STATUS OF COLLABORATIVE RESEARCH PROGRAM BETWEEN PNNL AND RISØ NATIONAL LABORATORY - D. J. Edwards (Pacific Northwest National Laboratory)* and B. N. Singh (Risø National Laboratory, Denmark)

OBJECTIVE

The primary objective of this collaboration is to conduct fundamental studies of radiation effects on pure metals and alloys of interest to the fusion materials community. Pure copper and its alloys (all FCC metals) are the primary focus of this collaboration, but other metals and alloys such as pure Fe, Mo and ferritic steels (BCC materials) and Ti (HCP materials) are included for comparison.

SUMMARY

PNNL and Risø have been collaborating since 1994 on a series of irradiation experiments on pure copper and various alloys of interest to the fusion materials community. The collaboration has been of great benefit to both institutes by sharing resources and experience. Past research has concentrated on examining the microstructural evolution during neutron irradiation and the influence this microstructural change exerts on the deformation response. Post-irradiation annealing experiments of both irradiated pure copper and CuCrZr yielded unique insights into the relationship between the microstructure and the deformation response. The results of that experiment also raised further questions regarding the stability and structure of the small defects produced during irradiation, particularly regarding the stability of these defects during annealing and how they interact with mobile dislocations. The focus of ongoing work has now shifted to examining the issues of defect stability in irradiated materials, dislocation generation from stress concentrations at interfaces in irradiated materials, and a new experiment on in-situ straining during irradiation and how this affects microstructural evolution and the relationship to mechanical properties.

PROGRESS AND STATUS

Introduction

PNNL and Risø have been collaborating since 1994 on a series of irradiation experiments on pure copper, molybdenum, iron and other metals and alloys of interest to the fusion materials community. The collaboration has been of great benefit to both institutes by sharing resources and experience. Past research has concentrated on examining the microstructural evolution during neutron irradiation and the influence these microstructural changes exert on the deformation response. The irradiated materials have been investigated using a wide variety of techniques including transmission and scanning electron microscopy (TEM and SEM, respectively), tensile testing, electrical resistivity measurements and positron annihilation spectroscopy. The irradiation experiments have been both fundamental in nature as well as more engineering oriented, the latter in particular for those experiments involving materials being considered for use in ITER (International Thermonuclear Experimental Reactor).

One experiment in particular that yielded unique insights involved the post-irradiation annealing of pure copper irradiated at 100°C. The original intent of this experiment was to explore the possibility that in-reactor bakeouts (performed to restore the vessel vacuum in ITER) could remove or at least mitigate the radiation hardening that occurs in copper and its alloys during reactor operation. This radiation hardening involves substantial increases in yield strength and severe loss of uniform elongation and work hardening ability that manifests itself as a yield point phenomenon and early onset of plastic instability. In the more extreme cases the tensile curves for irradiated copper and some of its alloys can exhibit plastic instability

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upon yielding and immediately begin necking in tension. The annealing conditions of 300°C for 50 hrs were chosen to reflect this bakeout procedure. The results of the PI annealing experiment proved that the vacancy-type defects in the irradiated copper (stacking fault tetrahedra in this case) were more stable than expected, especially at doses of 0.1 dpa and above where the defect density had essentially saturated. Annealing produced observable changes in the microstructure including a new distribution of interstitial loops. However, more significant was the fact that the SFT distribution coarsened only slightly after annealing, that is, the density decreased slightly and the average size of the SFT increased, proving that the SFT microstructure was quite resistant to annealing. After annealing the tensile properties reflected these microstructural changes by losing the yield point phenomenon that occurred at doses of 0.1 dpa and higher and restoring some work hardening ability. However, the overall ductility of the PI annealed materials did not significantly improve after annealing if the specimens were irradiated to doses of ≥ 0.1 dpa. In the as-irradiated condition, the appearance of a yield point phenomenon is thought to be a consequence of suppression of homogenous production and propagation of dislocations by the pinning of pre-existing dislocations of small dislocation loops, clusters of defects and impurities formed during irradiation. The restoration of work hardening and removal of the yield point phenomenon is therefore related to the post-irradiation annealing lowering the degree of dislocation pinning, allowing more homogenous plastic flow. While the annealing lowered the yield stress and allowed some degree of homogenous deformation to promote work hardening, dislocation channeling still occurred in the post-irradiation annealed samples. The presence of even a small amount of dislocation channeling appeared to be more than enough to prevent the full recovery of ductility back to the unirradiated levels. The experiment demonstrated the bakeout condition to be of limited use for restoring the mechanical properties to unirradiated levels, particularly since subsequent exposure of the PI annealed material would involve a starting microstructure composed of pre-existing loops and SFTs not present in the unirradiated condition. For further details on this experiment the reader is referred to reference 1.

This experiment in turn produced new directions of research that have led to continued experimental collaborations between PNNL and Risø. One key issue is to examine the deformation microstructures after tensile testing and attempt to discover more about the dislocation channeling phenomenon such as where the channels originate, how they get started, what leads to the continued production of new channels with increasing strain and why existing channels appear to get shut down as new channels are formed. Deformation studies have been started in both pure copper and CuCrZr irradiated below 100°C to further investigate dislocation channeling. The stability of the SFT raised new questions and reopened issues related to how they interact with mobile dislocations, an issue of particular importance for modeling the generation and movement of dislocations to produce cleared channels. Finally, the past experiments led to a new experiment aimed at investigating the microstructure of irradiated metals that were strained in-situ and how this influenced the mechanical properties compared to materials that were only tested after being removed from the reactor.

A brief description of current experiments is provided in the following sections. The results of these experiments are to be presented either at the next ICFRM-11 in Japan or published separately in the Journal of Nuclear Materials.

Status of Present Experiments

Recently, a number of TEM samples were examined with the objective of characterizing the microstructures in pure copper and CuCrZr neutron irradiated at 60°C to 0.3 dpa. The CuCrZr alloy had been processed before irradiation to yield a much different size distribution of precipitates than produced during the conventional prime ageing heat treatment. In addition, the deformation microstructures were characterized for most of the irradiated conditions to better understand the formation and interaction of dislocation channeling, a phenomenon that severely limits the deformation to discrete volumes and substantially reduces the uniform elongation.

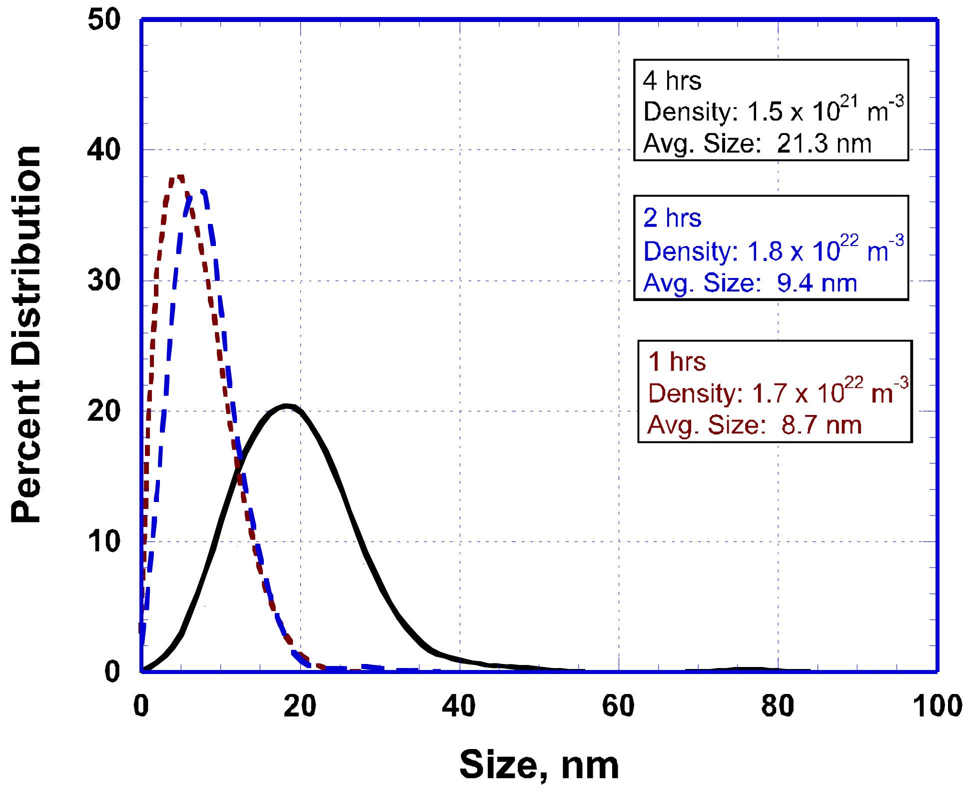

Figure 1. Size distributions were measured of the precipitates produced during the overageing treatment at 600°C. The samples aged for 2 and 4 hours were included in the irradiation experiment.

The irradiation experiment on the CuCrZr concluded a set of experiments started in 2001 that involved overageing the CuCrZr to produce a much coarser precipitate distribution than observed in prime aged CuCrZr, the normal condition when using this material. In 2001 a series of heat treatments were explored to choose two overageing conditions that would yield a reasonable density of precipitates of larger diameter that might alter the response of the alloy during subsequent post-irradiation testing. The hope was that a precipitate distribution could be produced that yielded average sizes on the order of 4-10 nm in diameter with a density around 10^{22} m^{-3}, a density similar to that of the oxide particles present in the oxide dispersion strengthened GlidCop alloy. Note that the prime aged condition for CuCrZr (this involves solution annealing, water quenching, then ageing at ~475°C for 3-4 hours) generally yields a precipitate distribution of 3-5 nm diameter precipitates in a density of ~10^{23} m^{-3}. Ultimately the goal was to see if it was possible to mitigate or remove the extreme effects of radiation hardening and restore some semblance of uniform elongation and work hardening to the CuCrZr alloy by manipulation of the starting microstructure before irradiation. The larger precipitates may be more stable and resistant to irradiation, therefore serving as effective obstacles to dislocation motion and prevent or minimize dislocation channeling. The exploratory research, which has been reported in prior Fusion Material Semi-Annual Reports [2,3], found that an additional thermal exposure of 600°C for 2 hrs and 4 hrs to samples initially given the prime aged heat treatment produced a precipitate distribution in the desired range indicated above. The size distributions are shown in Figure 1. These two conditions, along with samples of CuCrZr given only the prime aged heat treatment and samples of pure copper provided for a baseline comparison, were placed in neutron irradiation experiment at 60°C to a total dose of 0.3 dpa.

These samples were removed from reactor in 2002 and were tested and examined recently at Risø. The tensile results demonstrated that the alteration of the precipitate distribution before irradiation did indeed influence the tensile behavior and achieved some increase in work hardening, although the upper/lower yield point phenomenon was not removed. The microstructural characterization was performed on both the as-irradiated and the as-irradiated and deformed samples, however, the analysis of the results is still in progress and will be reported in detail at a later date. The initial impression, based on a strictly qualitative inspection of the images and the tensile response, is that the different precipitate distributions obviously influenced the deformation behavior, but the microstructural relationship is not so obvious and requires careful analysis.

In an experiment involving interrupted tensile tests on pure copper irradiated at ~50°C to 0.3 dpa, a new feature has been observed in deformed samples that offers potential insight into the deformation behavior of irradiated copper. The samples were tested at Risø and sent to PNNL for characterization in the SEM and TEM. In samples where the tensile test was stopped just before yield (~80% of the yield strength or ~270 MPa), distinct defect-free zones (DFZs) were observed in the TEM at many of the grain boundaries in the deformed pure copper. Four different examples of these DFZs are provided in Figure 2. By examining TEM samples taken from the grip area of the tested samples, the defect-free zones were confirmed to be a consequence of the applied stress during post-irradiation tensile testing. The lack of DFZs at the grain boundaries implies that the DFZs in the strained samples were due to grain boundary

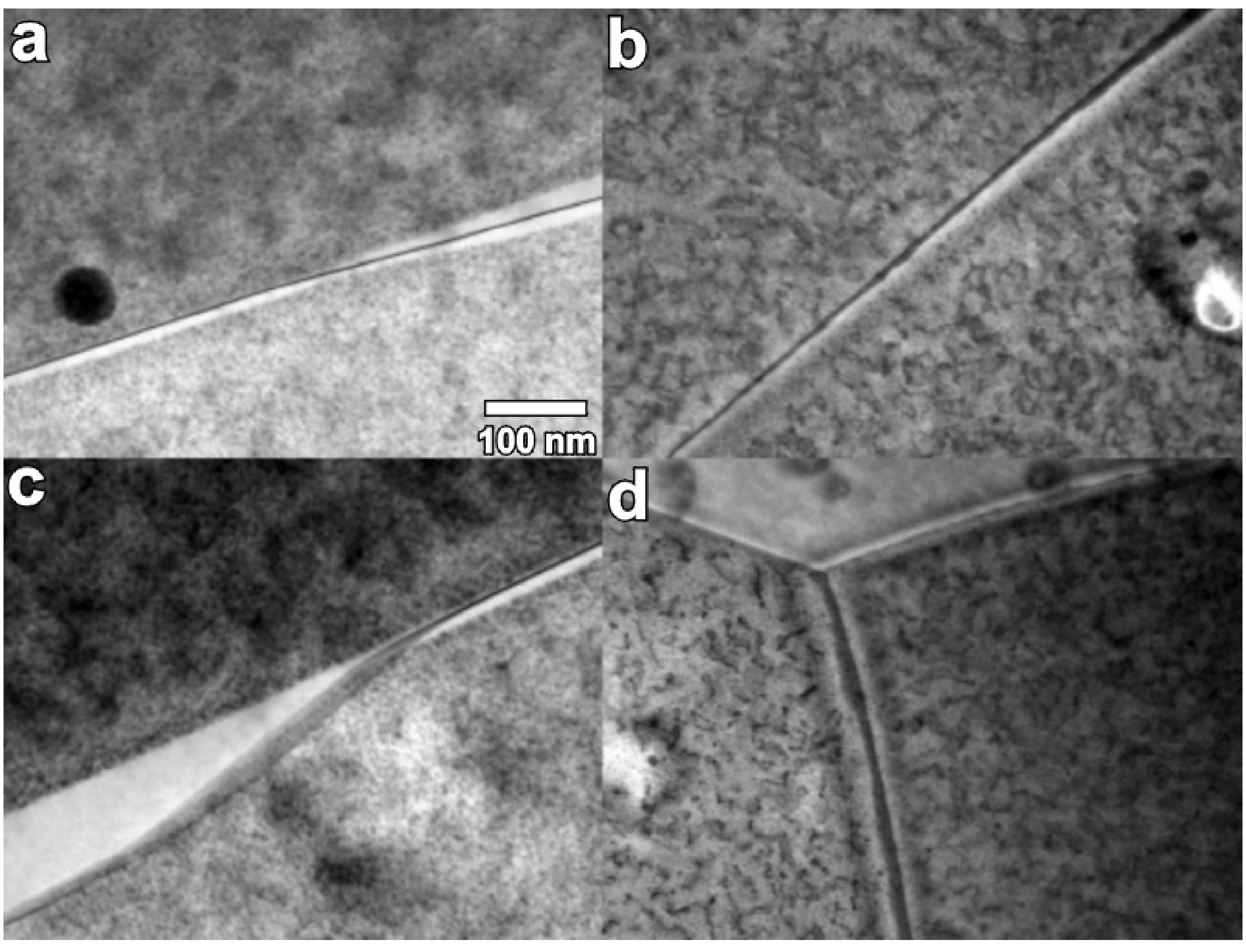

Figure 2. Examples are shown of defect-free zones observed along grain boundaries in irradiated OFHC copper. The sample was irradiated and tested at 50°C, but the test was stopped just before the macroscopic yield point. These defect-free zones were not observed in the untested samples. Note that the DFZ can undulate across the grain boundaries, varying in width at different positions.

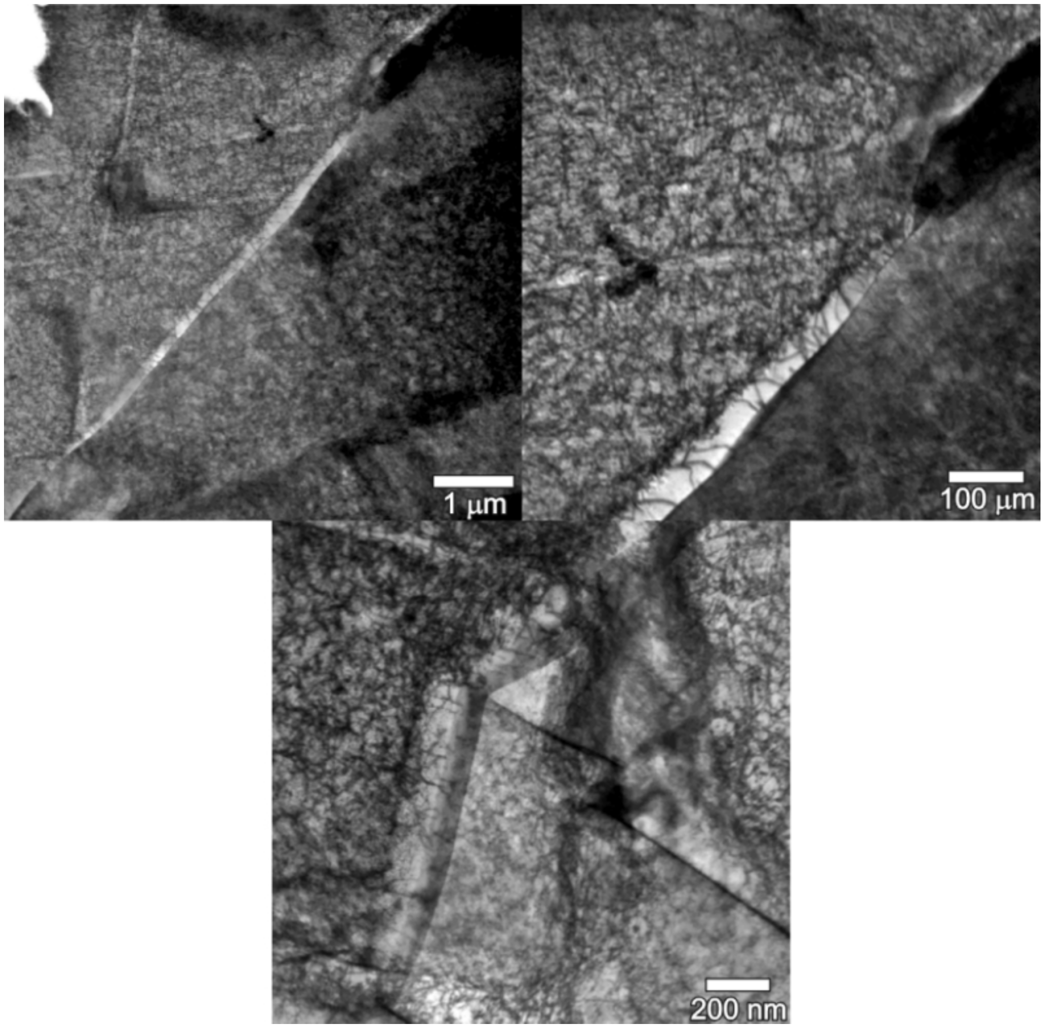

Figure 3. Three examples are shown for the DFZ as they appeared in sample where the tensile test was stopped at the ultimate tensile strength. Dislocation channeling was more prevalent at this level of strain, and the DFZ often contained dislocations produced by deformation. No wide scale homogenous deformation is present in the grain interiors, but the dislocations are present that are thought to have formed during deformation and percolated through the SFTs present in the matrix without removing a substantial fraction of these defects.

sliding and/or migration under the applied load. Note that the yield stress in the as-irradiated samples was near 300 MPa, so the applied loads at which the DFZs were first observed was quite high for pure copper. At this stage of the tensile test, dislocation channeling, the dominant deformation mechanism observed at higher strains, was very rare, often limited to 1-2 channels per grain in the area examined with no deformation-induced dislocation motion evident in grain interiors. Figure 3 shows DFZs in a sample irradiated and tested under the same conditions, but in this case the tensile test was stopped just before the ultimate tensile strength. Dislocation channeling was far more prevalent in this condition and the DFZs often contained line dislocations possibly produced from a source near or within the grain boundary. Note that even though the matrix contained a significant density of dislocations resulting from the irradiation, no homogenous annihilation of the defects could be identified, indicating that most of the strain was accommodated within the dislocation channels and the dislocations were only able to "percolate" through the SFTs.

The DFZs were found to be present in both the pure copper and the CuCrZr samples mentioned earlier that were irradiated at 60°C. However, because the samples examined had been taken to failure and were not interrupted tests, the DFZs were difficult to see because the impingement of the dislocation channels distorted the grain boundary areas and produced large plastic strains in the softer DFZ regions. In a few isolated cases, grain boundaries were found that had not been heavily deformed by channel intersection and the DFZs were more obvious. These results offer further confirmation of the DFZs being a generic feature in irradiated and tested copper, and illustrate that it would be easy to overlook these DFZs in samples taken to failure. The impact of these DFZs requires further evaluation, but the immediate implication is that deformation occurred at the grain boundaries at macroscopic stresses lower than that needed to initiate significant dislocation channeling. The relationship between the dislocation channeling and the DFZs is unknown at this time as many of the grain boundaries had clear DFZs around them, but only rarely were channels found in the grains and these often came from boundaries with no DFZs.

Another experiment recently completed extended the previously described post-irradiation annealing experiment to TEM samples of pure copper that were neutron-irradiated at 200 and 250°C. Post-irradiation annealing was then conducted on separate specimens at 300, 350, 400 and 450°C for 2 hours for each irradiation temperature. These two irradiation temperatures bracket a transition in microstructural evolution where void swelling and small defects form during irradiation at 250°C, but only small defects (stacking fault tetrahedra and small loops) form at 200°C. The objective of this experiment was to investigate the stability of the stacking fault tetrahedra (SFT) in the absence or presence of voids, another sink/source of vacancies during the annealing. The importance of this type of research is two-fold since it first helps to understand why in-situ annealing treatments may be ineffective as a means for mitigating radiation hardening, especially in those situations where the component will be irradiated in the next cycle. Secondly, understanding the stability of the SFT may provide insights into their structure and how they can be destroyed by the passage of dislocations during deformation. In the post-irradiation annealing experiment conducted on samples irradiated at 100°C, it was noticed that the SFT appeared to become more “perfect” after annealing, i.e. more triangular in appearance, suggesting that the SFT produced from displacement cascades were not as “structurally perfect” as often assumed. This is an issue that requires further verification since a high fraction of non-perfect SFT could alter the overall deformation response if they are more easily destroyed by mobile dislocations. Recent modeling by Wirth et al. [4] suggested that mobile dislocations could more easily interact with a truncated SFT and eventually destroy it, which is important when trying to model the formation of cleared channels in irradiated copper. The experimental characterization of the different annealing conditions listed above is finished, with the analysis of the data expected to be completed over the coming months. Initial results from the samples irradiated at 200°C to 0.3 dpa are presented in Figure 4 showing images of the SFT microstructure in the as-irradiated condition and after post-irradiation annealing at 350 and 450°C. The size distributions for the as-irradiated condition and the four different annealed conditions listed above are shown in Figure 5. The size distributions and images show that the size distribution increases with annealing temperature, but even at 450°C the SFT are still present in a significant density.

Another issue that is being investigated in this collaboration concerns the clearing of defects within the dislocation channels in both pure copper and CuCrZr. In the case of pure copper, many of the channels have been found to be essentially free of the stacking fault tetrahedra observed at a very high density in the regions adjacent to the channels. Some debris remains inside the channels left over from the passage and interaction of many dislocations. In contrast, the channels found in the deformed CuCrZr exhibited a somewhat higher residual population of dislocation segments and dipoles as well as the original defects and precipitates, but overall the channels are still relatively clear of the defects produced during irradiation. Since it is not known how many dislocations have moved through a given channel, it is not possible using the current data to make quantitative comparisons between individual channels within a given sample, let alone different samples or samples from different materials.

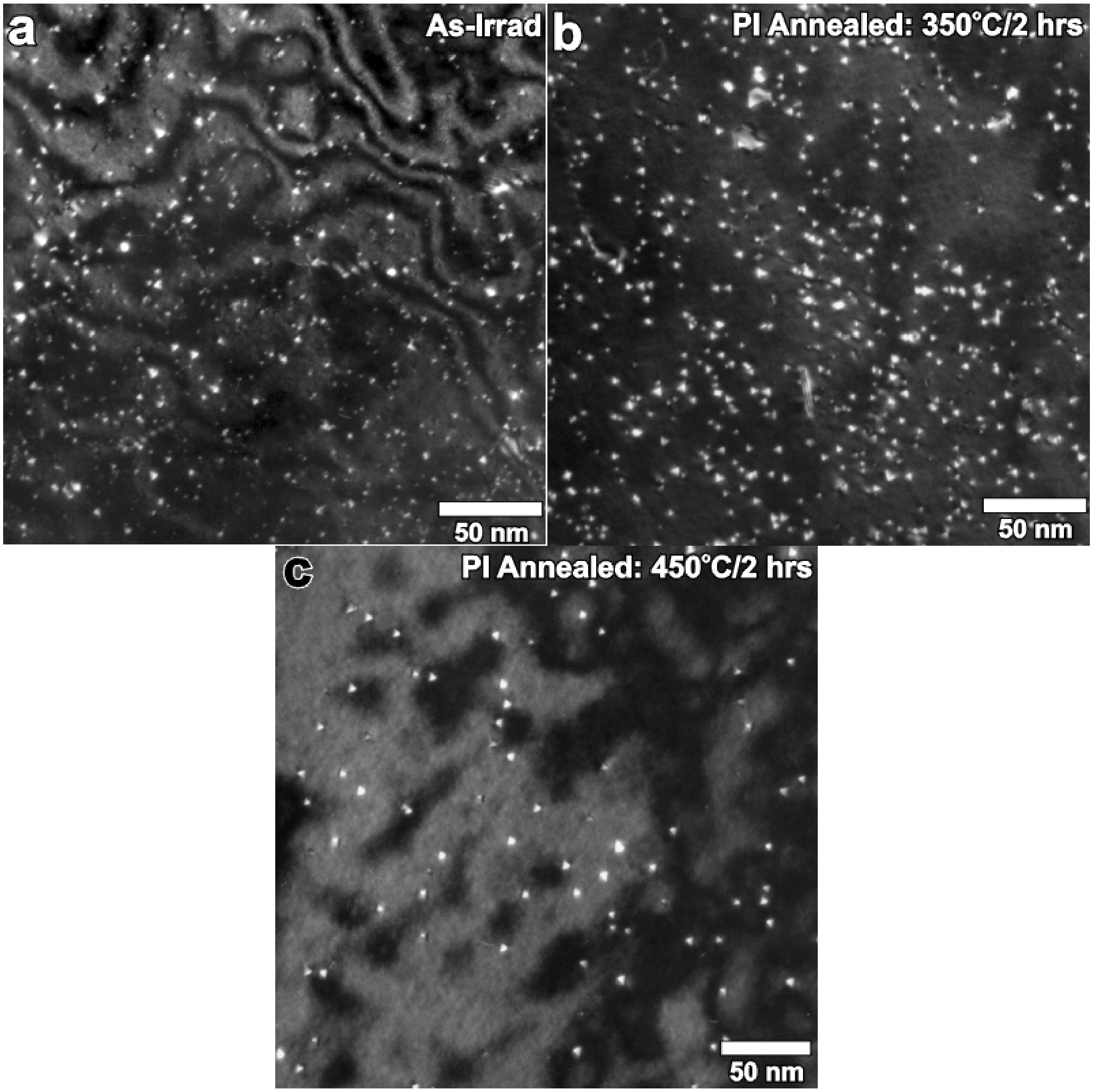

Figure 4. Examples of the SFT microstructure after post-irradiation annealing are shown above. The density decreased as the annealing temperature increased, and the size distributions shown in Figure 5 indicate a significant shift in the size distributions.

As further work is conducted to investigate the phenomenon of dislocation channeling, there is a growing recognition concerning the difficulty of trying to quantify the spacing, size and extent of dislocation channeling using TEM. Very few observations have ever captured the point at which a channel has been initiated, and the strain gradients that occur from grain to grain in a tested polycrystalline sample mean that the limited data obtained from one grain cannot necessarily be applied globally to the entire sample. A final point to consider is that the grain size in many pure metals and single phase alloys examined in these irradiation experiments ranges from several microns up to ~30 mm. A typical TEM foil is generally only 100-200 nm thick, so the very thin volume of material characterized in the TEM limits the chances of finding the point at which a channel is initiated and how it propagates into the grain interior. A greater

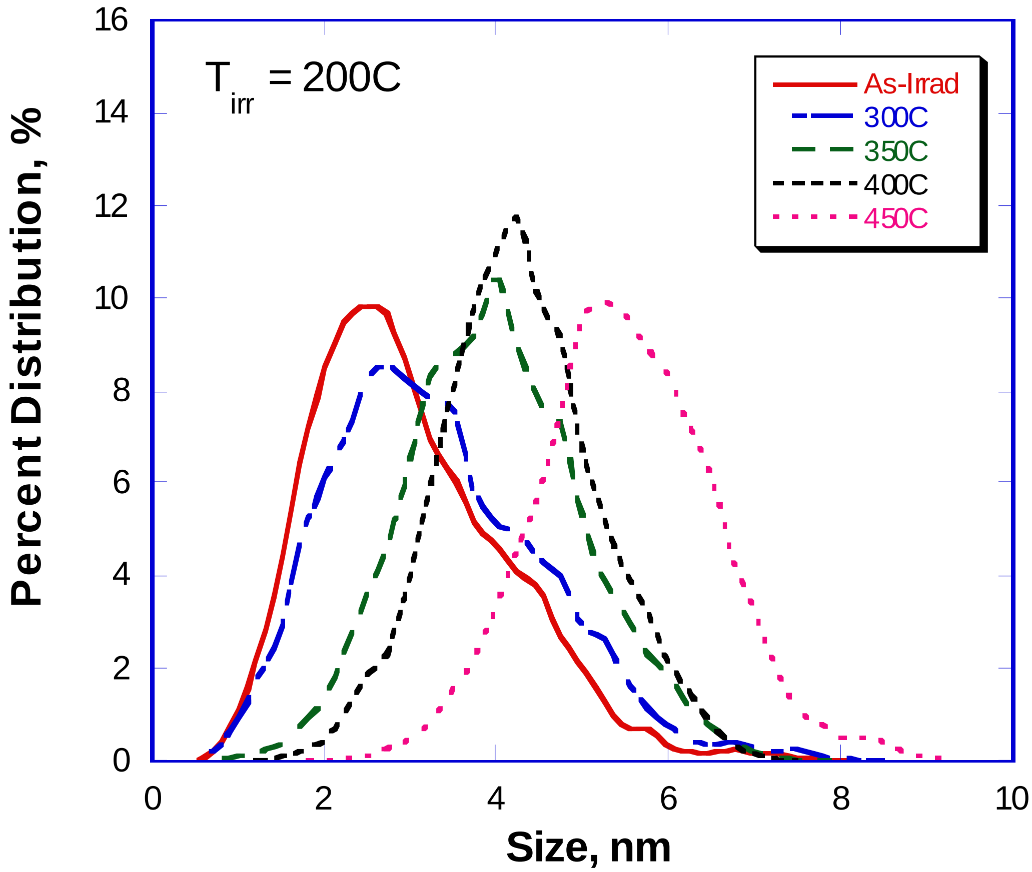

Figure 5. Size distributions from pure copper, irradiated at 200°C and annealed for 2 hours at the temperatures indicated on the plot.

effort is therefore needed to utilize bulk methods in conjunction with TEM and other techniques to explore this more fully, possibly including in-situ straining in the TEM to try and capture channel initiation events.

FUTURE WORK

The collaboration between PNNL and Risø will continue to examine some of the issues described above. A new set of experiments has been initiated involving the in-situ straining of pure copper, and the samples from that experiment will be available mid-2003. Subsequent irradiations will irradiate CuCrZr under the same conditions, then later experiments are slated to irradiate Fe and a ferritic steel. The main goal of these experiments is to compare the differences in microstructure and mechanical behavior that result from applying tensile strain from the start of irradiation cycle and comparing it side by side to samples that were not loaded until near the end of the irradiation cycle. Additional work will delve further into the issue of where channels are initiated in polycrystalline materials, in particular investigating the role of interfaces such as grain boundaries and twin boundaries.

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