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Effects of neutron irradiation on microstructure and deformation behaviour of mono- and polycrystalline molybdenum and its alloys

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Abstract

The influence of neutron irradiation on microstructural evolution and mechanical properties of mono- and polycrystalline molybdenum and its alloys has been investigated. Tensile specimens and 3 mm diameter discs of monocrystals of pure molybdenum and Mo–5%Re were irradiated with fission neutrons at ~320 K to displacement doses in the range 5.4×10^{-4} to 1.6×10^{-1} dpa (NRT) in the DR-3 reactor at Risø National Laboratory. For comparison, polycrystalline specimens of Mo–5% Re and TZM were also irradiated together with the monocrystalline specimens. Both unirradiated and irradiated specimens were tensile tested at 295 K. Post-irradiation microstructures were quantitatively characterized using a transmission electron microscope (TEM). Fracture surfaces were examined in a scanning electron microscope (SEM). The results of tensile testing as well as of transmission and scanning microscopy are presented and discussed in terms of intracascade clustering of self-interstitial atoms and the role of one-dimensional glide of these clusters in controlling microstructural evolution and the resulting mechanical properties. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Traditionally, molybdenum alloys (e.g. TZM and Mo–Re) have been considered as potentially useful structural materials for components subjected to high neutron (and heat) fluxes [1]. The attractive properties of these alloys relate to their high strength, good thermal conductivity and resistance to void swelling. However, Mo alloys are sensitive to irradiation induced embrittlement [2].

Commonly, the problem of embrittlement has been investigated after irradiation at relatively high temperatures [2–4]. In recent years, however, results have been reported on the deformation behaviour of these alloys irradiated at lower temperatures with fission neutrons [5,6] and 600 MeV protons [7,8]. These investigations have demonstrated that the ability of Mo, TZM and Mo–5%Re to deform plastically in a homogeneous fashion is seriously impaired by irradiation with fission neutrons and 600 MeV protons at temperatures in the range of ∼300–600 K. Furthermore, this impairment occurs after irradiation to dose levels of even less than 0.1 dpa.

The analysis of the tensile results, pre- and post-deformation microstructures and fracture surfaces of the irradiated samples have revealed the following important features [6]: (a) the lack of homogeneous deformation and the initiation of plastic instability (i.e. necking) which seems to be related to the formation of cleared channels, (b) the increase in the yield stress due to irradiation which appears to be related to difficulty in dislocation generation rather than dislocation motion and (c) the drastic decrease in the uniform elongation (i.e. ductility) which seems to be caused not by grain boundary embrittlement but by grain boundary sliding and separation.

To clarify whether grain boundaries play a significant role in the irradiation induced reduction in the ductility

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of these alloys, it was decided to investigate the effect of neutron irradiation on the deformation behaviour of Mo and Mo–5%Re alloy in the monocrystalline state. The present paper describes and discusses these results.

2. Materials and experimental procedure

Molybdenum and two molybdenum alloys (i.e. TZM and Mo–5%Re) were studied. Monocrystals of 99.999% pure Mo were grown with (1 1 1) axis orientation. The monocrystal of Mo–5%Re was prepared from nominally 99.99% pure Mo and Re also with (1 1 1) axis orientation. From these monocrystals, tensile specimens and 3 mm discs with ⟨1 1 0⟩ surfaces were sliced using the spark erosion technique.

The two polycrystalline molybdenum alloys were TZM and Mo–5%Re (hereafter referred to as MoRe) supplied as hot-rolled 0.3 mm thick sheet by Metallwerk Plansee, Austria. Compositions, in wt% were, TZM; Ti 0.55, Zr 0.12, Fe 0.01, W 0.03, O 0.03, N 0.002, C 0.04. bal. Mo and MoRe; Re 5±0.5, Fe 0.01, W 0.03, O 0.005, N 0.001 C 0.003, bal. Mo. Tensile specimens were machined from the as-supplied sheet and then mechanically polished to remove as-fabricated surface layers (~10 μm) prior to irradiation and tensile testing. Optical microscopy showed the average grain size in the TZM and MoRe samples to be ~24 and ~21 μm, respectively.

Tensile specimens and 3 mm diameter discs of mono- and polycrystalline Mo and Mo-alloys were irradiated in helium-filled capsules with fission neutrons in the DR-3 reactor at Risø National Laboratory. Irradiations were carried out at ~320 K to neutron fluences of 5×10^{21} to 1.5×10^{24} n/m^2 ($E > 1$ MeV) (corresponding to displacement damage levels of 5.4×10^{-4} to 1.6×10^{-1} dpa (NRT)). The neutron flux was ~2.5×10^{17} n/m^{2}s ($E > 1$ MeV) corresponding to a damage rate of 2.7×10^{-8} dpa/s.

Both unirradiated and irradiated specimens were tensile tested at 295 K in an Instron machine at a strain rate of 1.2×10^{-3} s^{-1}. For electron microscopy investigations, 3 mm diameter discs were electropolished at 20 V in 20% perchloric acid in methanol at ambient temperature. Thin foils were examined in a 200 keV JEOL 2000FX transmission electron microscope (TEM). To examine the deformed microstructures, TEM samples were taken from the zones as close as possible to the tensile fracture surfaces. Fracture surfaces were examined in a scanning electron microscope (SEM).

3. Experimental results

3.1. Irradiation-induced microstructural evolution

Thin foils of monocrystalline Mo and MoRe and polycrystalline MoRe and TZM irradiated at different doses at ~320 K were examined for the irradiation-induced accumulation and evolution of defect microstructures. TEM examinations showed high densities of small defect clusters and loops in all irradiated specimens. The dislocation line density in all cases was found to be very low.

The variation of cluster/loop density with irradiation dose for all materials investigated is presented in Fig. 1. The loop densities and sizes for all the specimens investigated in the present work are summarized in Table 1.

The main features of the microstructural evolution presented in Table 1 may be summarized as follows:

(i) Clusters/loops in the monocrystalline Mo coarsen rapidly with increasing dose and begin to form rafts of loops already at a dose level of 5.4×10^{-3} dpa. This leads to a marked segregation of the microstructure into rafts of loops and isolated loops. Consequently, the microstructure becomes very heterogeneous at a dose level of 0.16 dpa. The loop density in the monocrystalline Mo first increases with dose, reaches a maximum at 5.4×10^{-3} dpa and then begins to decrease with dose. The cluster/loop size, on the other hand, does not change with dose. The density of rafts reaches a maximum at 5.4×10^{-2} dpa and then begins to decrease (Fig. 1, Table 1). The raft length, on the other hand, increases with dose.

(ii) In contrast to the observation in monocrystalline Mo, the loop coarsening in the monocrystalline MoRe is very slow and there is no indication of segregation of loops in the form of rafts. The loop density is substantially higher in the monocrystalline MoRe than in pure Mo at all doses (Fig. 1)

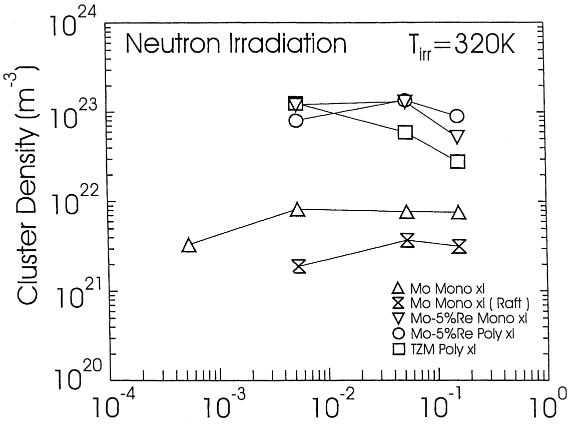


Fig. 1. Cluster density as a function of displacement dose for monocrystalline Mo and Mo–5% Re and polycrystalline Mo–5% Re and TZM, irradiated at 320 K. Variation of the density of rafts in monocrystalline Mo is also shown.

Table 1
Loop and raft densities and sizes in neutron irradiated mono- and polycrystalline Mo and Mo-alloys at 320 K

Materials	Neutron fluence (n/m^2 (E > 1 MeV)	Dose (NRT dpa)	Loop density (10^{22} m^{-3})	Loop size (nm)	Raft density (10^{22} m^{-3})	Raft length (nm)
Mo (Monocrystal)	5×10^{21}	5.4×10^{-4}	0.33	4.5	–	–
	5×10^{22}	5.4×10^{-3}	0.82	4.6	0.19	24.2
	5×10^{23}	5.4×10^{-2}	0.77	4.7	0.37	40.9
	1.5×10^{24}	1.6×10^{-1}	0.76	4.1	0.32	46.1
Mo–5% Re (Monocrystal)	5×10^{22}	5.4×10^{-3}	12.0	1.3	–	–
	5×10^{23}	5.4×10^{-2}	13.1	3.0	–	–
	1.5×10^{24}	1.6×10^{-1}	5.2	5.6	–	–
Mo–5% Re (Polycrystal)	5×10^{22}	5.4×10^{-3}	8.0	1.3	–	–
	5×10^{23}	5.4×10^{-2}	13.6	2.3	–	–
	1.5×10^{24}	1.6×10^{-1}	9.0	4.3	–	–
TZM (Polycrystal)	5×10^{22}	5.4×10^{-3}	12.6	1.7	–	–
	5×10^{23}	5.4×10^{-2}	5.9	4.6	–	–
	1.5×10^{24}	1.6×10^{-1}	2.8	4.7	0.64	25.0

and decreases with dose beyond 5.4×10^{-2} dpa. It is interesting to note here that the average loop size at 0.16 dpa is larger in MoRe than that in the pure Mo monocrystal (Table 1).

(iii) The loop density in the polycrystalline TZM at 5.4×10^{-3} dpa is similar to that in MoRe (both mono- and polycrystalline) but almost an order of magnitude higher than that in the monocrystalline Mo. As in the case of monocrystalline Mo, the loop density in TZM decreases with dose starting already from the dose level of 5.4×10^{-3} dpa. Furthermore, a relatively high density of rafts is formed in TZM at 0.16 dpa; the raft density is higher and the size smaller than that in monocrystalline Mo at the same dose level (Table 1).

(iv) It is interesting to note that irrespective of loop density, the loop size at 0.16 dpa is found to be very similar in all of the materials in the present work (Table 1).

3.2. Pre- and post-irradiation tensile properties

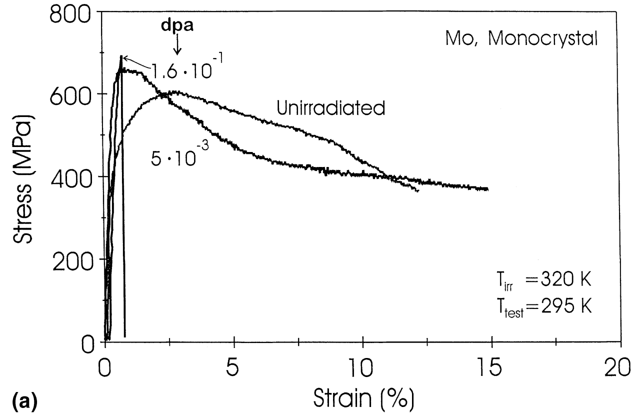
First of all, it should be mentioned that because of the lack of irradiation space, tensile specimens of only monocrystalline Mo and MoRe were irradiated at different doses; polycrystalline specimens were irradiated at only one dose (i.e. at 0.16 dpa).

The results of tensile tests on the unirradiated and irradiated specimens are shown as stress–strain curves in Figs. 2–4 and tensile data is summarized in Table 2.

The results show that yield stress increases due to irradiation as expected. For monocrystalline MoRe, the increase is clear even at the low dose of 5×10^{-4} dpa (Fig. 3). Interestingly, defect clusters could not be resolved at this dose in the monocrystalline MoRe alloy; defect clusters were not visible until the dose level of 5×10^{-3} dpa (Fig. 1, Table 1). The results on the monocrystals of pure Mo and MoRe also show that the uniform elongation is reduced due to irradiation and that already at 5×10^{-2} dpa, monocrystalline MoRe suffers from plastic instability (i.e. lack of work hardening and onset of localized plastic deformation). In the case of monocrystalline pure Mo irradiated to a dose of 0.16 dpa no plasticity is observed and the specimen fails in a brittle manner (Fig. 2(a)). Fig. 2(b) shows plastic instability in polycrystalline Mo after irradiation with 600 MeV protons to a dose level of 6×10^{-2} dpa. Similar behaviour is observed in neutron irradiated polycrystalline MoRe alloy (Fig. 4).

3.3. Post-deformation microstructure

In order to gain further insight into the deformation processes operating during tensile testing of the irradiated monocrystals of Mo and MoRe, post-deformation microstructures were investigated by TEM. Fig. 5 shows typical examples of the observed microstructures in the deformed monocrystal of Mo irradiated to dose levels of (a) 5.4×10^{-3} dpa (NRT) and (b) 1.6×10^{-1} dpa (NRT) at 320 K and tested at 295 K. It can be seen in Fig. 5(a) that even at this low dose the microstructure is dominated by "cleared" channels. Only a few dislocation segments can be seen, suggesting that most of the plastic deformation has occurred in a localized and inhomogeneous fashion and concentrated in the cleared channels. It should be noted that the presence of rafts of loops across the cleared channels provides the interaction sites for the gliding dislocations in the channels (channel B, Fig. 5(a)). However, it seems as if the gliding dislocations in the channels eventually succeed in destroying the raft and forming dislocation free clear channels (channels A, C, Fig. 5(a)). Also, there is no indication of dislocation multiplication in the volumes between the rafts or between the cleared channels.



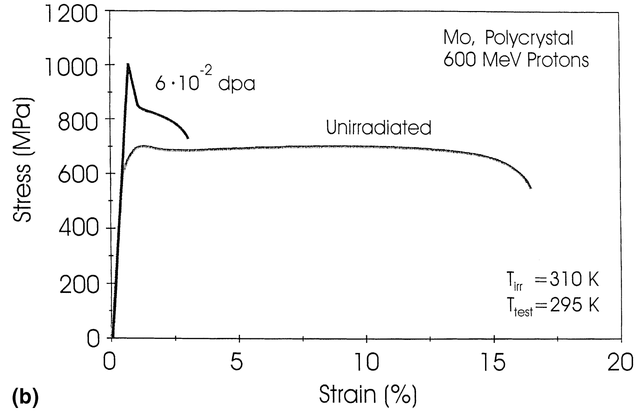


Fig. 2. (a) Stress–strain curves for the unirradiated and irradiated monocrystals of Mo irradiated at 320 K and tensile tested at 295 K. (b) Stress–strain curves for the unirradiated and irradiated polycrystals of Mo irradiated with 600 MeV protons at 310 K and tested at 295 K.

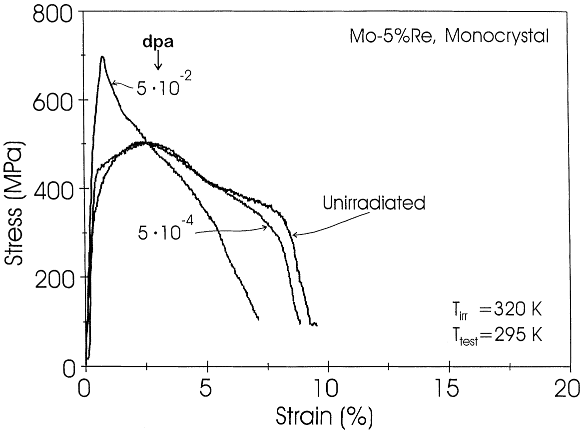


Fig. 3. Stress–strain curves for the unirradiated and irradiated monocrystals of Mo–5% Re irradiated at 320 K and tensile tested at 295 K.

Fig. 5(b) shows the post-deformation microstructure of the Mo monocrystal irradiated to a dose level of 1.6×10^{-1} dpa (NRT) at 320 K and tested at 295 K. The microstructure is practically identical to that observed in the as-irradiated crystal (i.e. without any deformation). The microstructure shown in Fig. 5(b) clearly

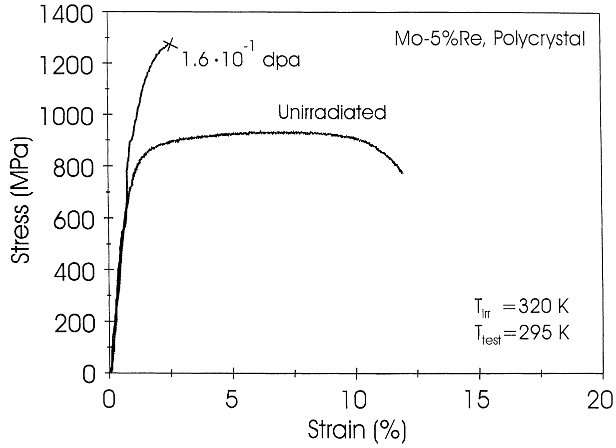


Fig. 4. Stress–strain curves for the unirradiated and irradiated polycrystals of Mo–5%Re irradiated at 320 K and tested at 295 K.

demonstrates that even at a stress of ~700 MPa practically no dislocations are generated during the tensile test. By contrast, the unirradiated monocrystal of Mo begins to deform plastically already at a stress level of ~400 MPa.

SEM of the fracture surfaces of the irradiated Mo monocrystals showed that the specimen irradiated to the low dose of 5.4×10^{-3} dpa (NRT) failed in a ductile manner, whereas the specimen irradiated to 1.6×10^{-1} dpa (NRT) failed in a very brittle manner, showing clean cleavage (Fig. 6(a)). The low dose (5.4×10^{-4} dpa (NRT)) specimen of MoRe monocrystal showed ductile failure with macroscopic shear fracture and facet formation. The failure mode of the MoRe monocrystal irradiated to the dose level of 5.4×10^{-2} dpa (NRT) was, on the other hand, completely brittle (Fig. 6(b)).

4. Discussion

The present results on the dose dependence of the microstructural evolution in monocrystalline pure Mo and MoRe alloy reveal two interesting features: (a) A rapid coarsening and segregation of loops in the form of rafts of loops in Mo starting already at a relatively low dose level of 5.4×10^{-3} dpa; (b) Substantially higher loop density in MoRe than in Mo and the lack of formation of rafts of loops in MoRe.

The rapid coarsening of loops and the formation of rafts of loops in the monocrystalline Mo clearly show that the diffusional glide of small SIA clusters produced in the cascade must be very efficient in this material. Once the rafts are formed a fraction of the loops generated subsequently in the cascades will rapidly glide to the existing rafts. This would lead to a low density of loops in the volume between the rafts and growth of the existing rafts, as found in the present experiments (Fig. 1, Table 1).

The phenomenon of raft formation by gliding loops was treated by Brimhall and Mastel [9] already some years ago. However, their treatment was limited to higher temperatures where both prismatic glide and conservative climb were considered to contribute to raft formation. Brimhall and Mastel [9] assumed that prismatic gliding of loops did not occur at 323 K. Recent molecular dynamic simulations, however, have demonstrated that

Table 2
Yield strength ($\sigma_{0.2}$), ultimate strength (σ_{max}), uniform plastic strain (ε_u^p) and total elongation (ε_t) for mono- and polycrystals of Mo and Mo–5% Re in unirradiated and irradiated (at 320 K) states and tensile tested at 295 K

Material	Dose (dpa)	$\sigma_{0.2}$ (MPa)	σ_{max} (MPa)	ε_u^p (%)	ε_t (%)
Mo (M)	0	430	610	2.5	12
Mo (M)	5.4×10^{-3}	650	655	1.1	15
Mo (M)	1.6×10^{-1}	–	690	0.1	0.6
Mo–5%Re (M)	0	375	500	2.5	9.0
Mo–5%Re (M)	5.4×10^{-4}	445	502	2.5	8.5
Mo–5%Re (M)	5.4×10^{-2}	625	700	0.3	7.0
Mo–5%Re (P)	0	820	925	7.0	11.7
Mo–5%Re (P)	1.6×10^{-1}	1050	1275	1.3	2.5

M – Monocrystal, P – Polycrystal.

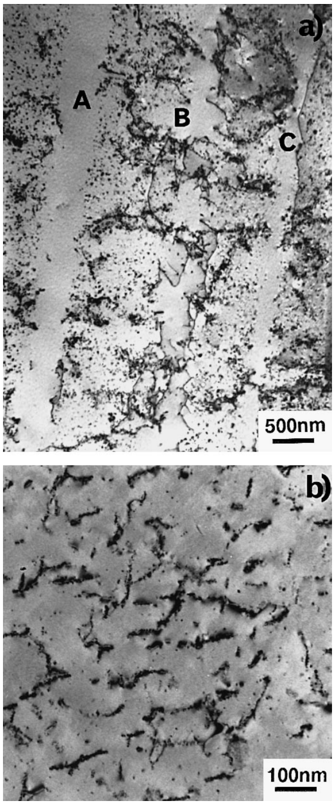


Fig. 5. Post-deformation microstructure of monocrystalline Mo irradiated at 320 K to (a) 5.4×10^{-3} dpa (NRT) and (b) 1.6×10^{-1} dpa (NRT).

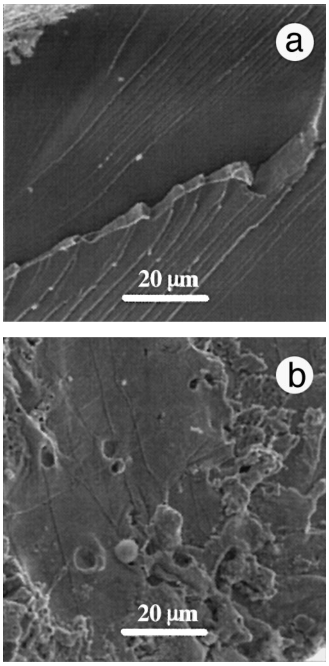


Fig. 6. SEM fractographs of fracture surfaces of monocrystals of (a) Mo irradiated at 320 K and tensile tested at 295 K to a dose of 1.6×10^{-1} dpa (NRT) and (b) Mo–5% Re irradiated at 320 K and tensile tested at 295 K to dose levels of 5.4×10^{-2} dpa (NRT).

small SIA loops glide rapidly via correlated diffusion of SIAs in the cluster/loops [10]. The SIAs in these clusters act like a bunch of coupled crowdions. Recently, Trinkaus et al. [11] have shown that it is indeed one-dimensional glide of SIA clusters which is responsible for the decoration of dislocations by SIA loops.

The second feature showing the lack of raft formation and the high density of loops in both mono- and polycrystalline MoRe indicates that the presence of impurity atoms may play a role in reducing the mean free path of the one-dimensional glide of SIA clusters. It seems quite plausible that impurity atoms having some degree of binding with the SIAs would interfere with the correlated motion of SIA clusters responsible for the one-dimensional glide. That the rafts are formed in the less impure TZM (compared to MoRe) and that raft density is higher and length shorter than in pure monocrystalline Mo, lends qualitative support to the above argument.

Finally, it should be pointed out that the present results help confirm the phenomenon of one-dimensional glide of SIA clusters/loops under cascade damage conditions. This implies that any realistic theoretical treatment aimed at describing the defect accumulation under cascade damage conditions must specifically consider the consequences of one-dimensional glide on damage accumulation and hence the physical and mechanical properties of materials under irradiation.

The tensile results confirm the traditional effects of irradiation on hardening and ductility. The irradiation-induced increase in the yield stress in the monocrystalline Mo, for example, becomes clearly noticeable already at a displacement dose level of 5×10^{-3} dpa. In the case of monocrystalline MoRe, the increase in the yield stress can be seen at a dose level as low as 5×10^{-4} dpa even though the defect clusters responsible are too small to be resolved in the TEM.

Another characteristic effect of irradiation on deformation behaviour of metals and alloys is the known phenomenon of yield drop. The yield drop is caused by a sudden release of a large number of dislocations. Such a release in a heterogeneous fashion would localize the subsequent deformation and would lead to plastic instability, necking and early fracture (see [12] for a recent review). It has been shown earlier that polycrystalline Mo, TZM and MoRe irradiated at relatively low temperatures do exhibit yield drop and lack of uniform elongation (i.e. ductility) in the post-irradiation tensile tests [5–8].

The irradiation-induced reduction in ductility has been interpreted as arising either from grain boundary embrittlement by segregated impurity atoms (e.g. [2]) or as a result of grain interiors being unable to deform plastically in a homogeneous fashion [6]. In the latter interpretation it has been argued that while the yield strength of the grain interiors remains high due to source hardening (difficulties in dislocation generation), the localized nature of deformation may initiate fracture process at the relatively weak grain boundaries causing grain boundary sliding and separation [6].

The question then arises as to how the irradiated materials would deform and fracture in the absence of grain boundaries? The tensile results clearly show that the neutron irradiated monocrystalline Mo as well as MoRe deform practically in the same way as the polycrystalline Mo and MoRe. Thus, the presence or absence of grain boundaries does not seem to affect the reduction in ductility due to irradiation.

In fact, the most crucial information which may help understand the problem of irradiation-induced embrittlement at temperatures below the recovery stage V emerges from the post-deformation investigations of the microstructure and examination of the fracture surfaces. These investigations have firmly established two very important features: (a) the localization of plastic deformation in the cleared channels and (b) a complete lack of global dislocation generation in a homogeneous fashion even at very high stress levels. These observations are not limited only to the present investigation. Similar observations have been reported for copper [13,14] TZM and MoRe [6] and pure iron [15]. The localization of plasticity leads to plastic instability and necking during deformation, but does not necessarily cause brittle fracture. It has been shown, however, that in the case when the cleared channels begin to intersect and there is no global dislocation generation, then the fracture surfaces show that failure has occurred in a brittle manner [15].

However, when all dislocation sources are blocked and there is no global dislocation generation, crack nucleation is no longer determined by plastic deformation. Under these conditions, the crack nucleation can only occur at internal or surface flaws in the material. Once nucleated, the crack will propagate very rapidly through the material without much hindrance since the material is unable to generate dislocations (i.e. to deform plastically) at the crack tip. This implies that the irradiation induced loss of ductility and embrittlement at low irradiation temperatures is likely to depend on the presence of flaws. The present observations in the neutron irradiated mono- and polycrystalline Mo and MoRe are consistent with the above argument.

5. Conclusions

The results of the present investigations lead to the following main conclusions:

(a) The generation of glissile SIA clusters in displacement cascades plays a decisive role in the evolution of the irradiation-induced microstructure (e.g. density, size and distribution of clusters/loops and rafts). The presence of impurity atoms or alloying elements may affect the glide process and the microstructural evolution.

(b) The one-dimensional glide of SIA clusters causes decoration of dislocations by SIA clusters/loops and the formation of rafts. This leads to locking of dislocation sources and localization of plastic deformation in the form of cleared channels.

(c) The localization of the plastic deformation in the form of cleared channels gives rise to plastic instability, reduction in ductility and brittle fracture.

(d) When all dislocation sources are locked by the irradiation-induced SIA clusters/loops, the crack nucleation is no longer caused by plastic flow but must initiate at internal or external flaws in the material. Once nucleated, the crack is likely to propagate rapidly through the irradiated material since the material is unable to deform plastically.

Acknowledgements

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References

[1] V.V. Rybin, D.L. Smith, J. Nucl. Mater. 191–194 (1992) 30.
[2] I.V. Gorynin, V.A. Ignatov, V.V. Rybin, S.A. Fabritsiev, V.A. Kazakov, V.P. Chakin, V.A. Tsykanov, V.R. Barabash, Y.G. Prokofyev, J. Nucl. Mater. 191–194 (1992) 42.
[3] K. Abe, M. Kikuchi, K. Tate, S. Morizume, J. Nucl. Mater. 122/123 (1984) 671.
[4] Y. Hiraoka, M. Okada, H. Irie, J. Nucl. Mater. 155–157 (1988) 381.
[5] B.N. Singh, A. Horsewell, P. Toft, J.H. Evans, J. Nucl. Mater. 212–215 (1994) 1292.
[6] B.N. Singh, J.H. Evans, A. Horsewell, P. Toft, D.J. Edwards, J. Nucl. Mater. 223 (1995) 95.
[7] G.V. Müller, D. Gavillet, M. Victoria, J.-L. Martin, J. Nucl. Mater. 212–215 (1994).
[8] G.V. Müller, Ph.D. Thesis, EPFL Lausanne, Switzerland, 1997.
[9] J.L. Brimhall, B. Mastel, Radiat. Eff. 3 (1970) 203.

[10] A.J.E. Foreman, C.A. English, W.J. Phythian, Philos. Mag. A 66 (1992) 655.
[11] H. Trinkaus, B.N. Singh, A.J.E. Foreman, J. Nucl. Mater. 249 (1997) 91.
[12] B.N. Singh, A.J.E. Foreman, H. Trinkaus, J. Nucl. Mater. 249 (1997) 103.
[13] Y. Dai, Ph.D. Thesis, EPFL, Lausanne, Switzerland, 1995.
[14] B.N. Singh, D.J. Edwards, P. Toft, J. Nucl. Mater. 238 (1996) 244.
[15] B.N. Singh, A. Horsewell, P. Toft, presented at 8th Int. Conf. on Fusion Reactor Materials, Sendai, Japan, 1997.