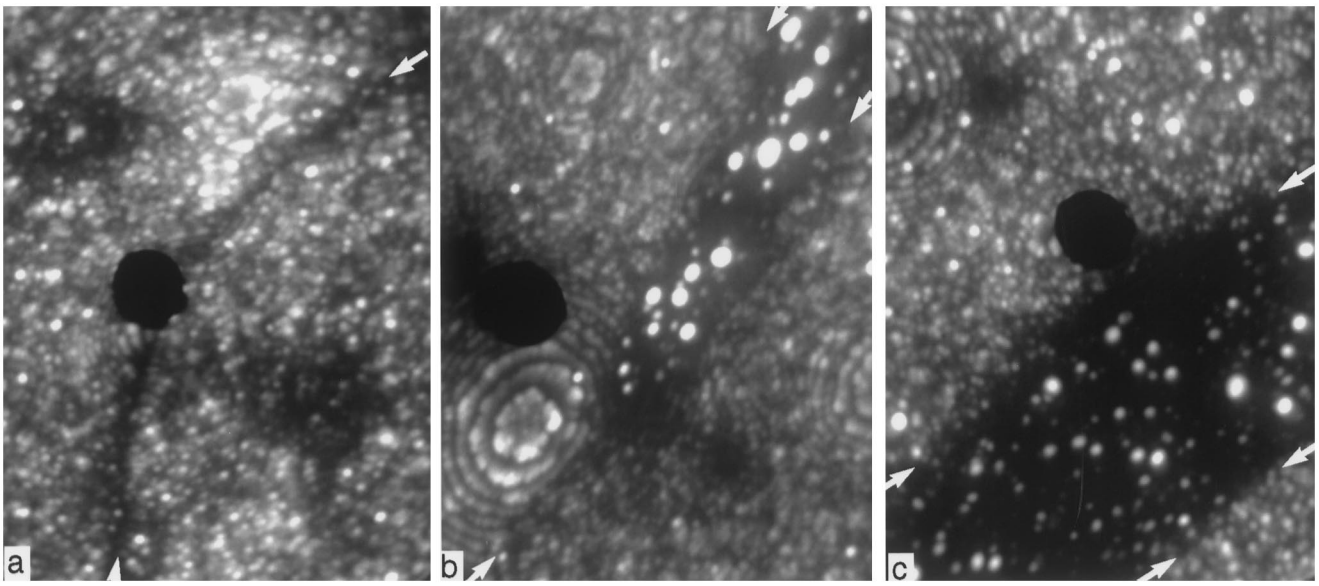

Fig. 2. Field ion images of grain boundaries. (a) Precipitate free grain boundary in the material heat-treated for 1 h at 600°C (arrowed). (b) Thin intergranular carbide (arrowed) in the material heat-treated for 4 h at 600°C. (c) Large carbide (arrowed) in the material heat-treated for 213 h at 600°C.

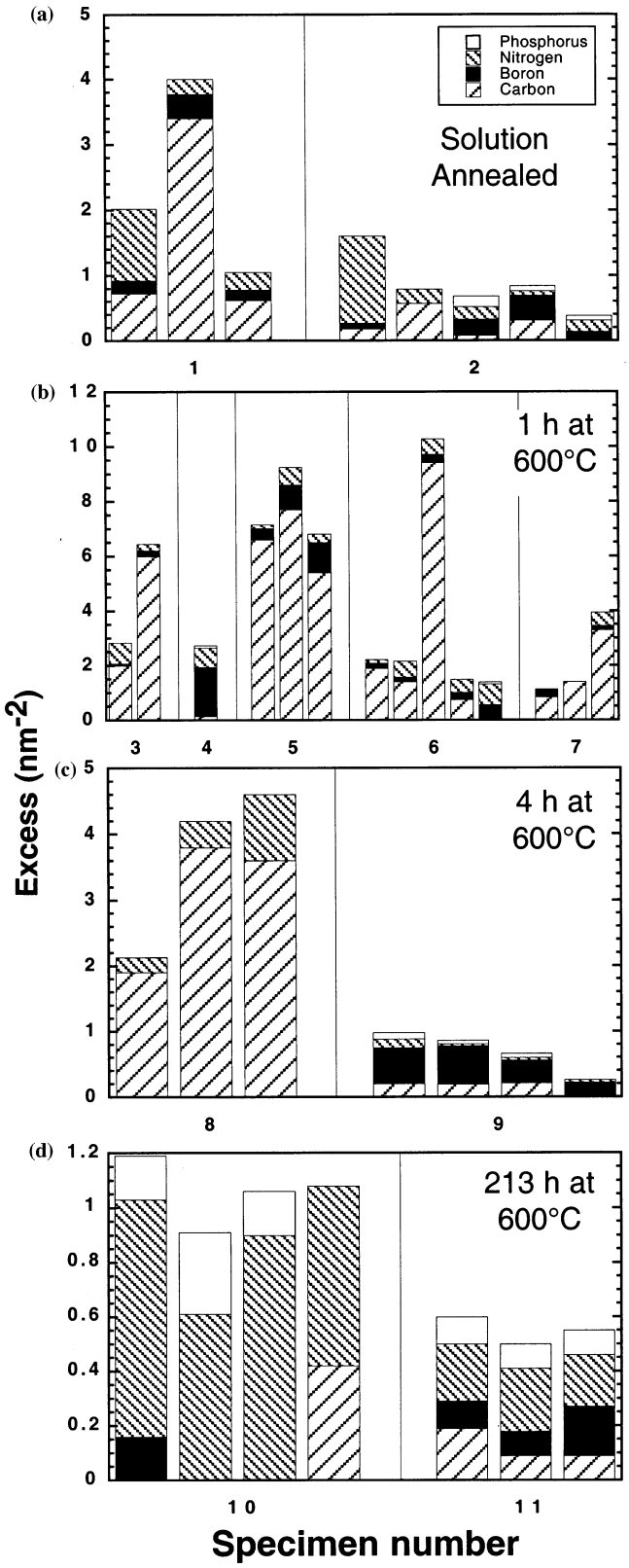

Fig. 4. (a)–(d). Histograms showing the Gibbsian interfacial excess in all analyses. Each bar represents one analysis of the grain boundary. Note the different scales on the ordinate.

In the material heat-treated for 1 h, the specimens having a large excess of carbon (specimen no. 3, 5 and 7) had relatively high chromium concentrations, 19% Cr on average. In contrast, specimen no. 4 contained almost no carbon and chromium was depleted to 13% Cr. Concentration profiles obtained from the third and fourth analyses of specimen no. 6 are presented in Fig. 5. Again, the correlation between carbon and chromium is evident in this early stage of precipitation. A similar pattern was observed in the material heat-treated for 4 h. The grain boundary in specimen no. 8, containing approximately three carbon atoms nm^{-2}, had a chromium concentration of $\sim$21% Cr, whereas in specimen no. 9, almost free of carbon, chromium was depleted to $\sim$8% Cr. This seems to indicate that the nucleation process has not been completed, even though relatively large carbides have already formed. In the material heat-treated for 213 h, chromium was still slightly depleted, to $\sim$11% Cr. A chromium concentration profile from the grain boundary into the matrix is shown in Fig. 6.

Another interesting observation is that phosphorus was only present at the grain boundary when the carbon concentration was low. In fact, phosphorus was detected in all ageing conditions, but only when the

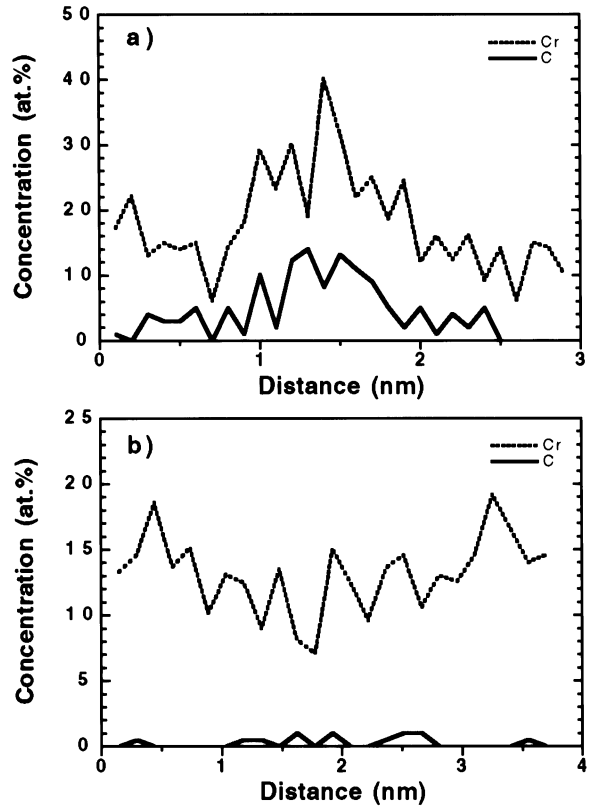

Fig. 5. Concentration profiles obtained from the same grain boundary (specimen no. 6) in the material heat-treated for 1 h at 600°C. (a) Simultaneous enrichment of carbon and chromium, indicating early stage of precipitation. (b) Depletion of chromium and very low amount of carbon.

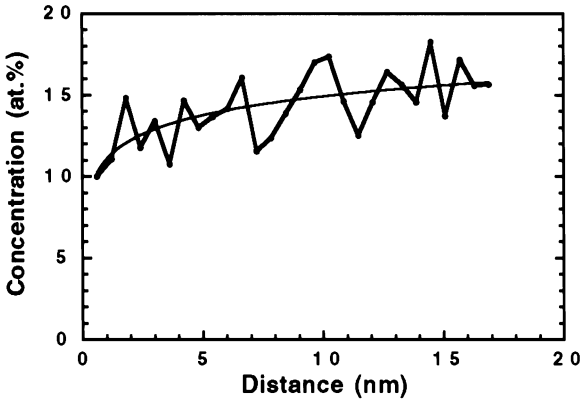

Fig. 6. Chromium profile obtained from across a grain boundary and into the matrix, showing the depletion in the material heat-treated for 213 h at 600°C.

excess of carbon was below 0.3 nm^{-2}. This effect has previously been established in steel [11].

A grain boundary in the material heat-treated for 1 h at 600°C was analysed in the ECOPoSAP. In the atom map shown in Fig. 7, the boundary appears to be ~3 nm thick. However, this large thickness is most probably an artifact, caused by complex trajectory effects in the vicinity of the grain boundary, and to a much smaller extent by an inaccuracy in the reconstruction algorithm due to the carbon atoms being on interstitial sites in the crystal lattice. Such effects are expected to be most prominent when the angle between the grain boundary normal and the specimen axis is large. In this specimen, the angle was ~70-80°. Carbon and boron were uniformly distributed at the boundary. It is notable that phosphorus appeared to be enriched a few nanometers from the boundary, likely rejected from the boundary because of the enrichment of carbon.

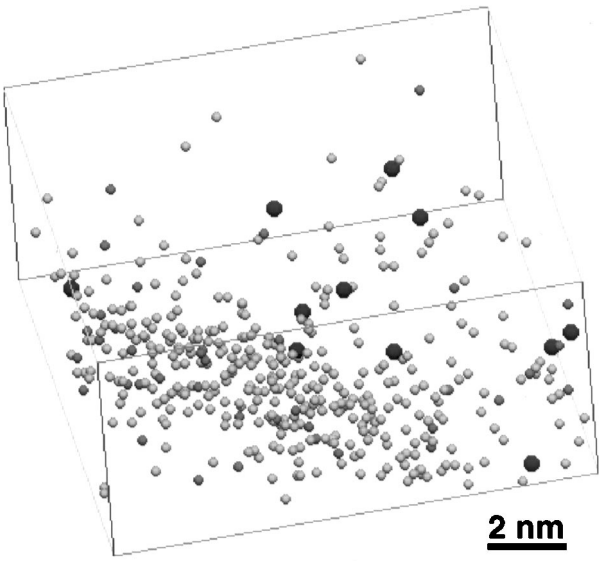

Fig. 7. Three-dimensional atom map of a grain boundary in the material heat-treated for 1 h at 600°C, showing the distribution of carbon, boron and phosphorus atoms.

All these experimental observations were obtained at 600°C, rather than the typical conditions that occur in a steam generator. It is possible to extrapolate the diffusion data, obtained at higher temperatures, for carbon [12] and chromium [13] to the typical service temperature. These extrapolations indicate that 1 h at 600°C would correspond to ~1 year for carbon and ~500 years for chromium at the service temperature of 350°C. This simple calculation suggests that an increase in carbon segregation is possible during the lifetime of a steam generator tube, but that chromium is too slow for significant precipitation to take place. On the other hand, a simultaneous rearrangement of carbon and chromium could occur, considering fast grain boundary diffusion.

4. Conclusions

During heat treatment of the investigated model Alloy 600 material at 600°C, the highest amount of carbon segregation to the grain boundaries occurred after 1 h, when the Gibbsian interfacial excess on average was 3.4 nm^{-2}. Locally, the amount of carbon segregation was correlated with the grain boundary chromium concentration, a consequence of the chromium carbide precipitation process. After prolonged heat treatment, the carbide precipitation resulted in a substantial decrease of the amount of grain boundary segregated carbon. Phosphorus was only detected at the grain boundaries when the excess of carbon was lower than 0.3nm^{-2}. Boron and nitrogen were also found to segregate to the grain boundaries in all material conditions and no correlation with heat treatment was observed.

Acknowledgements

This research was sponsored by the Division of Materials Sciences, US Department of Energy, under contract DE-AC05-960R22464 with Lockheed Martin Energy Research Corp. This research was conducted, in part, utilising the Shared Research Equipment (SHaRE) User Program facilities at Oak Ridge National Laboratory.

References

[1] S.M. Bruemmer, G.S. Was, J. Nucl. Mat. 216 (1994) 348.
[2] G.P. Airey, Corrosion 41 (1985) 2.
[3] K. Stiller, J.-O. Nilsson, K. Norring, Metall. Trans. A 27A (1996) 327.
[4] G.P. Airey, Metallography (1980) 21.
[5] G.S. Was, Corrosion 46 (1990) 319.

[6] G. Sui, J.M. Titchmarsh, G.B. Heys, J. Congleton, Corr. Sci. 39 (1997) 565.
[7] M. Thuvander, K. Stiller, E. Olsson, Mat. Sci. Tech. 15 (1999) 273.
[8] J.J. Kai, C.H. Tsai, T.A. Huang, M.N. Liu, Metall. Trans. A 20A (1989) 1077.
[9] G.S. Was, H.H. Tischner, R.M. Latanision, Metall. Trans. A 12A (1981) 1397.
[10] M.K. Miller, G.D.W. Smith, Appl. Surf. Sci. 87/88 (1995) 243.
[11] H. Vieflhaus, B. Richarz, Werkstoffe und Korrosion 46 (1995) 306.
[12] J. Cermak, J. Soupousek, K. Stransky, Scripta Metall. Mater. 29 (1993) 1581.
[13] D.D. Pruthi, M.S. Anand, R.P. Agarwala, J. Nucl. Mat. 64 (1977) 206.