PRE-IRRADIATION SPATIAL DISTRIBUTION AND STABILITY OF BORIDE PARTICLES IN RAPIDLY SOLIDIFIED BORON-DOPED STAINLESS STEELS

N. Kanani, L. Arnberg and O.K. Harling

Nuclear Reactor Laboratory and Department of Materials Science and Engineering
M.I.T., Cambridge, Massachusetts 02139, U.S.A.

The time temperature behavior of boride particles has been studied in rapidly solidified ultra low carbon and nitrogen modified 316 stainless steel with 0.088% boron and 0.45% zirconium. The results show that the as-splat-cooled specimens exhibit precipitates at the grain boundaries and triple junctions. For temperatures up to about 750°C no significant microstructural changes occur for short heat treatment times. In the temperature range of 750-950°C, however, particles typically 100-500 Å in diameter containing Zr and B are formed within the grains. Higher temperatures enhance the formation of such particles and give rise to particle networks. The results show that a fine and uniform distribution of the boride particles almost exclusively within the grains can be achieved if proper annealing conditions are chosen. This type of distribution is an important requirement for the homogeneous production of helium during neutron irradiation in fast reactors.

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1. INTRODUCTION

The relatively low energy neutrons of fission reactors used as irradiation test facilities for fusion materials are not in general capable of producing the higher helium production rates expected in fusion reactors. Nickel containing materials are an exception to this since they can be tested in mixed flux reactors to produce helium and dpa simultaneously with reasonably correct ratios, albeit for a limited range of damage and helium generation rates. Furthermore, the largest high flux test volumes are available in fast reactors where it is not possible to achieve adequate He generation for any of the candidate CTR alloys, including Ni containing alloys. This work is directed toward the development of a technique for the simultaneous production of helium and displacement damage in first wall structural materials during irradiation in fission reactors, with emphasis on high flux fast test reactors such as EBR-II and FFTF.

2. APPROACH

One possible simulation technique is to dope the material of interest with helium-producing elements such as ^{10}B , which has a high neutron cross section for helium production. The boron doping technique may allow the use of existing fast reactors to produce approximately the correct amounts of helium via the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction in candidate CTR materials, while they are being damaged by the reactor's fast neutrons [1]. Boron, however, cannot be kept from diffusing out of the solid solution to segregate at grain boundaries since the equilibrium solubility of boron in most elements and alloys is very low [2,3]. The maximum solubility of boron in stainless steel similar to Type 316 is about 500 appm at 1100-1150°C [4]. To keep adequate amounts of boron in

solution, it is necessary to quench directly from the melt, using high cooling rates. Finally, to keep the boron finely distributed and to achieve a homogeneous helium distribution during reactor irradiation at service temperatures, zirconium can be added to produce a fine (relative to the 2.6 μm range of the α particle) dispersion of stable ZrB_2 precipitates.

3. ALLOY SELECTION AND TREATMENT

In order to perform the pre-irradiation characterization of microstructure and spatial distribution as well as to study the time temperature behavior of the boride particles, two alloys with different concentrations of boron were rapidly solidified ($\sim 10^5\text{K/s}$) from the melt by means of a roller quencher [5,6]. The composition of the base material was (in w/o) Cr 16.7, Ni 16.5, Mo 2.27, Mn 1.21, Si 0.149, O 0.0052, C 0.0052, S 0.0035 and N 0.0016, Fe bal. An alloy with 0.088 w/o natural B and 0.45 w/o Zr was chosen for the present investigation. The microstructural characterization of the other alloy, which had lower B and Zr concentrations, has been presented elsewhere [7].

The alloy was studied in the form of $\sim 0.1\text{ mm}$ thick roller quenched foils. The grain size of these foils was between 2 and 4 μm . In order to investigate the spatial distribution as well as the time temperature characteristics of the boride particles, TEM discs were prepared and heat treated. The temperatures ranged between 550°C and 1050°C and the heat treatment time was between 15 min and 30 days. To be certain that no oxidation occurred, the heat treatment was performed in a stationary argon atmosphere with specimens wrapped in 316SS shim stock and loaded in boats containing titanium sponge as oxygen getter. In some cases the specimens were heat

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Fig. 1. TEM bright field micrograph of rapidly solidified 316 stainless steel + 5000 appm (B + Zr), showing grain boundary and triple junction precipitates in as-splat-cooled foils.

treated under a vacuum of approximately 10^{-7} torr.

4. INVESTIGATION OF BORON DISTRIBUTION

To determine the spatial distribution of boron in the boron doped stainless steel alloys in an unheat-treated condition, suitable specimens were prepared and investigated by neutron autoradiography [8]. A uniform spatial distribution of tracks was observed by optical microscopy in all specimens investigated. No boron segregation in any heat-treated samples could be detected on the level of 2-3 μm , which was the resolution of the neutron autoradiography technique employed.

5. MICROSTRUCTURAL CHARACTERIZATION

The microstructure of the boron doped alloy was examined by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). The TEM investigations were carried out on a Siemens Elmiskop 101 and a Philips EM300 operated at 100 kV. The STEM studies were performed on a Vacuum Generators HB5 equipped with an electron energy loss spectrometer (EELS) and an energy dispersive X-ray spectrometer (EDXS). The specimens were thinned to electron transparency by electrochemical methods.

The microstructural characterization of the alloy in its as-quenched condition is outlined below.

The splat-cooled foils consist of very small grains of the order of 2-4 μm and contain precipitates almost entirely located at grain

Fig. 2. STEM micrograph of grain boundary precipitates in rapidly solidified 316 stainless steel + 5000 appm (B + Zr).

boundaries and triple junctions. The particles have different morphologies and are of a complex nature, containing Ni, Cr, Fe and Mo with or without Zr. The TEM micrographs in Fig. 1 and Fig. 2 illustrate the locations and morphologies of some of these particles, whereas the EDX spectra in Fig. 3 indicate, by way of example, the composition of the two particles from Fig. 2.

Fig. 3. EDXS from particles A and B shown in Fig. 2.

Fig. 4. a) STEM micrograph showing precipitates in (B + Zr) doped rapidly solidified 316 stainless steel annealed at 550°C for 3 days.

b) Zr X-ray ($L_{\alpha+\beta}$) map showing the Zr distribution (light) in the area shown in Fig. 4a.

The examples given in these figures are representative of the as-splat-cooled foils. Fig. 4 displays a STEM micrograph and the corresponding Zr X-ray map. One can clearly see that in addition to the very small zirconium containing precipitates alongside the grain boundaries, there also exists a relatively larger particle with a high concentration of zirconium at the triple junction. The grain boundary and triple junction precipitates were not sufficiently thinned by the polishing solution to give reliable electron energy loss spectra and boron could, therefore, not be detected in these particles. Another difficulty with regard to the analysis of the particles arises from the fact that the difference between the critical absorption energies of B ($K\alpha = 187$ eV) and Zr ($M_{IV}, V^{0II, III} = 182$ eV) is equal to about one half the resolution of the energy loss spectrometer.

Further microstructural investigations were carried out on heat treated specimens to examine the thermal behavior without irradiation. The results obtained show that, for temperatures as high as 800°C, the characteristics of the material remain almost unchanged. There still exist precipitates at grain boundaries and triple junctions in specimens that were heat treated at 550°C for up to 30 days. This is also true for specimens held at 700 to 800°C for three days. Fig. 5 shows a representative TEM micrograph taken from a specimen kept at 800°C for three days. From this figure one can see a large number of precipitates decorating the grain boundaries and triple junctions. According to the results obtained by EDXS, such precipitates are complex compounds containing zirconium, molybdenum and other major alloying elements of the

stainless steel.

One significant event, however, that clearly occurs for the first time in the temperature range of 750-800°C and above, is the formation

Fig. 5. TEM bright field micrograph of (B + Zr) doped rapidly solidified 316 stainless steel, annealed at 800°C for 3 days showing grain boundary precipitates.

Annealed
at 800°C
for 3 days

Annealed
at 850°C
for 30 min

Fig. 6. EDXS and EELS from boride particles in (B + Zr) doped rapidly solidified 316 stainless steel.

of a new phase occurring as small particles within the grains which can be seen in Fig. 5. Many of these particles were identified as being borides with complex compositions containing zirconium. Fig. 6a and Fig. 6b show X-ray and electron energy loss spectra from such particles (diameter about 500 Å) in samples heat treated at 800°C, 3 d. and 850°C, 30 min, respectively.

Annealing of the boron doped specimens at higher temperatures, e.g. 980°C, for 1/2 h leads to formation of more and more easily distinguishable boride particles in the grains. The TEM micrograph in Fig. 7 shows one example illustrating the size and distribution of the boride particles. As can be seen from this micrograph the diameter of the boride particles is generally somewhere between 100 and 500 Å. The apparently random distribution of the boride particles has been confirmed repeatedly. Such particles can, however, not be found in as-splat-cooled foils. Neither can they be observed in specimens annealed at lower temperatures in the range of 700–800°C unless long holding times of the order of a few days are chosen.

The absence of such particles in specimens heat treated at lower temperatures and their formation in those annealed at higher temperatures cannot be explained satisfactorily at the present time. However, the following observations seem to be noteworthy in this connection. The emergence of the boride particles within the grains goes hand in hand with a gradual decrease in size and number and in many cases even the disappearance of the aforementioned grain boundary particles, while no significant changes in grain size occur. There is some evidence that this finding may be due to a dissolution of the grain boundary

precipitates during the heat treatment process, possibly an Oswald ripening process. This supposition is also supported by the fact that the decrease and disappearance of these precipitates is enhanced with increasing heat treatment temperatures and times. The observations made so far indicate that it is possible to obtain a uniform distribution of the boride particles in the grains with almost no grain boundary precipitates if proper annealing conditions are chosen.

Fig. 7. TEM bright field micrograph of intra-granular B-rich particles in (B + Zr) doped rapidly solidified 316 stainless steel annealed at 980°C for 30 min.

Fig. 8. TEM bright field micrograph of (B + Zr) doped rapidly solidified 316 stainless steel showing precipitate coarsening and grain growth after annealing at 980°C for 72 h.

Further studies were conducted in order to investigate the behavior of the boride particles for stability, distribution and coarsening as well as the grain growth with time. These experiments were carried out at 980°C, which had proved in previous investigations to be the appropriate temperature for a uniform distribution of small boride particles. The time was, however, extended to 72 hours. Some of the results obtained from these experiments are presented in Fig. 8 and Fig. 9. The TEM micrograph in Fig. 8 is illustrative of considerable grain growth. It also demonstrates a uniform distribution of the boride particles. Furthermore, it can be deduced from this micrograph that particle coarsening occurs under these conditions as well. While rather uniformly distributed boride particles have been observed repeatedly in heat treated specimens, occasionally an arrangement of particles alongside preferential directions, probably originally dendrite boundaries, can be found as suggested by Fig. 9. This effect seems to be enhanced with increased temperature.

6. CONCLUSIONS AND FUTURE WORK

The results obtained from microstructural characterization of boron doped rapidly solidified stainless steel alloys indicate that the boron doping technique, using zirconium boride, provides the possibility for including useful amounts of boron in candidate CTR alloys. They also suggest that a uniform distribution of the boride particles within the grains can be achieved, provided the proper heat treatment conditions are used. Therefore, a homogeneous dispersion of helium produced through neutron capture during the irradiation of such boron doped stainless steel alloys in fission reactors can be expected. Stability of the zirconium containing boride particles under irradiation and the simultaneous helium and damage production, at ratios which approximate the CTR environment,

Fig. 9. TEM bright field micrograph of the same material as in Fig. 8 showing nonuniform particle distribution.

will be examined in the near future on specimens being irradiated in the AD-2 irradiation experiment in EBR-II.

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