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ANNEALING BEHAVIOR OF RADIATION HARDENING IN MOLYBDENUM NEUTRON IRRADIATED AT 600℃

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The tensile properties at room temperature in molybdenum irradiated to a fast neutron fluence of 8.0×10^{19} n/cm^2 at 600°C were investigated in terms of changes in microstructure with the irradiation and subsequent heat treatment. The irradiation produced large dislocation loops and small defect clusters, which caused the hardening of about 4 kg/mm^2. Upon post-irradiation annealing for 1 h at 800°C, the hardening increased to 18 kg/mm^2, which resulted from formation of small voids with the density of 3×10^{16} /cm^3. As the annealing temperature was raised above 800°C, the yield stress decreased gradually with decrease in the void number density. On annealing for 1 h at 1200°C, the hardening recovered to the as-irradiated level; the void number density was 3×10^{13} /cm^3. The defect structure after annealing at a temperature of 800 1000°C consisted of coarsely distributed dislocation loops and rather inhomogeneously distributed voids.

高温照射したモリブデンの引張性質の回復挙動

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モリブデンの室温における引張性質が約600℃，高速中性子量 8.0×10^{19} n/cm² の照射および照射後の熱処理によって変化する様子を電子顕微鏡組織と関連させて調べた。中性子照射によって約4 Kg/mm² の硬化が起るが，これは照射中に比較的大きな転位ループと小さな照射欠陥集合体が生成することによる。照射した試料を800℃で1時間熱処理すると硬化量はさらに増化し18Kg/mm² となる。この硬化は熱処理中に 3×10^{16}/cm³ の密度で小さなボイドが生じることによるものである。熱処理の温度を上げるとボトドの密度は減少し，1200℃，1時間の熱処理後には 3×10^{13}/cm³になる。この熱処理によって降伏強さは照射したままの試料とほぼ同程度の大きさまで回復する。照射後800～1100℃の温度範囲で熱処理した試料には比較的大きな転位ループとやや不均一な分布をしたボイドが観られる。

目 次 な し

1. Introduction

Molybdenum is considered as a candidate material for the first wall in fusion reactor designs. In such application, the material is subject to exposure to high energy neutrons at high temperature. This has stimulated to study of the effect of radiation induced defect clusters on the mechanical properties of molybdenum.

The microstructure change in molybdenum with neutron irradiation at elevated temperatures has been studied by a number of investigators. The results have been reviewed by Eyre (1): Irradiation below 450°C results in the formation of a fine distribution of vacancy loops as well as coarsely-distributed interstitial loops and the distribution is influenced by impurities. For irradiation temperature above 450°C and below 1000°C, the damage structure consists of a coarsely distributed interstitial component plus a much finer distribution of voids. The voids tend to arrange themselves into a three-dimensional array possessing bcc symmetry in specimens following irradiation to total doses in excess of 10^{22} n/cm^2. More recently, investigations of the effect of neutron irradiation on the microstructure in molybdenum have been reported with particular emphasis placed on void formation (2-5).

In contrast with the microstructure study, a few data are available for mechanical properties of molybdenum irradiated at elevated temperature (6-8). In addition, studies on radiation anneal hardening (9,10) and deformation characteristics (11) have been made with reactor ambient temperature irradiated samples. The effects of neutron irradiation on mechanical properties of molybdenum have been little understood, especially in relation to the microstructure.

The present paper describes hardening upon post-irradiation annealing of molybdenum neutron irradiated at about 600°C and discusses the hardening in terms of microstructure.

2. Experimental procedure

The material used in this study was nominally 99.95% pure molybdenum in the form of 0.25 mm thick sheet obtained from Materials Research Corporation (MRC). The chemical impurities in the molybdenum are according to the manufacturer; 30 wt ppm oxygen, 25 wt ppm carbon, 20 wt ppm silicon and 30 wt ppm iron. Prior to neutron irradiation, specimens for tensile tests (5 mm wide and 28 mm gauge length) and for electron microscopy were annealed for 1 h at 1400°C in a vacuum better than 2×10^{-7} torr. After the heat treatment the tensile specimen had an average grain diameter of 64 μm with pronounced [100] or [111] textures. The tensile and electron microscopy specimens were irradiated in an in-core position of the JRR-2 reactor at Tokai-mura to a fast neutron fluence of 8.0×10^{19} n/cm^2 (En $\geq$ 1 MeV) at an average temperature of 600°C in the range 560~640°C. The specimens were placed in a helium-filled stainless steel capsule in such a way that all the specimens were in direct thermal contact with the capsule wall. Irradiation temperature was maintained by gamma heating and an air gap between the capsule and outer aluminum envelope. The temperature was measured with a thermocouple located at the center of the stainless steel capsule. Post-irradiation annealing was carried out for 1 h at temperature ranging from 700 to 1200°C in the vacuum.

Tensile tests were performed at room temperature with an Instron tensile-testing machine at a strain rate of 2.8×10^{-4} /sec, The yield stress was evaluated at the upper yield point or at the maximum stress around yielding determined from the tensile load-elongation curves. When no yield point was apparent, the stress at 0.2% plastic strain was used in order to determine the yield stress.

Thin foils for electron microscopy were prepared electrolytically, using solution of 30% H_2SO_4 in methanol at 15°C. In order to observe clearly the damage structures of voids and of dislocation components, the foils at an area of about $0.06 \sim 0.1$ μm and 0.15 μm thick were, respectively, examined a JEM-200A electron microscope operating at 200 kV. The foil thickness was determined by counting the number of equal thickness fringes from the specimen edge or at the grain boundary.

3. Experimental results

The stress-strain curves at room temperature for irradiated and annealed specimens and for an unirradiated specimen are shown in fig. 1. Neutron irradiation causes an increase in the yield stress and a decrease in the elongation. The as-irradiated specimen exhibited two stage work hardening without yield drop; distinct yield drop was present in the unirradiated specimen. The yield stress was further increased upon postirradiation annealing at 800 and 900°C; the stress-strain behavior was characterized by small yield drop and little work hardening. When the irradiated specimens were heated at 1200°C, the yield stress recovered to the as-irradiated condition. The yield stress and total elongation at room temperature are plotted in fig. 2 as a function of neutron irradiation and postirradiation annealing temperature.

As the damage structure, dislocation loops and voids were observed in the irradiated and annealed specimens. The change in dislocation component of the structure with postirradiation annealing temperature is shown in fig. 3. The damage structure in the as-irradiated specimen consists of small dislocation loops surrounded by irregular shaped large loops (fig. 3a). The small loops becomes larger and decrease in number density with increasing annealing temperature; the irregular shaped loops revert to hexagonal in shape and develop to be dislocation segements.

Diffraction contrast analysis (12) was carried out to determine the Burgers vectors and the nature of the loops. The resolvable dislocation loops observed in the specimens irradiated and annealed at 700, 900 and 1100°C were prismatic $a/2\langle 111\rangle$ loops. Both interstitial and vacancy type loops were present in the specimen annealed at 700 and 900°C. Interstitial loops were found in all parts of the size spectrum, but all of the analyzed vacancy loops were small. Although only a few loops were analyzed (about 40 loops in a specimen) and the accuracy could not be claimed, ratio of vacancy loops to the analyzed loops were about 20 per cent; all the dislocation loops seen in fig. 3d were identified as interstitial in nature.

Voids appeared upon postirradiation annealing at temperatures of 800 to 1200°C, while the void could not be observed in the as-irradiated specimen. The change in the void component of the microstructure with postirradiation annealing is shown in fig. 4. When the annealing was carried out at lower temperatures (800 and 900°C), small voids of less than 40 Å in diameter were seen in very high density of about 10^{16} voids/cm^3. The voids are not completely homogeneously distributed as seen in the figure. As increase in the annealing temperature, the voids grew larger with decrease in the density; the anneal also increased the size distribution range. The histograms of void number frequency as a function of diameter are shown in fig. 5 for the samples annealed at temperature ranging from 800 to 1200°C. The large voids seen in the specimen annealed at 1200°C appeared to be dodecahedral bounded by $\{110\}$ planes and truncated by $\{100\}$ planes as reported by Rau, et al. (13).

Changes in the density and average size of radiation-produced defect clusters, dislocation loops and voids, are shown in fig. 6, as a function of annealing temperature. It is apparent in the figure that the density of the loop is much smaller than that of the void in the specimen annealed at temperatures of 800 to 1000°C.

4. Discussion

The microstructure of dislocation component observed in this experiment is in substance agree with the results reported in the literature (1,3,14,15). The raft characterized by a complex structure consisting of large loops surrounded by small loops in various stage of interaction was reported to be seen in molybdenum neutron irradiated at 575°C to a fluence of $3 \sim 6 \times 10^{19}$ n/cm^2 (15). In the specimen irradiated at 600°C to a neutron fluence of 3.5×10^{19} n/cm^2, large dislocation loops of ~1000 Å in diameter are present with unresolvable small defect clusters (14). Dislocation segments and loops observed in the specimen irradiated in DFR to a total dose of 3.15×10^{22} n/cm^2 at 640°C are frequently irregular and population of the loop are predominantly interstitial in nature; a significant number of vacancy loops of smaller size are also present (3). It is also reported that the large loops present in 400°C irradiated molybdenum after 900 and 1000°C anneals were predominantly interstitial in nature for JM material and predominantly vacancy type for MRC material (15).

With regard to void component of radiation-produced microstructure, Sikka and Moteff (5) have tabulated the void size and density data reported in the literature as well as the data obtained from their own experiment; voids of 20~64 Å in average diameter with $2 \times 10^{16} \sim 1 \times 10^{17}$ /cm^3 density have been observed in molybdenum neutron irradiated at around 600°C. In the specimen irradiated at 430°C to a neutron fluence of 7.5×10^{19} n/cm^2, Brimhall, et al. (4) have observed small voids of 20 ~ 25 Å in average diameter with the density of $2 \sim 4 \times 10^{16}$ /cm^3. In this experiment, voids could not be observed in the as-irradiated specimen; neutron irradiation was performed at about 600°C (0.3 Tm) to a fast neutron fluence of 8.0×10^{19} n/cm^2 (En $\gtrsim$ 1 MeV). An anneal for 1 h at 800°C resulted in formation of voids visible in the electron microscope. The density and average diameter of the voids are 3×10^{16} /cm^3 and 17 Å, respectively, which are equivalent to the number shown in the table made by Sikka and Moteff (5). The voids are considered to appear during the anneal, at least the voids which cause to rise the yield stress do not present in the as-irradiated specimen as discussed later.

It is revealed by Evans, et al. (16) that voids can be produced in molybdenum by annealing for 1 h at 900°C after neutron irradiation at 60°C to a fission dose of 5×10^{19} n/cm^2. The parameters of the voids structure are 19 ~ 37 Å in average void radius and $1.5 \times 10^{16} \sim 1.0 \times 10^{17}$ /cm^3 in number density; the void density varies widely from specimen to specimen (17). Based on position annihilation study of molybdenum neutron irradiated at 60°C to a fluence of 1.5×10^{18} n/cm^2, Peterson, et al. (18) interpreted annealing stages ranging 580 to 750°C and 750 to 940°C, respectively, as coarsing of voids through the transfer of vacancies from dislocation loops and growth of large voids at the expense of the smaller ones. With experiments on recovery of lattice parameter in high purity molybdenum neutron irradiated at 450°C to a fast fluence of 3×10^{21} n/cm^2, Kulcinski and Kissinger (19) reported that the lattice parameter recovery in the 500 to 600°C range is attributable to release of vacancy from traps, and that the lack of sufficient deep traps for isolated vacancies above 600°C may be resposible for apparent temperature threshold for void formation in molybdenum. Thus, the formation of voids in molybdenum during neutron irradiation at around 600°C (0.3 Tm) is strongly affected by interstitial impurity content, neutron flux and neutron fluence as well as irradiation temperature.

In this experiment, the yield stress of irradiated molybdenum was further increased by postirradiation annealing at temperatures of 800 to 1000°C (fig. 2). The anneal produced small voids in rather high density and lowered dislocation loop density to the order of 10^{13} /cm^3 (fig. 6). Thus, the hardening after the anneal is considered to be due mainly to voids visible in the electron microscope. The increase in the yield stress, $\Delta\sigma_y$ caused by the presence of voids can be expressed as

$$\Delta\sigma_y = 2\,\alpha\mu b\,(Nd)^{\frac{1}{2}} \quad , \tag{1}$$

where α is a dislocation-void interaction parameter, μ is the shear modulus, b is the Burgers vector, N is the void density and d is the void diameter (20,21). The equation has been verified to be suitable for predicting the strengthening caused by voids in neutron irradiated 304 stainless steel (22) and nickel (23) with α =1. With hardness measurements of molybdenum irradiated at 430°C to a fast neutron fluence of $\sim 1 \times 10^{22}$ n/cm^2, Sikka and Moteff (24) reported that the hardening after anneal at temperatures of 800 to 1450°C is mainly due to radiation produced voids. In the present study, $\Delta\sigma_y$ was calculated with α =0.5, μ =12.2 × 10^3 kg/mm^2 and b=2.73 Å and the values are compared with that obtained in the experiment in table 1. The agreement is fairly well for the samples annealed at temperatures of 800 to 1000°C, considering accuracy of void number density and non-random distribution of the voids. In addition, substantial increase in yield stress due to gas bubbles formed during postirradiation annealing was observed in aluminum-lithium alloys (25).

The hardening of as-irradiated sample is attributable to dislocation loops. The radiation hardening of 4.2 kg/mm^2 can be provided by loops of 50 Å in an average diameter with 1.3 × 10^{15} /cm^3 in density (fig. 6), if the equation

$$\Delta\sigma_y = \alpha\mu b\,(Nd)^{\frac{1}{2}} \tag{2}$$

with α =0.5 is used for the loop hardening (26). Transmission electron micrographs of deformed specimens shown in fig. 7 also suggest that hardening mechanism is different among the specimens; cell structure is seen in the unirradiated specimen (a), straight dislocation lines in the as-irradiated specimen (b), dislocation tangles in the specimen irradiated and annealed at 900°C(c), and cell structure again in the specimen irradiated and annealed at 1200°C (d). However, the specimens were too much deformed to explore the hardening mechanism. In the specimen irradiated and annealed at 1200°C, elongation to fracture recovered to unirradiated level and microstructure after deformation to fracture is somewhat similar to that observed in unirradiated specimen.

5. Conclusion

Tensile tests at room temperature and electron microscope observations were made on pure molybdenum that was neutron irradiated to a fast neutron fluence of 8.0×10^{19} n/cm^2 at about 600°C and annealed for 1 h at temperatures up to 1200°C. The investigation leads to the following conclusions:

(1) The defect structure of as-irradiated specimen consists of large dislocation loops of ~ 2000 Å in diameter with unresolvable small defect clusters of 1.5×10^{15} /cm^3 in density; radiation hardening due to the loop is about 4 kg/mm^2.

(2) Postirradiation annealing for 1 h at 800°C produces small voids of 17 Å in average diameter and 3.0×10^{16} /cm^3 in density; the hardening observed after the annealing is about 18 kg/mm^2.

(3) On annealing at higher temperatures the voids grow larger with decrease in density; the hardening is also decreased by the annealing.

(4) The defect structure after anneal at temperatures ranging from 800 to 1100°C consists of coarsely distributed dislocation loops and rather inhomogeneously distributed voids.

(5) The hardenings provided by postirradiation annealing at 800 1000°C are larger than that of as-irradiated condition and are attributable to the voids.

(6) The stress-strain curve of the specimen annealed at 800and 900°C is characterized by small yield drop and little work hardening.

(7) The yield stress of the specimen annealed 1 h at 1200°C is almost equal to that of the as-irradiated specimen.

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Table 1

Density and size of voids and their contribution to the hardening

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annealing temperature (°C)	void density N (cm^{-3})	void diameter, d (Å)		$\Delta\sigma_y$ (kg/mm^2)	
		range	average	calculated	experimental
800	3.0×10^{16}	15~ 20	17	23.7	18.0
900	9.1×10^{15}	15~ 50	20	14.2	17.1
1000	5.0×10^{15}	15~ 90	39	14.7	9.1
1100	1.5×10^{15}	25~90	55	9.6	—
1200	3.2×10^{13}	60~300	107	1.9	5.5

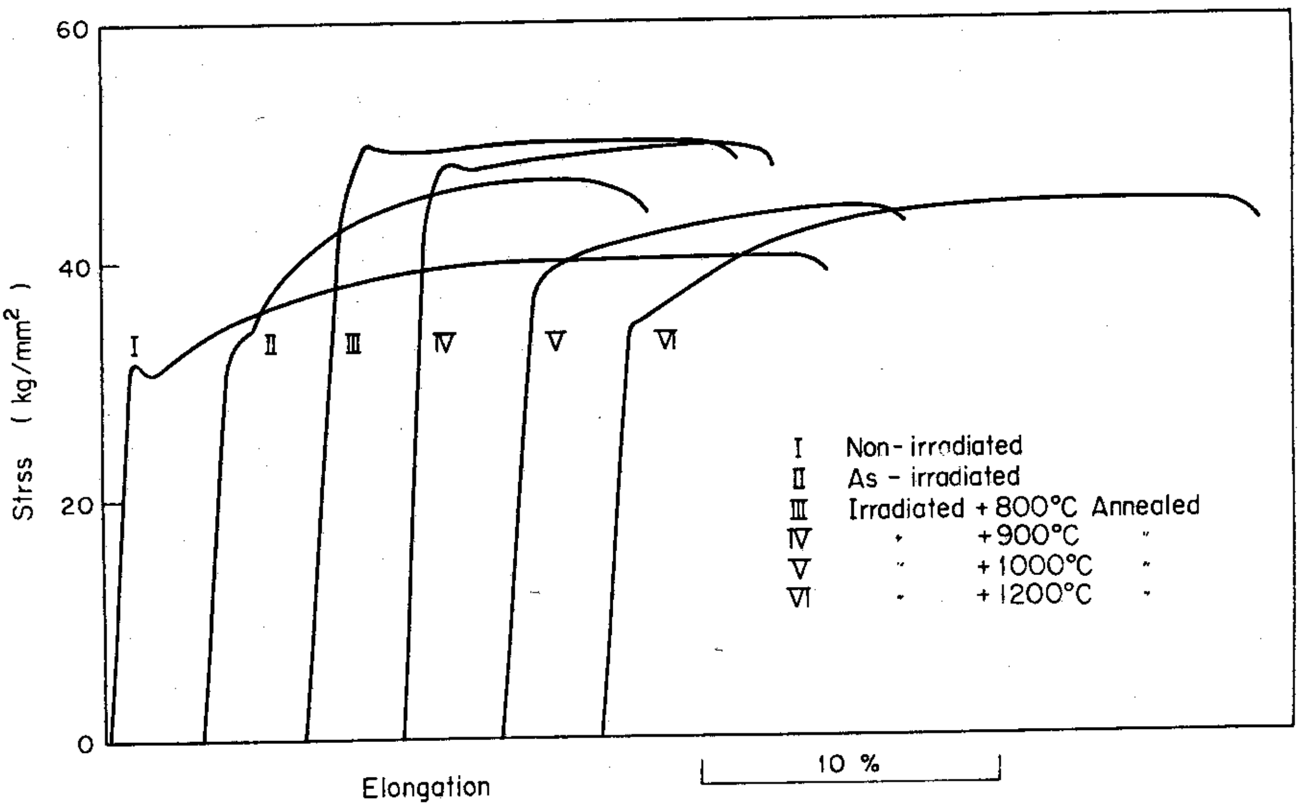

Fig. 1 Variation in stress-strain curve with neutron irradiation and postirradiation annealing temperature in molybdenum.

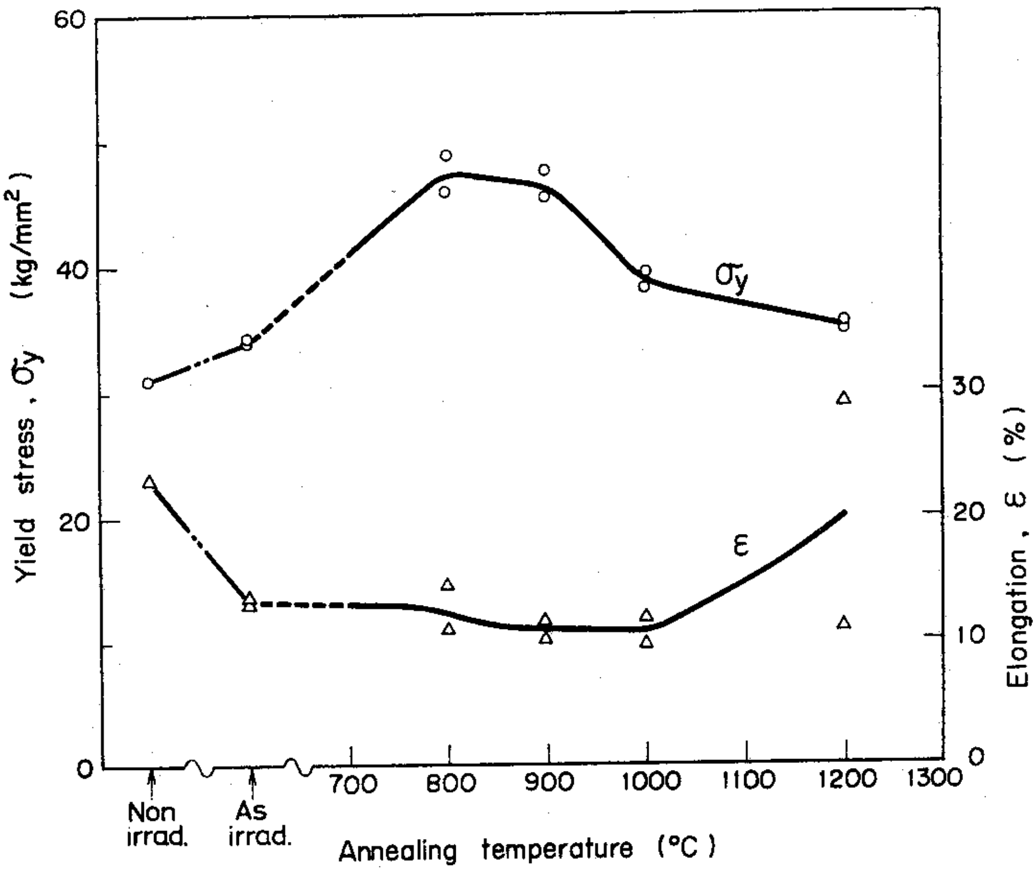

Fig. 2 Change in tensile properties at room temperature with irradiation and anneal temperature in molybdenum.

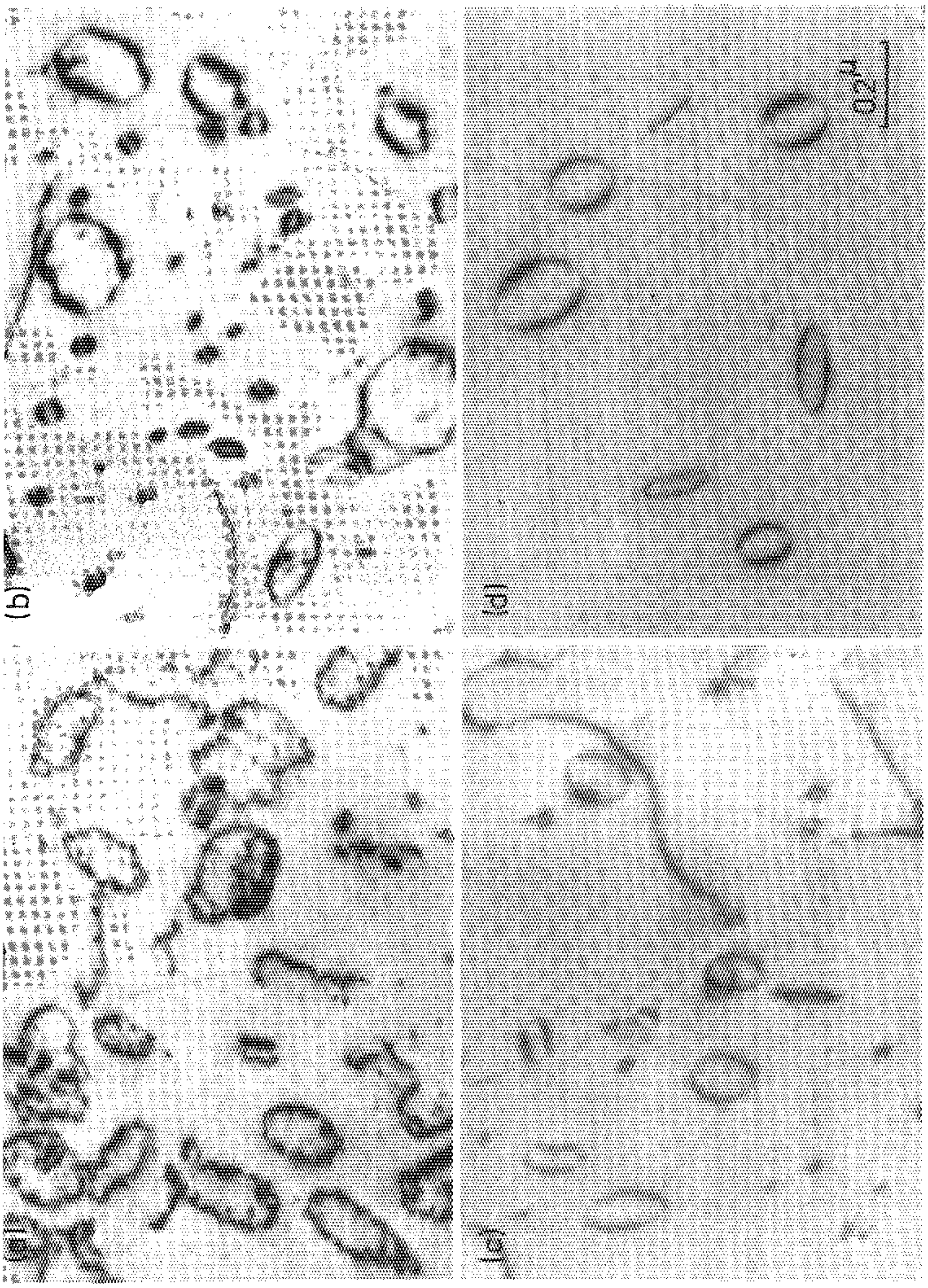

Fig. 3 Dislocation loops in molybdenum irradiated to a fast neutron fluence of 8.0×10^{19} n/cm^2 at about 600 °C (a), and annealed for 1 h at (b) 700 °C; (c) 900 °C; and (d) 1100 °C.

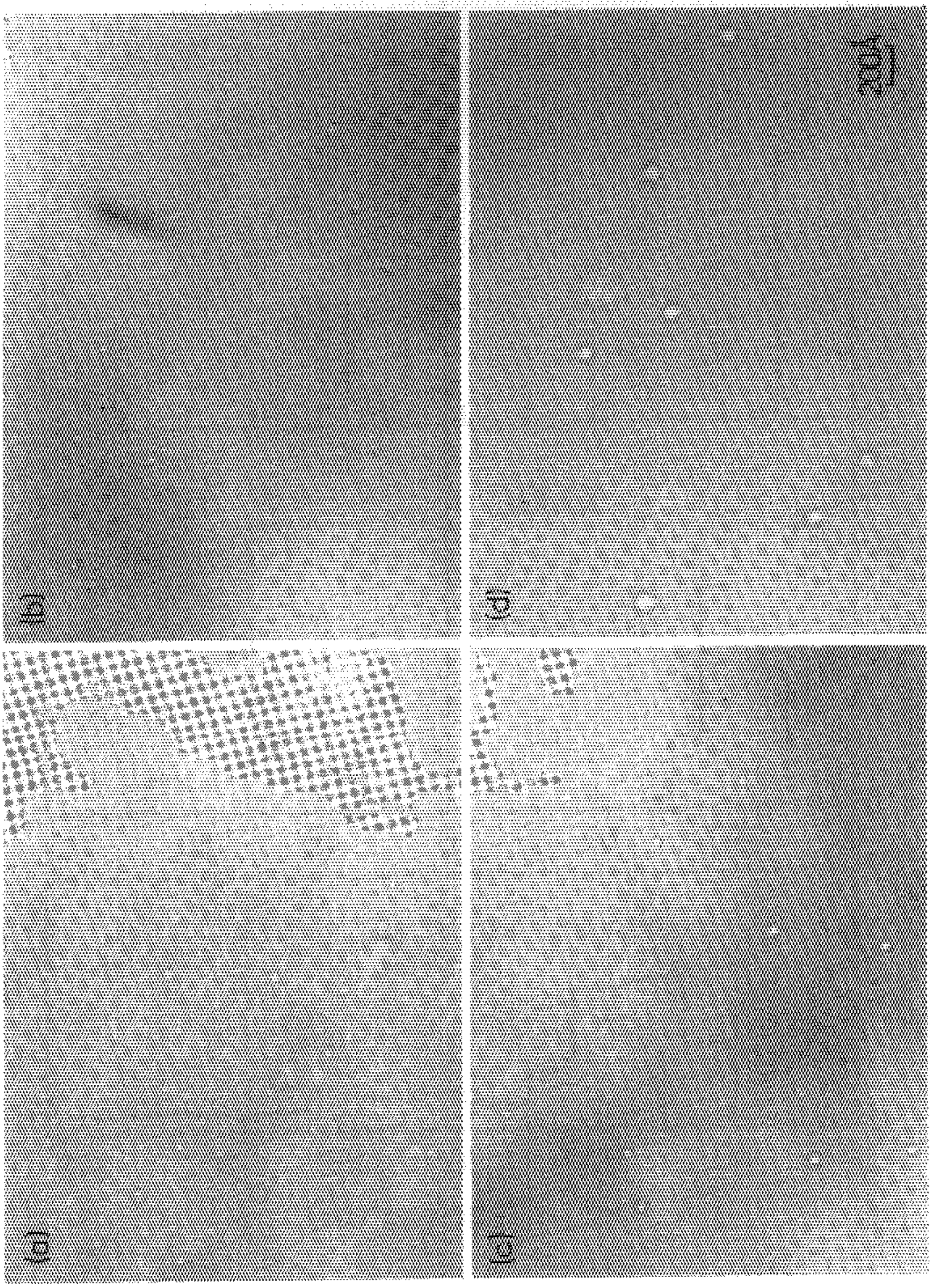

Fig. 4 Voids in molybdenum irradiated to a fast neutron fluence of 8.0×10^{19} n/cm^2 at about 600 °C and annealed for 1 h at (a) 800 °C; (b) 900 °C; (c) 1000 °C and (d) 1200 °C.

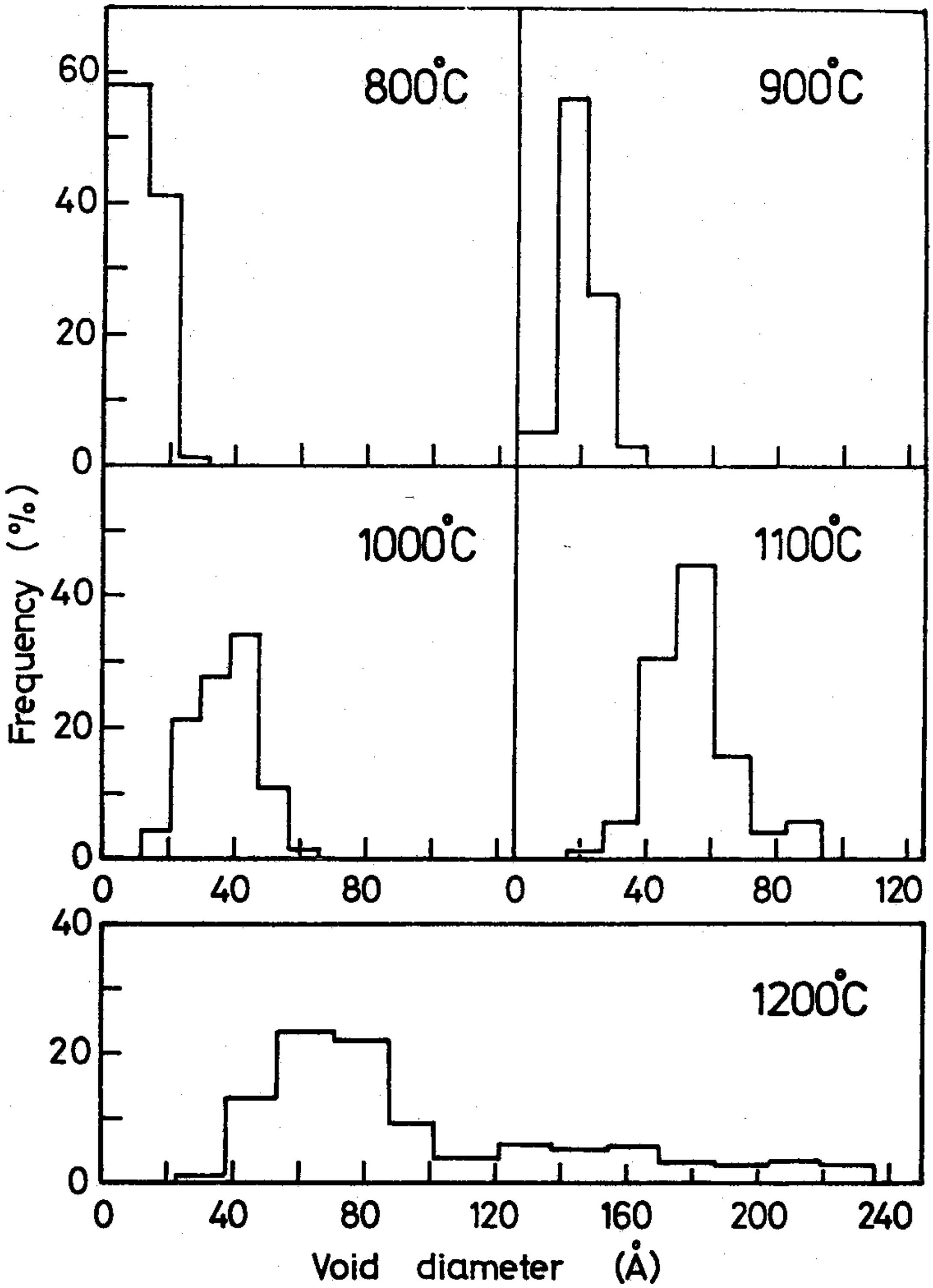

Fig. 5 Void size distribution for in molybdenum irradiated to a fast neutron fluence of 8.0×10^{19} n/cm^2 at about 900 °C and annealed at five different temperatures.

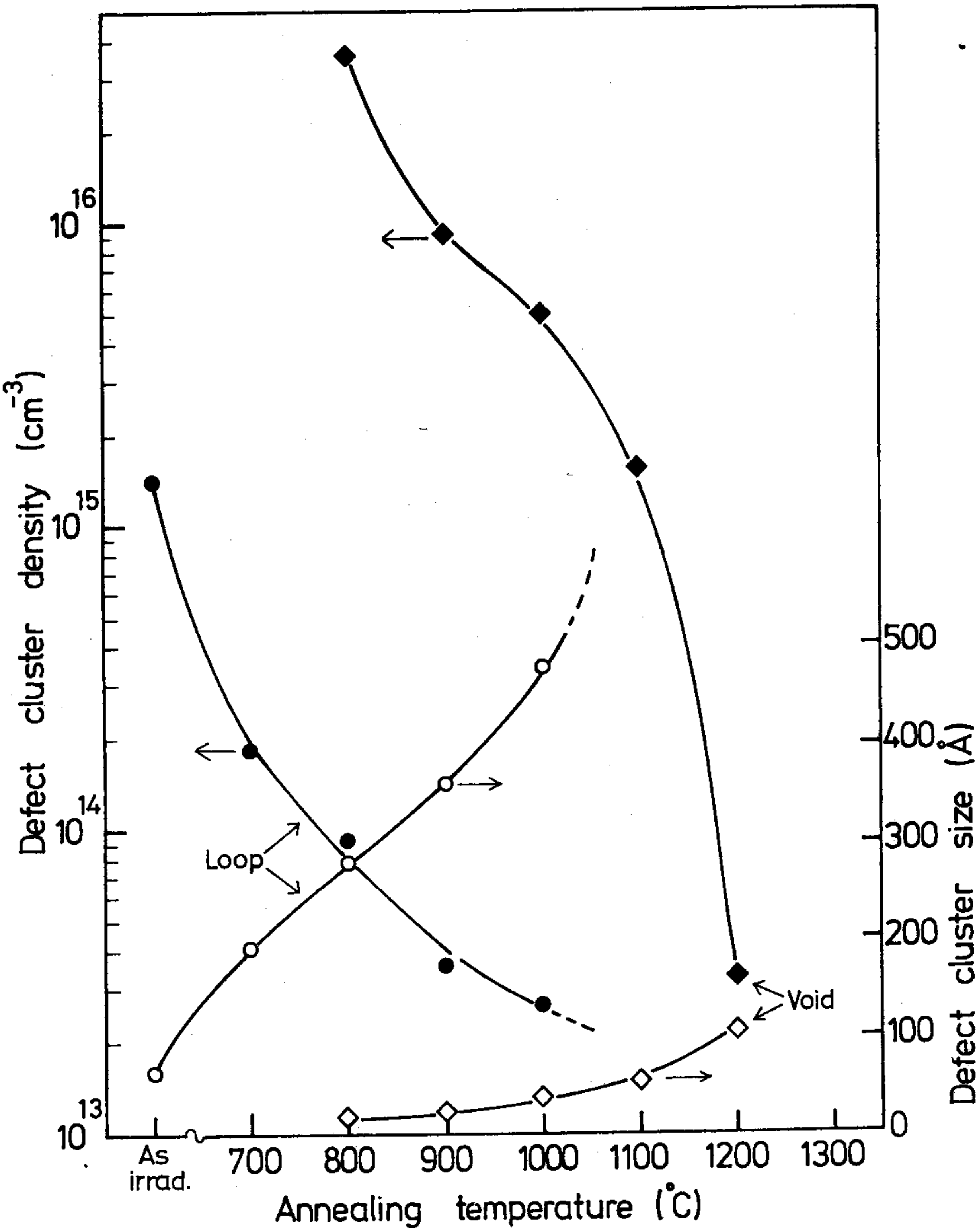

Fig. 6 Changes in defect cluster density and average size with annealing temperature in molybdenum irradiated to a fast neutron fluence of 8.0×10^{19} n/cm^2 at about 600 °C.

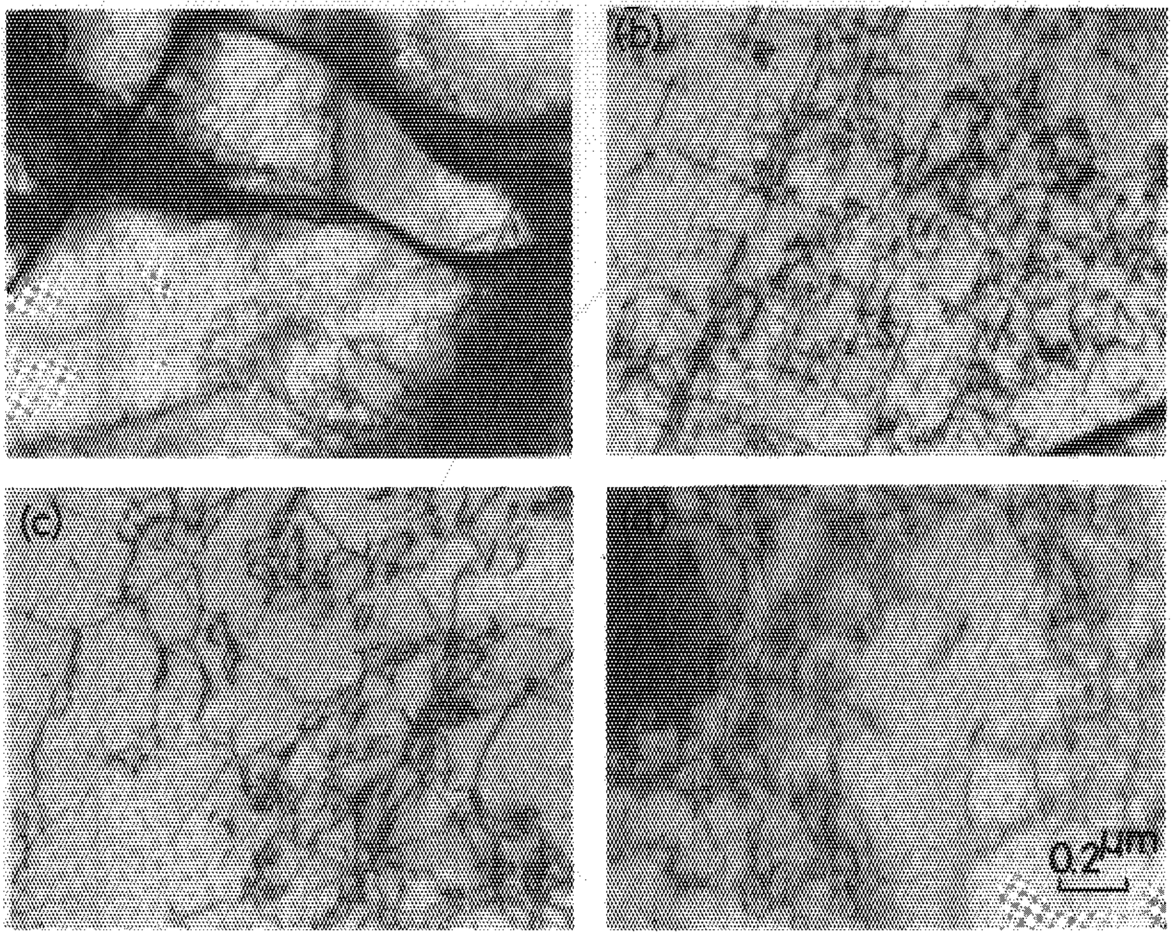

Fig. 7 Transmission electron micrographs deformed specimens of (001) orientation.

(a) Unirradiated specimen deformed about 25%

(b) Irradiated and deformed about 14%

(c) Irradiated and annealed for 1 h at 900 °C and deformed about 12%

(d) Irradiated and annealed for 1 h at 1200 °C and deformed about 28%