OVERAGING OF OUTOKUMPU CUCRZR - D.J. Edwards (Pacific Northwest National Laboratory)* and B.N. Singh (Risø National Laboratory)

OBJECTIVE

The objective of this work is to study the effect of overaging on the microstructure of CuCrZr, its effects on mechanical properties, and how it affects performance under neutron irradiation.

SUMMARY

Aging at 850°C for 4 hours essentially removed the fine-scale precipitates produced during the prime aging treatment. Aging at 700°C lead to large scale coarsening that produced denuded zones along grain and twin boundaries, grain boundary precipitates, and removed all of the fine-scale defects to produce precipitates 20 nm in size or larger. Aging at 600°C lead to somewhat similar microstructure compared to the 700°C aged specimens, however the average size of the precipitates was not quite as large and the density appears to be somewhat higher. Denuded zones formed along all boundaries, but the grain boundary precipitation was not as extensive as in the case of the specimens aged at 700°C. Further characterization will be conducted to determine the identity and chemistry of the precipitates observed in the aged microstructures.

PROGRESS AND STATUS

Introduction

Over the past 6 years a series of studies [1-5] have been conducted exploring the effects of neutron irradiation on pure copper and various copper alloys, most notably the precipitation strengthened CuCrZr and CuNiBe alloys and the ODS alloy GlidCop Cu-Al_2O_3,. Depending on the irradiation and operating conditions, each of these alloys has problems that limit their current applicability for service in advanced fusion power system designs. From a fracture toughness perspective, CuCrZr is an alloy that may possess potential since it retains a greater fraction of its fracture toughness at elevated temperatures and after irradiation. Seppo et. al. [6] found the room temperature fracture toughness of unirradiated Outokumpu CuCrZr to be more than double that of the GlidCop Al25 and CuNiBe alloys (220 kJ/m^2 vs 80-100 kJ/m^2), and at temperatures in the range of 200-350°C the toughness still remains at roughly 80% of the ambient values. Neutron irradiation to 0.3 dpa over the same temperature range produces some degradation in toughness, but even at 350°C, the toughness of the irradiated CuCrZr is near 100 kJ/m^2, whereas for both the GlidCop and CuNiBe it is near zero. The latter two materials begin to exhibit intergranular failure at temperatures above 250°C, whereas the CuCrZr alloy fails in a ductile manner.

The one limitation to the CuCrZr alloy is that in the absence of cold working, it is difficult to heat treat the alloy to produce the same levels of strength as compared to the other two alloys. Under irradiation, however, the CuCrZr hardens dramatically when irradiated below 250°C, but this hardening is accompanied by loss of uniform ductility and work hardening and can produce a tensile instability in the most extreme case. Given the fracture toughness behavior, this tensile behavior does not appear to be important since the toughness remains reasonably high, and may be related to the fact that despite the hardening and loss of uniform ductility, it exhibits good reduction in area and ductile failure at elevated

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temperatures and after irradiation. One final point is that precipitate stability can be an issue when the irradiation temperature exceeds 280°C, which can lead to loss of strength, and at high enough temperatures, the material begins to swell from void formation. The CuNiBe alloy also suffers from this problem. The ODS GlidCop by comparison exhibits excellent stability with respect to the microstructure and appears to be swelling resistant even when irradiated at 430°C to doses as high as 150 dpa [7].

The CuCrZr alloy will likely be joined to other materials depending on its application since it may not possess the strength to be a standalone structural material. Therefore it is wise to consider the potential effect of heat treatments that may produce less than optimum properties and see how these different microstructural states affect the performance under irradiation. In this report, we describe a set of heat treatments given to CuCrZr and briefly describe the microstructure. These materials will be tested in the near future in the unirradiated condition and will be placed in an irradiation experiment in the DR-3 reactor at Risø in Denmark.

Experimental

Tensile specimens fabricated from Outokumpu CuCrZr (produced by Outokumpu Oy) were given four separate heat treatments to study the effect of overaging on the microstructure and mechanical properties. The heat treatments are listed below in Table 1. All heat treatments were done in vacuum ($<10^{-4}$ torr). The microstructure was examined by transmission electron microscopy using a JEOL 2000FX.

TABLE 1 Heat treatments used to study overaging in Outokumpu CuCrZr

Prime Aged: Solution annealed at 960°C / 3 hrs / WQ + aged 460°C / 3 hrs / WQ
850°C treatment: PA + 850°C / 4 hrs / WQ
700°C treatment: PA + 700°C / 4 hrs / WQ
600°C treatment: PA + 600°C / 4hrs / WQ

Results

Prime aging (Figure 1)

The microstructure of this condition is comprised of a high density of small precipitates that appear similar to those measured in earlier studies [1,3,4]. Though the precipitate reactions that occur in CuCrZr are not clearly understood, it appears that at least two types of small precipitates are formed during the prime aging treatment, and larger precipitates of a much lower density. Small Gunier-Preston zones (G-P) are present that exhibit a lobe-lobe appearance with a line of no contrast perpendicular to the operating $(200)_{Cu}$ reflection, an appearance known to occur for very small, coherent spherical particles. There were other precipitates present in the microstructure that differed from the G-P zones in both size and appearance. These precipitates tended to exhibit Moiré fringes when imaged using a g $=200_{Cu}$ reflection, however, not all precipitates were clearly visible. These fringed precipitates are thought to be incoherent Cr-rich precipitates because of the lack of any strain

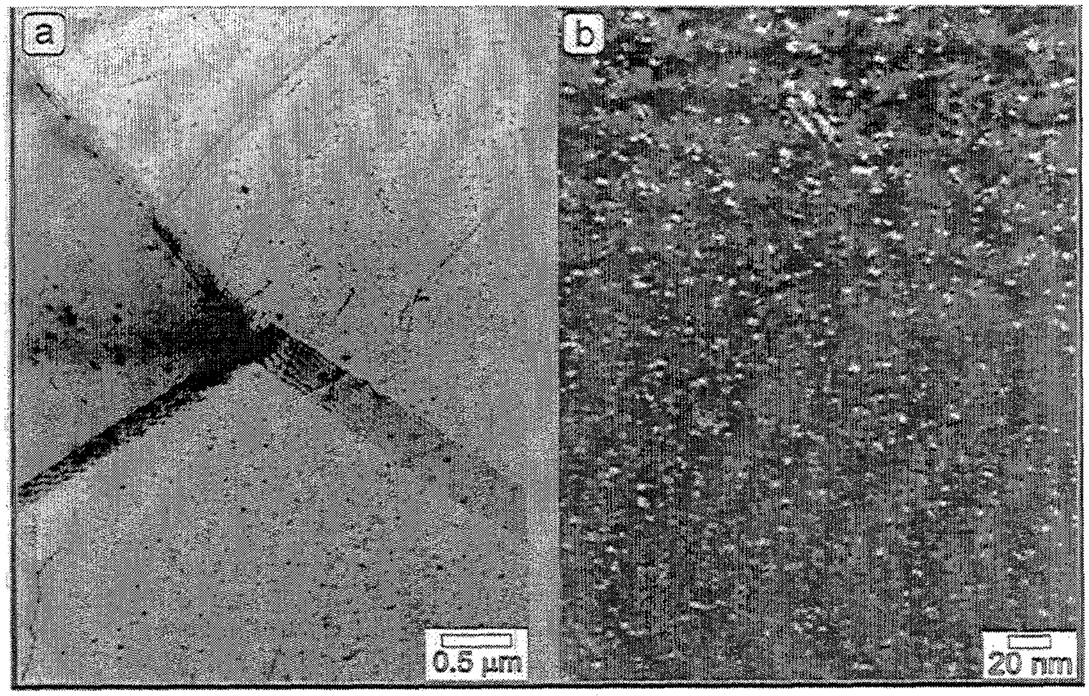

Figure 1. The prime aging treatment leads to (a) precipitation denuding along grain boundaries, dislocations, and twin boundaries. A low density of large inclusions are present, and some grain boundary precipitation occurs at the grain boundaries. A close-up of the fine scale precipitation is shown in (b).

fields around them. The fringed precipitates were oriented in 3 different directions, suggesting that they may be the same type of precipitate but with more than one orientation relationship or habit plane visible in the image. It is not clear whether they are a BCC or a metastable FCC as has been proposed in the literature [8-10]. Large precipitates were also found in a lower density and much larger size than the G-P zones. Selected area diffraction patterns revealed no discrete reflections that would permit identification of any the phases present, so further work is planned on high resolution analytical TEM's to study the precipitation. The grain boundaries contain a low density of small precipitates, and denuding is present along dislocations and boundaries. Large inclusions are scattered about in the matrix, and are assumed to be large Cr particles formed during the solution annealing or original processing that did not dissolve.

850 °C Treatment (Figure 2)

The microstructure in this case is much simpler since the aging heat treatment removed the fine-scale precipitation. A few stacking fault tetrahedra can be found that formed during the water quenching from 850°C. The severe overaging produced large-scale grain boundary precipitates that formed when the small scale dispersion either coarsened or dissolved.

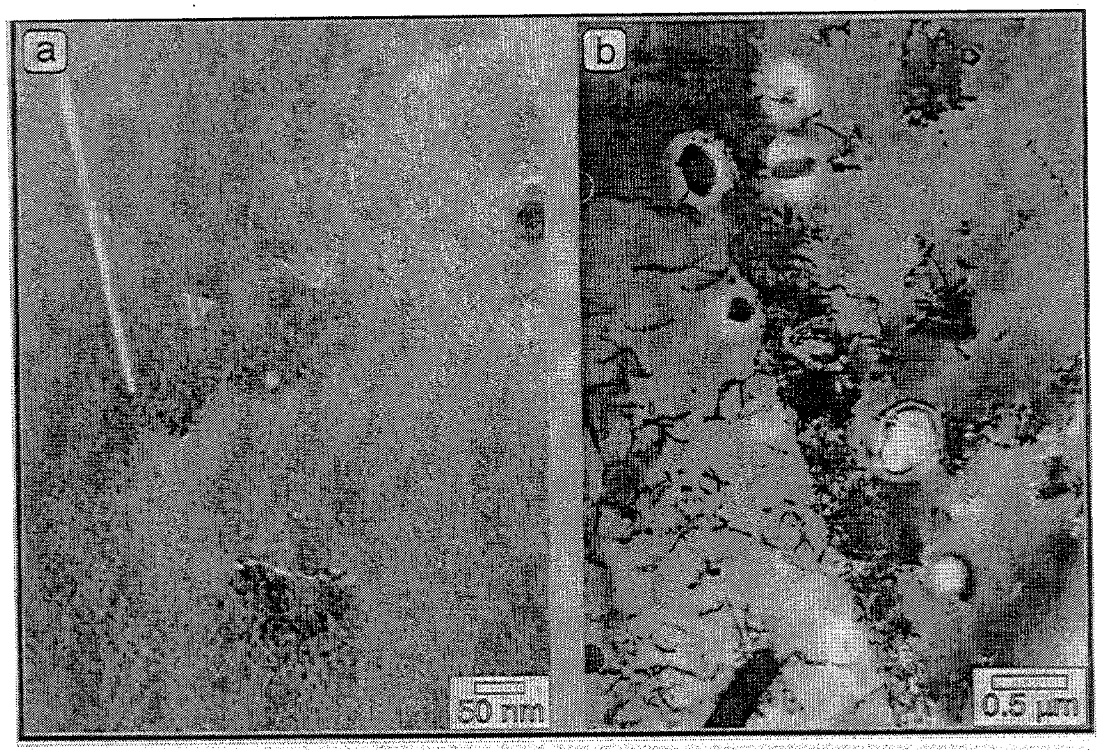

Figure 2. The overaging appears to have reverted the material back to an annealed condition, forming the stacking fault tetrahedra shown in (a) during the water quenching. Other than dislocations the matrix is free of any the fine-scale defects shown in Figure 1a. The extensive grain boundary precipitation formed in this condition (b) may point to where the solute went during the overaging.

700 °C Treatment (Figure 3)

This treatment causes severe coarsening of the fine-scale precipitates, effectively removing the G-P zones and other precipitates shown in Figure 1a. Larger precipitates have formed or coarsened in the matrix to produce an overaged condition of lower overall precipitate density. Grain boundary precipitation and denuding occurs in this condition also, as well as at twin boundaries. The identity of the different phases remains to be determined, requiring careful analysis of their composition.

600 °C Treatment (Figure 4)

The overaging that occurs at this temperature is not as severe as shown for the 700°C treatment. However, there is still extensive precipitation and denuding along the grain boundaries and twins as shown in Figure 4a. The fine-scale precipitates have been replaced by a much coarser dispersion of particles, the composition and identity of which will be determined in future work.

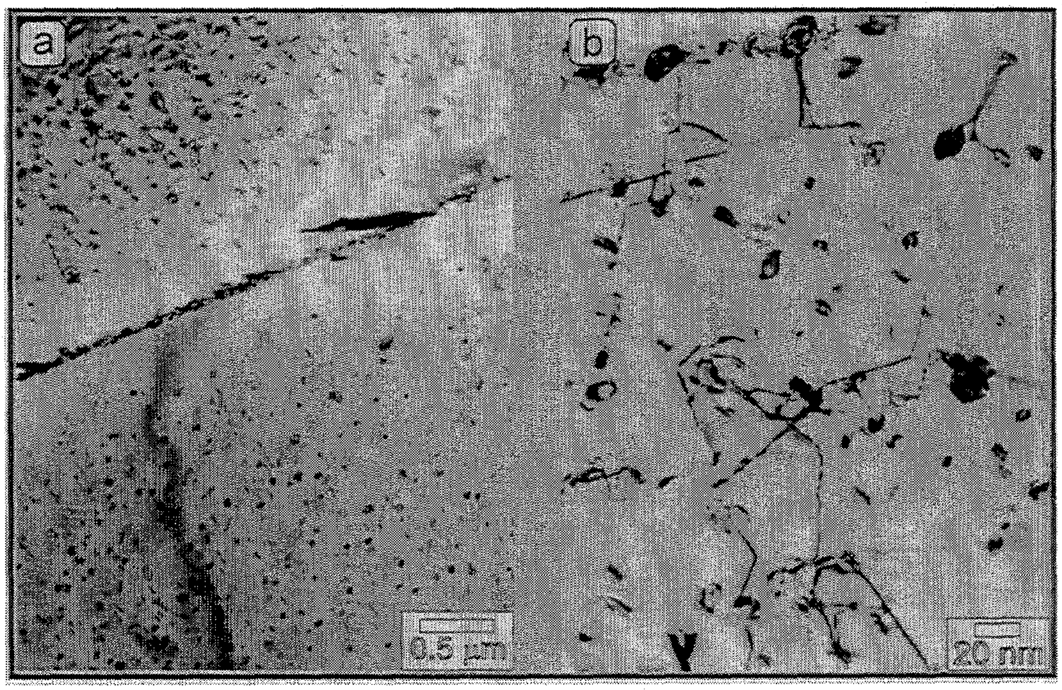

Figure 3. Strong denuding occurs at the boundaries with the material as shown in (a). This denuding is also accompanied by grain boundary precipitation that occurs equally on twin boundaries and grain boundaries. The fine-scale G-P zones and other precipitates shown in Figure 1a have disappeared to be replaced by the larger precipitates shown in (b). Their identity remains to be determined.

FUTURE WORK

Further work is necessary to characterize the precipitate types that have formed in the different aging treatments. Samples of the unirradiated material will be shipped to PNNL to be characterized in 2010 Field Emission Gun ATEM. Tensile testing and electrical resistivity measurements will be conducted at Risø on the unirradiated samples to determine the effect of the aging treatments and how it relates to the observed microstructure. Samples will also be included in future irradiation experiments to study the effect of irradiation on the microstructure, mechanical and physical properties.

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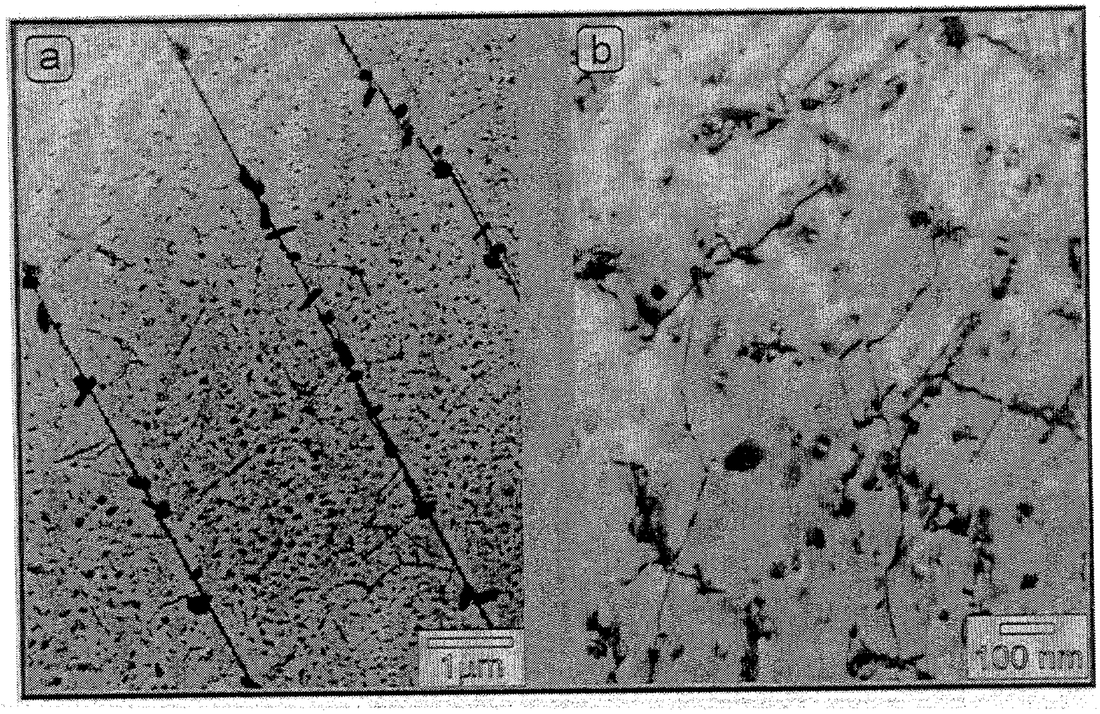

Figure 4. Denuding and precipitation (a) on twin and grain boundaries occurs on a finer scale than that observed in the specimens given the 700°C treatment. As in the 700°C, though, the G-P zones and other small precipitates have been replaced with the coarser distribution of precipitates shown in (b).

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