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THE DUCTILITY IN BENDING OF MOLYBDENUM ALLOYS IRRADIATED BETWEEN 425 AND 1000°C*

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Molybdenum and the alloys Mo-0.5% Ti and TZM were irradiated at four temperatures between 425 and 1000°C, to a displacement level of 11 dpa at a fluence of 2.5×10^{26} n m^{-2} (> 0.1 MeV). Vacuum bend tests at elevated temperatures showed the ductile-to-brittle transition temperature (DBTT) to be above room temperature for all irradiation temperatures. Irradiation at 585°C produced the highest DBTT, 550 to 700°C. Differences among the three materials were minor.

1. INTRODUCTION

Molybdenum, or molybdenum alloys, were among the first materials suggested for use as first wall and other structures in fusion reactors. This suggestion has frequently been repeated in conceptual designs. The most recently proposed use of a molybdenum alloy, and the most thorough evaluation of its potential, is the use of TZM for the first wall of the UWMAK-III reactor design study of 1976 [1]. The chief attraction of molybdenum alloys is their potential for high-temperature service, 1000°C or higher, and the resulting high thermal efficiency possible in the power generation system. The chief difficulty with these alloys is their tendency toward brittle failure. The ductile-to-brittle transition temperature (DBTT) can be raised by impurities in the metal, by fabrication, by welding, and by irradiation. The least understood of these is the effect of neutron irradiation at proposed service temperatures. Previous work has shown that neutron irradiation at 425°C can raise the DBTT (defined by tensile test) to at least 550°C [2]. Other relevant literature on the effect of neutron irradiation on this process has been reviewed by Badger et al. [1].

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Molybdenum in service as the first wall of a tokamak, with a lithium–stainless steel blanket, will experience displacement damage and gas generation from transmutation reactions. The defect production rates are 7.5 dpa, 47 at. ppm He, and 95 at. ppm H per MW y/m^2 of reactor operation [3].

The purpose of this work was to evaluate the effect of irradiation at temperatures between 425 and 1000°C on the DBTT. The geometry of the available samples restricted the possible testing to three-point bending over a range of test temperatures. The DBTT was judged by a bend-or-break criterion, supplemented by scanning electron microscopy (SEM) fractography to determine the fracture mode. The as-irradiated microstructures of these samples had been characterized and reported previously [4].

2. EXPERIMENTAL

Three materials — low-carbon arc-cast molybdenum, Mo–0.5% Ti, and TZM — were included in this experiment. The chemistry of the materials and the annealing temperatures used to produce fully recrystallized microstructures are given in Table 1. Sheet specimens, ∿0.4-mm thick, were irradiated with a number of other materials in static gas-filled capsules in the EBR-II fast reactor. The irradiation parameters for this experiment are given in Table 2, and more detail on the irradiation experiment is given elsewhere [2,4]. The specimens used for bend tests were cut to 2.5 × 3 mm with an abrasive saw. These pieces were electropolished just before testing to produce a smooth surface on the tension side of the beam.

A three-point bending device was designed to accommodate these rectangular specimens, with distance between supports of 2.03 mm (0.080 in.) and maximum bend angle near 45°. Sections of 0.51 mm (0.020-in.) dia tungsten

Table 1. Material Parameters for Molybdenum Alloys

Alloy	Alloy Additions (wt %)	Weight Parts per Million C	O	N	Annealing Temperature (°C)
Mo	(none)	30	20	<5	1200
Mo–0.5 Ti	0.5% Ti	230	12	<5	1400
TZM	0.5% Ti, 0.09% Zr	230	20	<5	1500

Table 2. Parameters for Irradiation in Row 2 of EBR-II

Temperature Nominal (°C)	Temperature Nominal (T/T_m)	Temperature Uncertainty or Range[a] (°C)	Gas in Static Atmosphere	Fluence (>0.1 MeV) (n/m^2)	Displacement Level (dpa)[b]	Helium Level (at. ppm)[b]
425	0.24	±10	He	$2.5 \cdot 10^{26}$	11	0.4
585	0.30	±20	He	2.5	11	0.4
790	0.37	±25	Ar	2.5	11	0.4
1000	0.44	950 to 1050, ±30	Ar	4.4	19	0.7

[a]Uncertainty due to uncertainty in the nuclear heating rate. These capsules were not instrumented.

[b]Compare to fusion reactor rate of 7.5 dpa and 47 at. ppm He per MWy/m^2 of operation.

wire were used for the load bearing points. The text fixture is shown schematically in Fig. 1. The test system is mounted in a turbomolecular pumped vacuum system on an Instron Universal test machine. Test temperatures were achieved by thermocouple-controlled induction heating. Load deflection curves showed either specimen break or the end-of-travel of the test system, but did not give useful yield point information for specimens that bent without breaking. Most tests were run at a crosshead speed of 8.5 µm/s, for an approximate strain rate at the tensile surface of 4×10^{-4} s^{-1}. Specimens for elevated-temperature tests were held at temperature for 30 min before testing. The temperature uncertainty was approximately ±5°C, and the vacuum was typically 3 MPa (2×10^{-5} torr).

Fractographic examination was conducted in a scanning electron microscope at 25 kV with secondary electron imaging. The entire fracture surface was surveyed quickly, and critical or typical areas examined more carefully and photographed at direct magnifications between 100 and 1000×.

3. RESULTS

Bend specimens break or crack when brittle, but may deform and then crack or bend a full 45° if they are tested above the DBTT. Since cracking is not conclusive evidence of the DBTT, scanning electron microscopy (SEM) of the fracture surface was used to confirm the failure mode. In some of these cases, the SEM showed regions of ductile dimple fracture. This was interpreted as evidence that the sample had some very limited ductility, with the limited ductile tearing preceding the final brittle fracture propagation.

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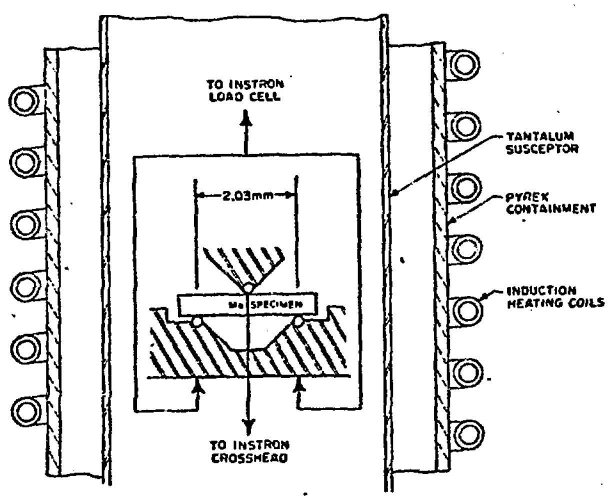

Fig. 1. Schematic illustration of the elevated-temperature three-point bend test fixture. Tungsten wire, 0.5 nm (0.020 in.) dia, was used for the specimen loading points.

The SEM fractography showed that for all three materials the preirradiation annealing had produced a recrystallized structure with a sheet texture, with the smallest grain dimension in the sheet thickness direction. There was no indication that the texture affected the results.

The bend test and SEM results are summarized in Fig. 2. Several important observations can be drawn from these results.

1. The unirradiated DBTT is below room temperature for all three materials.

2. Differences in the behavior of the three materials are smaller than differences due to irradiation conditions.

3. The shift in the DBTT is a strong function of the irradiation temperature.

4. For the available irradiation temperatures, the greatest degradation of properties was produced by the 585°C irradiation.

5. For all four irradiation temperatures and for all three materials, the DBTT is above room temperature.

A number of observations were also drawn from the SEM fractography. The fracture appearance changes from predominantly cleavage to mainly grain boundary separation and finally to ductile tearing as the test temperature is increased from below the DBTT to above the DBTT. Figure 3 demonstrates this change from cleavage to ductile tearing in Mo–0.5% Ti. The failure mode also changed across the thickness of some specimens, as shown in Fig. 4. The mode in this fracture changes from ductile tearing near the tensile surface to cleavage deep within the crack.

Molybdenum generally shows more grain boundary separation than Mo–0.5% Ti or TZM when tested at the same temperature, although there was some cleavage area in all brittle fractures. In tensile tests of control specimens at –196°C, M 8464

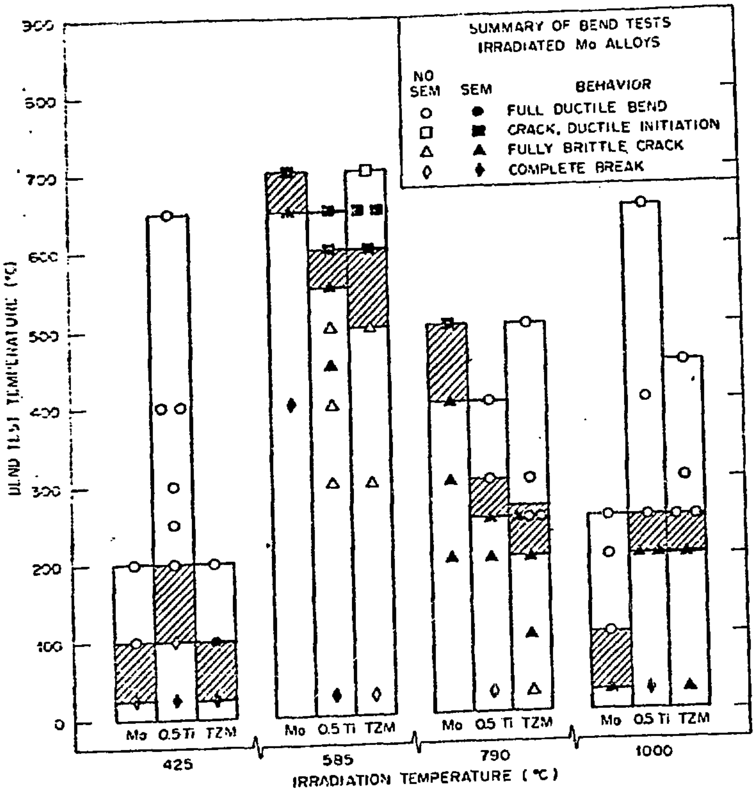

Fig. 2. Summary of the bend test results obtained on three molybdenum alloys, irradiated at the four temperatures shown on the abscissa and then tested at the temperatures shown on the ordinate. Open symbols indicate behavior determined by macroexamination only; filled symbols indicate SEM examination of the fracture surface. The shaded zone contains the DBTT.

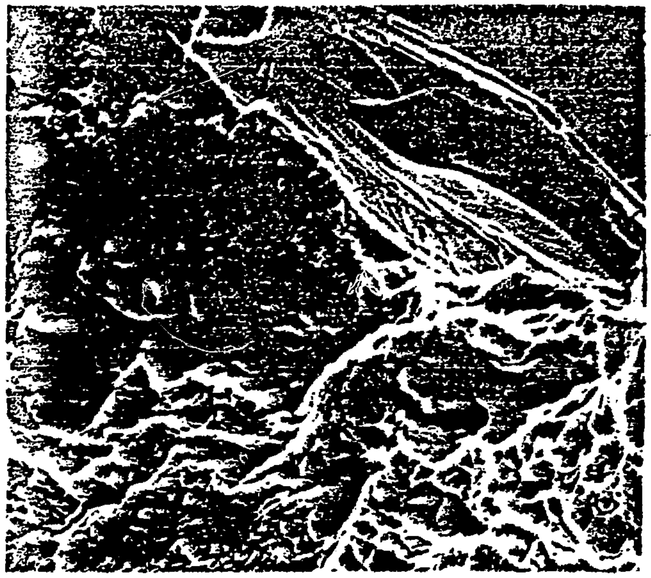

Fig. 4. Fracture surface on a sample of TZM irradiated at 585°C and bend tested at 650°C. The tensile edge of the crack shows ductile dimple rupture, with a transition to cleavage fracture deep within the crack. 1000×.

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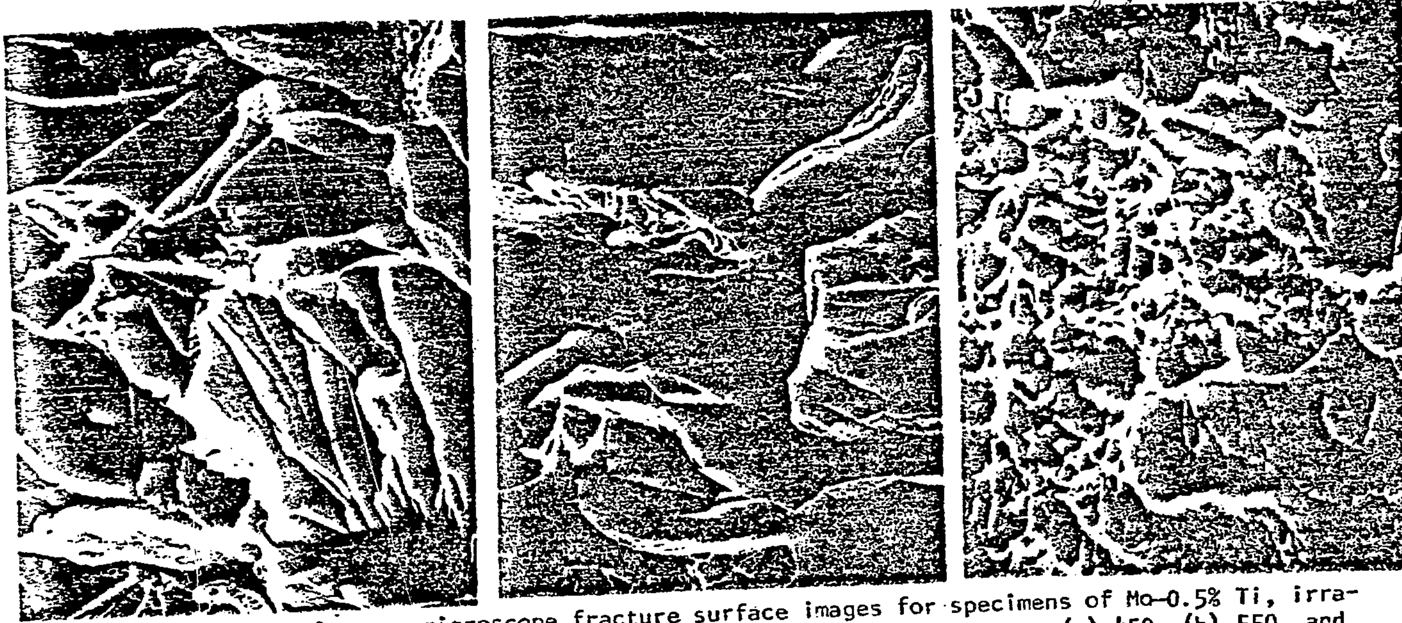

Fig. 3. Scanning electron microscope fracture surface images for specimens of Mo–0.5% Ti, irradiated to 2.5×10^{26} n/m^2 (>0.1 MeV) at 585°C and bend tested to failure at (a) 450, (b) 550, and (c) 650°C. 1000×. — (in final) ... (Note)

FIG 3, 4
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the molybdenum fracture surfaces showed 10 to 20% grain boundary separation; the balance of the area cleavage facets. For the same conditions, Mo—0.5% Ti showed 100% cleavage. In Fig. 5, fracture surfaces for the three alloys irradiated at 790°C and then tested at 200°C are shown. The sample set in Fig. 6 was irradiated at 1000°C and tested at 22°C. In samples irradiated at 585°C, molybdenum tested at 400°C showed ∿22% cleavage facets on the fracture surface, while Mo—0.5% Ti (tested at 450°C) showed ∿47% cleavage facets. The remainder of the exposed area in both samples was grain boundary faces.

In samples where cleavage facets were identified, there was no indication of a unique initiation feature for the failure. Most of the cleavage initiation points were subsurface, not linked by cleavage paths to the tensile stress face of the sample. While these facets indicated a direction of propagation that was approximately across the sample, there was a large variation in local propagation direction.

On the mixed-mode fracture surfaces, cleavage has occurred predominantly through larger than average grains, and grain boundary separation occurred for grains of average or smaller than average size.

4. DISCUSSION

The results show that irradiation temperature has a strong influence on the DBTT of irradiated molybdenum and molybdenum alloys, but that composition (within the range examined) has only a minor effect. For a fixed irradiation temperature, the fracture mode can include a combination of cleavage, grain boundary separation, and ductile dimple fractures. Cleavage is predominant at the lowest temperatues, grain decohesion at the intermediate temperatures, and ductile failure at the highest temperatures.

Fig. 5. The fracture mode below the DBTT depends somewhat on ~~alloys.~~ material composition. For samples irradiated at 790°C and tested at 200°C, Mo (a) shows much more grain boundary separation than does Mo–0.5% Ti (b) or TZM (c). The two alloys show mainly cleavage facets on the fracture surface, with less than 50% area coverage by grain boundaries. 1000× (in final)

(a), (b), (c) & micron marker will be used on final copy.

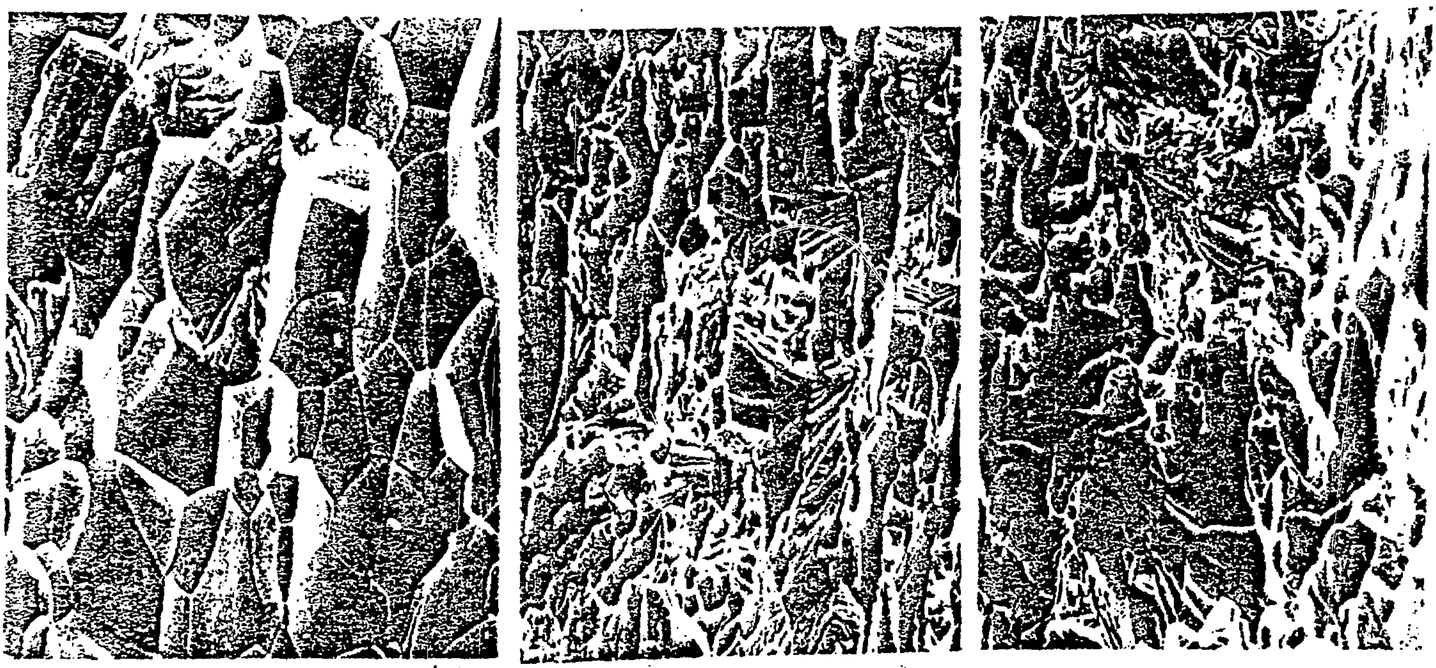

Fig. 6. Fracture surfaces of (a) Mo, (b) Mo–0.5% Ti, and (c) TZM, bend tested at 22°C after irradiation at 1000°C. 300×

The criterion used to define brittle failure in this work is far less restrictive than in many other investigations. In this work, a test that resulted in a crack, but with some ductile failure at the tensile face of the fracture, was defined as being above the DBTT. In contrast, Webster et al. [5] defined specimen fracture in a tensile test with less than 50% reduction in area as brittle behavior. This type of difference in definition of "brittle fracture," and the many other experimental differences, makes comparison of the present results with the few available published results difficult.

Results for the two lowest irradiation temperatures indicate a very strong irradiation temperature dependence of the DBTT in this range, with 425°C irradiation having produced a DBTT in the range of 50 to 200°C, but 585°C irradiation shifting the DBTT to above 550°C. Tensile tests on rod specimens from this same irradiation experiment showed that for a strain rate of $3 \times 10^{-4}\ s^{-1}$, irradiation at ∿450°C resulted in a DBTT between 550 and 650°C [2]. Since the two test types are quite different, this result is within the range defined in the current experiments, and also suggests that the dependence on irradiation temperature may be strongest in the 400 to 500°C range. Only two rod specimens of molybdenum from the earlier experiment had been irradiated at a higher temperature. These samples were irradiated at about 1000°C; the two tensile tests showed the DBTT to be above 22°C but below 400°C, which is also consistent with the current results.

Webster et al., [5] tensile tested samples of irradiated Mo and TZM at room temperature and at the irradiation temperature, for irradiation temperatures of 465 to 680°C. They reported brittle failures for all tests at room temperatures, with elongation less than 0.4% in all cases and not measurable in most cases. They inferred DBTTs in the range of 450 to 720°C for various test and material conditions. The current results are in approximate agreement with these results, but detailed comparison is not possible because of the differences in definition of DBTT, and because Webster et al. conducted tests only at the irradiation temperature. The Webster et al. irradiations were also for fluences well below those achieved in the current experiment.

All of the specimens in this experiment had a fully recrystallized microstructure before irradiation. This undoubtedly had a major influence on the high amount of grain boundary separation in many of the brittle failures, but probably is not a determining factor between ductile or brittle behavior. Since there was an appreciable fraction of cleavage fracture, even in failures that were mainly by grain separation, it appears that strengthening or elimination of grain boundaries could have raised the fracture stress in a given test, but would not have restored ductile fracture. Webster's [5] results indicated a similar effect. Recrystallized Mo and TZM failed by intergranular separation but cold worked or stress relieved specimens failed in a transgranular cleavage mode. The DBTT appeared to be relatively insensitive to fracture mode for these two brittle modes.

The effect of test temperature on the fracture mode suggests that while the cleavage stress is relatively temperature independent, the grain boundary decohesion stress decreases with increasing temperature, and drops below the cleavage stress over the testing range. The three fracture modes can be understood in terms of the modified Ludwig-Davidenkov diagram shown schematically in Fig. 7. At the lowest temperatures the cleavage stress is the lower of the three stresses shown, and cleavage

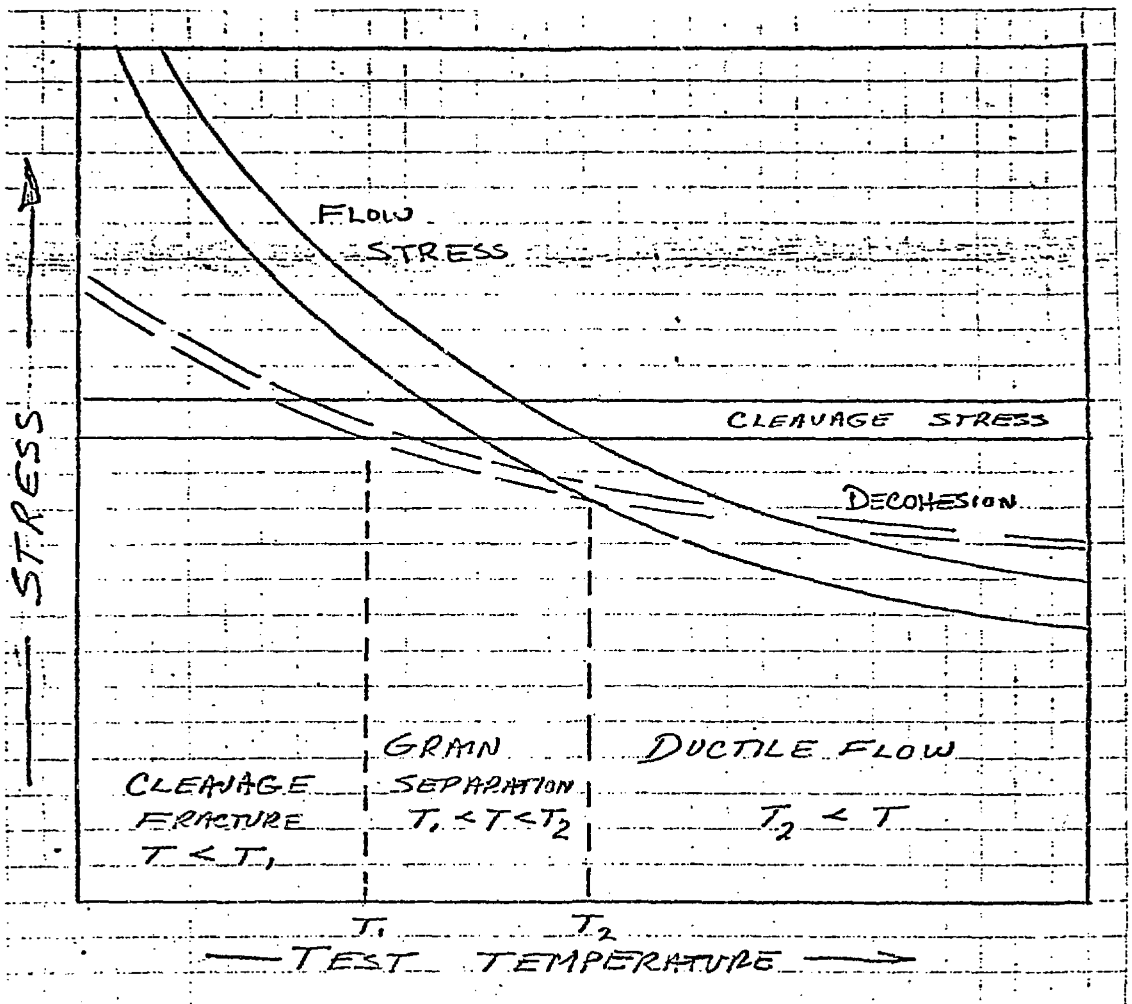

Fig. 7. A schematic Ludwig-Davidenkov diagram, with grain boundary decohesion stress added. The test temperature T_2 is the DBTT, T_1 is the boundary between cleavage and decohesion failure modes.

is the predominant failure mode. At increasingly higher test temperatures, the grain boundary decohesion stress drops below the cleavage stress and failure is initiated by the separation of the most highly stressed grain boundaries. The fracture progresses through connected separation of grain boundaries appropriately oriented, with cleavage failures through some grains to connect the opening boundaries. At still higher test temperatures the flow stress is lower than either of the brittle failure mode stresses and the sample deforms. The deforming sample may then either work harden to the cleavage stress, and brittle fracture will occur, or it may deform to produce fully ductile failure.

The cleavage stress of molybdenum and molybdenum alloys is little affected by irradiation [2]. The decohesion strength is assumed to be only weakly temperature dependent, is probably raised by alloying, and may be sensitive to irradiation. The flow stress is markedly increased by irradiation.

The effect of irradiation temperature on the DBTT is thus achieved through the effectiveness of the matrix hardening produced at each temperature. Hence raising the flow stress shifts the intersection with the brittle fracture stresses to higher temperatures, thus raising the DBTT (Fig. 7). The DBTT shifts measured in these experiments can only be qualitatively related to the previously reported microstructural features in these same samples. The highest void concentration was found after the irradiation at 585°C [4] with void concentrations decreasing in the order 425, 790, and 1000°C. The highest DBTT corresponds to the highest void density, but the other DBTT results do not correlate with observed void concentrations. The dominant microstructural feature after irradiation at 425°C was the very high concentration of small dislocation loops. The susceptibility of this microstructure to deformation by channeling, with high local ductility [2], is probably related to the lower DBTT after 425°C irradiation than after 585°C irradiation, where void hardening predominates. Void concentration differences among the three materials at any one irradiation temperature also do not correlate with the DBTT results. The other microstructural components that strengthen the matrix are dislocation loops and dislocation networks. These microstructural features were only described qualitatively. The dislocation density decreased with increasing irradiation temperature, and was higher in the two alloys than in the molybdenum. Loop concentrations after 425 and 585°C irradiation were too high to measure, and would be expected to provide the major part of the strengthening.

The differences in fracture mode between the Mo and the two alloys suggests that alloying has raised the decohesion strength, relative to that of unalloyed Mo. The cleavage stress in Mo and Mo-0.5% Ti was previously found to be almost identical, and essentially independent of temperature [2].

5. SUMMARY

Irradiation of Mo, Mo-0.5% Ti and TZM at temperatures from 425 to 1000°C, to fluences producing 11 dpa, resulted in DBTTs in bending of 100 to 700°C. All irradiation temperatures resulted in DBTTs above room temperature, but the exact level of the DBTT was a strong function of the irradiation temperature. The most severe embrittlement was produced by irradiation at 585°C, resulting in a DBTT between 550 and 700°C. Alloying at the concentrations in the two alloys tested had a relatively minor effect on the DBTT. For the two most embrittling irradiations, at 585 and 790°C, the alloys had lower DBTTs than did the unalloyed molybdenum. This may be related to the effect of the alloying on raising grain boundary decohesion stress. The DBTT shift with irradiation temperature could not be quantitatively related to the observed microstructures.

The increase in DBTT to above room temperature for all irradiation temperatures investigated suggests that molybdenum alloy structures in a fusion reactor could not survive a reactor shutdown. Unless molybdenum alloys more resistant to irradiation embrittlement could be developed, it is unlikely that they could be used for a fusion reactor first wall, or for any structural components in the high flux regions of the reactor.

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