FINAL REPORT

on

IMPROVEMENT OF CREEP STRENGTH AND LOW-TEMPERATURE DUCTILITY OF REFRACTORY METALS BY MEANS OF MECHANICAL TWINNING

to

NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

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by

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November 3, 1966

National Aeronautics and Space Administration
Office of Research Grants and Contracts
Office of Space Sciences
600 Independence Boulevard
Washington, D. C. 20546

Attention Mr. T. L. K. Smull

Gentlemen:

Contract No. NAS4-100(05), "Improvement of
Creep Strength and Low-Temperature Ductility
of Refractory Metals by Means of Mechanical Twinning"

Enclosed are 25 copies of the Final Report covering the entire contract period.

Sincerely yours,

J. W. Edington

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Metal Science Group

JWE:js
Enc. (25)

cc: Mr. J. Maltz (2)
Mr. G. M. Ault (1)
Mr. I. Machlin (1)

IMPROVEMENT OF CREEP STRENGTH AND LOW-TEMPERATURE DUCTILITY OF REFRACTORY METALS BY MEANS OF MECHANICAL TWINNING

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INTRODUCTION

It has been shown previously by Tardiff, et al., (1)* that there is an increase in microhardness with increasing twin density, and Reid(2) has shown that deformation twins harden single crystals of niobium more than do slip dislocations.

Furthermore, experiments have shown that mechanically twinned structures are more stable at high temperatures than slipped structures(3) and that the presence of mechanical twins can increase the recrystallization temperatures of the cold-worked metal(4). Finally, other research(5) has shown that the prior existence of twins in polycrystalline iron can prevent cleavage-crack propagation and so lower the ductile-brittle transition temperature.

Thus, it is conceivable that twins may improve the mechanical properties of bcc metals at both high and low temperatures. This report describes some investigations of the possible mechanical-property improvements outlined above using a range of different materials.

CONCLUSIONS

The conclusions which can be drawn from this work may be conveniently divided into two sections, one dealing with ductility improvement at low temperatures and one dealing with twin strengthening at high temperatures.

(a) Ductility Improvement

In the materials investigated it was found to be impossible to introduce mechanical twins without introducing cracks that rendered the material weak on subsequent testing.

(b) Twin Strengthening

The materials investigated exhibited different behavior. Twin strengthening occurred at 600 C in conventional tensile tests carried out in polycrystalline molybdenum-35 at. % rhenium alloy. Twin strengthening did not occur at elevated temperatures in conventional tensile tests carried out on polycrystalline niobium, a niobium-40 wt. % vanadium alloy, and a commercial FS 85 niobium alloy. Under creep conditions at elevated temperatures twin strengthening did not occur in the commercial FS 85 alloy.

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*References are given on page 15.

EXPERIMENTAL WORK

The materials chosen for these investigations were a niobium-40 wt. % vanadium alloy, niobium, tungsten, and an FS 85 niobium alloy (Nb-28Ta-10W-1Zr). The niobium-40 wt. % vanadium alloy was chosen for an evaluation of the high-temperature strengthening mechanism because it is known that closely spaced twins can be introduced by deformation at room temperature. The niobium and tungsten were used to evaluate the possible improvement of ductility at low temperatures, since a comparison of the behavior of materials known to behave in a ductile and in a brittle manner was considered to be important. The commercial FS 85 niobium alloy was included to test the hardening effect of deformation twins on a technologically important material.

The Nb-40V alloy was produced as a drop casting after melting niobium and vanadium in a nonconsumable-electrode electric-arc furnace. The niobium, tungsten, and FS 85 alloy were produced industrially, and all materials and alloy constituents were commercially pure.

The Nb-40V alloy was ductile at room temperature. After an initial 10 percent reduction in area by rod rolling and annealing for 1 hour at 1400 C, the material was rolled to 0.050-inch thickness before a final annealing treatment of 1 hour at 1300 C. The FS 85 alloy was obtained from the Navy Department Sheet Rolling Program in sheet form 0.040 inch thick that was recrystallized by annealing at 1750 C for 1 hour. Both the tungsten and the niobium were recrystallized by annealing at 1500 C for 1 hour.

RESULTS AND DISCUSSION

High-Temperature Strengthening

Preliminary Experiments

Previous work by Reid(2) has shown that mechanical twins give rise to a high-temperature strengthening in single crystals of niobium. The first step of this investigation was to evaluate the effect in polycrystalline material. For this work, polycrystalline niobium specimens were used to enable direct comparison with Reid's work. Two specimens were prestrained to 1 percent elongation at -196 and 30 C so that one specimen contained deformation twins and slip dislocations, while the other contained only slip dislocations. These specimens were tested in tension at 600 C. The stress-strain curves are shown in Figure 1. It will be noted that there is no significant difference in the mechanical properties of the two specimens. However, it is well known that the yield stress of niobium is relatively unaffected by changes in grain size, and so if deformation twins strengthen material in the same way as grain boundaries, their strengthening effect would be expected to be small in this material.

Preliminary tensile tests were carried out on a polycrystalline molybdenum-35 at. % rhenium alloy because this material twins readily like the niobium-vanadium alloy. Two mechanical tests were carried out. Specimen A was strained to 1 percent elongation at room temperature, then tested at 600 C. Specimen B was tested in the as-annealed condition at 600 C. The stress-strain curves are reproduced in Figure 2. It can be seen that, after equivalent total elongations, the flow stress of Specimen A was ~30 percent higher than that of Specimen B. Both the ultimate tensile strength and elongation to fracture of Specimen A were slightly greater than those properties of Specimen B. These tests demonstrate that twin strengthening occurs both in single crystals of niobium and in the polycrystalline molybdenum-35 at. % rhenium alloy but not in polycrystalline niobium.

Twin Stability at High Temperatures

After the initial investigation described above, it was necessary to determine the annealing characteristics of the mechanically twinned niobium-40 wt. % vanadium alloy that was to be used for most of the investigation so that testing temperatures could be chosen. A series of strip specimens 0. 050 inch thick were made as described previously, rolled to 5 percent reduction in thickness at room temperature, and annealed for 1 hour at temperatures between 900 and 1700 C. Figure 3 shows typical areas from some of the specimens. Pinching off of the twins at incoherent twin boundaries begins to occur at 1000 C, and the lengths of twins appear to be continually decreased during annealing at higher temperatures until above 1300 C grain growth occurs. Even after annealing at 1200 C, a few islands of twins remain.

The results of microhardness measurements carried out on these specimens are shown in Figure 4. It can be seen that there is a rapid softening of the material between 1000 and 1100 C, when the twins begin to anneal out. Surprisingly there is no correlation between hardness and twin density within grains in specimens annealed at 1100 C. Further softening of the material occurs when grain growth begins above 1300 C. In addition, microhardness measurements were obtained from material rolled to 5 percent reduction in thickness at 400 C and subsequently annealed in the same temperature range as the twinned specimens. This material did not contain twins, and recovery and recrystallization began at a lower temperature and were complete as the last twins in the twinned specimens annealed out.

Twinned, slipped, and annealed specimens were tested in tension under vacuum at 600 C and 950 C at a strain rate of 10^{-3} sec^{-1}. These temperatures were chosen on the basis of Figures 3 and 4, making due allowance for the fact that the presence of a stress on the specimen would tend to push the curves to the left, i. e., to accelerate the recovery and recrystallization processes. The test at 950 C was designed to fall within the region for which twins were stable but dislocations were undergoing climb. The test at 600 C was designed to determine whether the twinned structure was stronger intrinsically than the slipped structure at an elevated temperature at which both structures were stable. The gage length of each of the twinned specimens was examined after testing and the deformation twins were still present.

The results of these tests are summarized in Table 1.

The differences in behavior at 600 C are not very great although the twinned specimen appears to have a lower 0. 2 percent proof stress than the annealed and the slipped specimens. However, there is noticeably more elongation to fracture for the twinned specimen compared with the annealed specimen. In the tests at 950 C, the twinned specimen has the lowest yield stress and U. T. S., and the annealed specimen is the strongest. The elongations to fracture are not significantly different. In view of the fact

TABLE 1. MECHANICAL-PROPERTY DATA

From the Tests Carried Out at 600 and 950 C

Test Temperature, C	Specimen Condition	0.2 Percent Proof Stress, psi	U.T.S., psi	Percent Elongation to Fracture
600	Annealed	90,150	126,200	17.2
600	Slipped	91,650	130,000	20.8
600	Twinned	84,400	130,700	23.8
950	Annealed	77,400	92,400	6.4
950	Slipped	72,600	84,800	7.2
950	Twinned	65,200	81,400	7.2

that, in this material, the mechanical properties of the twinned and the slipped specimens were not significantly different from those of fully recrystallized material, it was inferred that the mechanical properties of this material are relatively structure insensitive. In order to check this conclusion, specimens of grain sizes 2d = 0.004 cm and 0.001 cm were tested at 30 and 400 C. In the test at 30 C, the coarse-grained specimen twinned at a stress of 132,500 psi while the fine-grained specimen slipped at 133,000 psi. At 400 C the coarse- and fine-grained specimens slipped at yield stresses of 101,000 and 107,000 psi, respectively. It was concluded that the yield strength of this material is relatively insensitive to changes in grain size. Thus, if deformation twins simply acted as grain boundaries by blocking dislocations, this material would not be expected to exhibit marked strengthening caused by twinning, as indeed it does not.

In view of the structural insensitivity of the mechanical properties of the niobium-40 wt. % vanadium alloy, attention was focused on the commercial FS 85 alloy. First, it was necessary to demonstrate that deformation twins could be produced in this alloy.

Initially, tensile specimens were ground from the as-supplied 0.040-inch-thick sheet. These specimens were annealed at 1750 C under vacuum for 1 hour, which produced an equiaxed grain structure. The specimens were then tested in an Instron testing machine at 77 K and at a strain rate of 10^{-3} sec^{-1}. The specimens showed <1 percent elongation before fracture and very few twins were found.

Consequently, it was decided to introduce twins by explosive loading. Sheet material was fully recrystallized by annealing at 1750 C under vacuum for 1 hour. The sheet was explosively loaded between two steel sheets at pressures of up to 400 kilobars. The assembly was detonated in air and recovered in a water tank, after which mechanical polishing and etching of the specimen were carried out so that the shocked structure could be examined by optical microscopy. The etchant used was a 70% HNO_3/30% HF solution. It was found that at shock pressures of 400 kilobars between 10 and 20 twins were produced in each grain without the formation of cracks. A typical area of a specimen shocked at 400 kilobars is shown in Figure 5. The invisibility of the twins in some grains is caused by an orientation dependence of the effectiveness of the etching procedure. Twins are in fact present in all grains. Annealing experiments in the temperature range 1100 to 1800 C were performed on material shocked to a pressure of

400 kilobars. Optical examination of the specimens showed that the twins were still present in a high density after annealing at 1400 C for 1 hour but that they were absent after annealing at 1600 C for 1 hour.

Test specimens were ground from sheet which had been shocked to a pressure of 400 kilobars and from fully annealed sheet. For comparison purposes, some fully annealed sheet was rolled to 20 percent reduction in thickness at room temperature in order to introduce a dislocation density in this material comparable to the very high dislocation density produced in the shocked material(6). For further comparison purposes, test specimens were also ground from the fully recrystallized material.

To give an immediate indication of the relative properties of the material in the three different conditions, tensile tests were carried out at a strain rate of 10^{-3} sec^{-1} in air at 30 and 400 C. The results of these tests are shown in Table 2.

TABLE 2. MECHANICAL PROPERTY DATA ON FS 85 MATERIAL

Specimen Condition	Test Temperature, C	0.2 Percent Proof Stress, psi	U.T.S., psi	Percent Elongation to Fracture
Annealed	30	65,200	87,700	33.2
Rolled	30	95,000	119,200	9.5
Shock Loaded	30	73,900	91,400	23.9
Annealed	400	27,300	48,300	23.9
Rolled	400	26,600	79,200	10.0
Shock Loaded	400	22,000	60,700	15.6

It can be concluded that at 30 C the cold-rolled specimen is much stronger than either the annealed or the shock-loaded specimen and has a much higher work-hardening rate. At 400 C there is little significant difference between the three conditions in terms of the 0.2 percent proof stress, although the ultimate tensile strength of the rolled specimen is the highest of the three and the rate of work hardening is also the highest.

Creep tests were kindly performed under vacuum at elevated temperatures by Mr. Robert Titran at NASA Lewis Laboratories, Cleveland, Ohio. One specimen in each condition was tested at 1100 and 1400 C. The high temperature was chosen because it was the highest temperature at which the twins were stable under straightforward annealing conditions. The lower temperature was chosen because, even if the applied stress and deformation accelerated the annealing rate of the deformation twins, the twins would be expected to remain stable throughout the test. The results of the creep tests are summarized in Table 3.

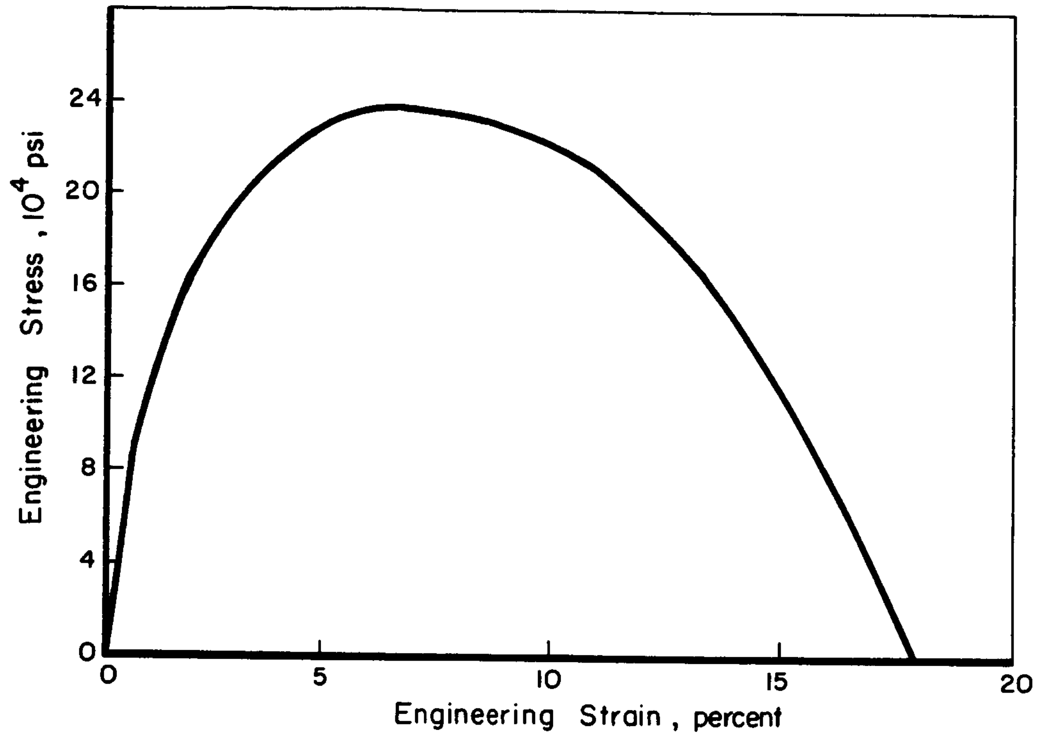
It can be concluded that the behavior of the three specimens tested at 1400 C was essentially the same, indicating that the original structure had annealed out during the course of the test. Metallographic examination of the gage length of the shocked and tested specimen demonstrated that this was indeed so; no deformation twins were observed. Metallographic examination of the gage section of all of the specimens tested at 1400 C showed that the grain boundaries were very irregular and that the grains were quite large, indicating that grain-boundary migration had occurred. The fracture took place by grain-boundary failure. Of the tests carried out at 1100 C it can be seen that the rolled specimen has the better creep properties, while those of the annealed and shocked specimen were essentially the same. Metallographic examination of the shocked specimen after testing showed that the deformation twins were still present, both in the gage length and at the fracture, see Figure 6, although in a greatly reduced density compared with the as-shocked state, see Figure 5. It was concluded that the reduction in density of the deformation twins during the test was brought about by fragmentation effects resulting from the motion of slip dislocations as described by Sleeswyk and Helle(7). Finally, it is concluded that, in this material, deformation twins are ineffective strengtheners under conventional tensile testing and under creep conditions. However, the preslipped specimen showed encouraging strengthening, particularly under creep conditions.

TABLE 3. CREEP TEST DATA ON FS 85 MATERIAL

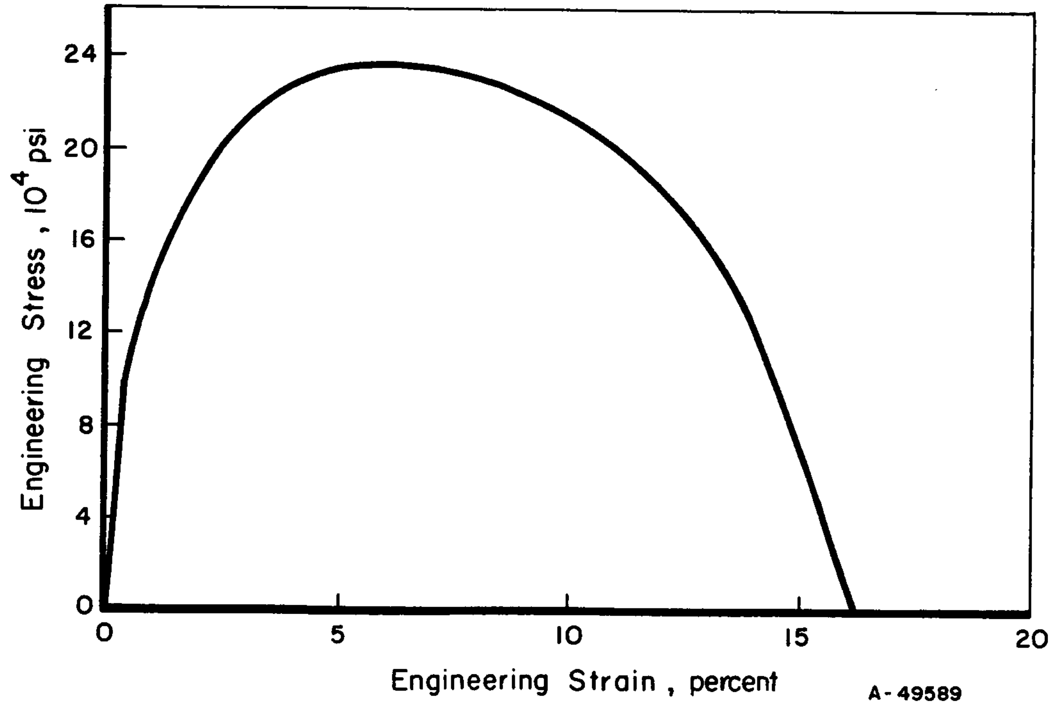
Specimen Condition	Load, psi	Test Temperature, C	Rupture	
			Time, minutes	Strain
Annealed	10,000	1400	1,364.4	64.6
Rolled	10,000	1400	1,230.4	57.9
Shocked	10,000	1400	1,085.0	62.4
Annealed	20,000	1100	8,675.4	37.2
Rolled	20,000	1100	13,678.8	20.5
Shocked	20,000	1100	8,352.3	27.5

Ductility Improvement at Low Temperatures

The experiments were designed to investigate the low-temperature behavior of ductile niobium and brittle tungsten. It is known that twins formed in tungsten at low temperatures always have cracks associated with them. Therefore, it was considered that twins without cracks may be introduced at higher temperatures by shock loading. As a result, compression specimens of tungsten and niobium were explosively deformed at room temperature under a load of 100 and 90 kilobars, respectively. Figure 7 shows typical photomicrographs of the specimens before and after shock loading. Mechanical twins are present in the niobium specimen but not in the tungsten specimen, while cleavage cracks are present in the niobium and extensive grain-boundary cracks are present in the tungsten. It appears, therefore, that the particular explosive deformation techniques as used at these temperatures cannot produce twins without cracks in either tungsten or niobium and thus renders ductilizing at low temperatures unpractical by this method.



a. Prestrained at -196 C



b. Prestrained at 30 C

FIGURE 1. THE STRESS-STRAIN CURVE FOR POLYCRYSTALLINE NIOBIUM SPECIMENS TESTED IN TENSION AT 600 C IN AIR

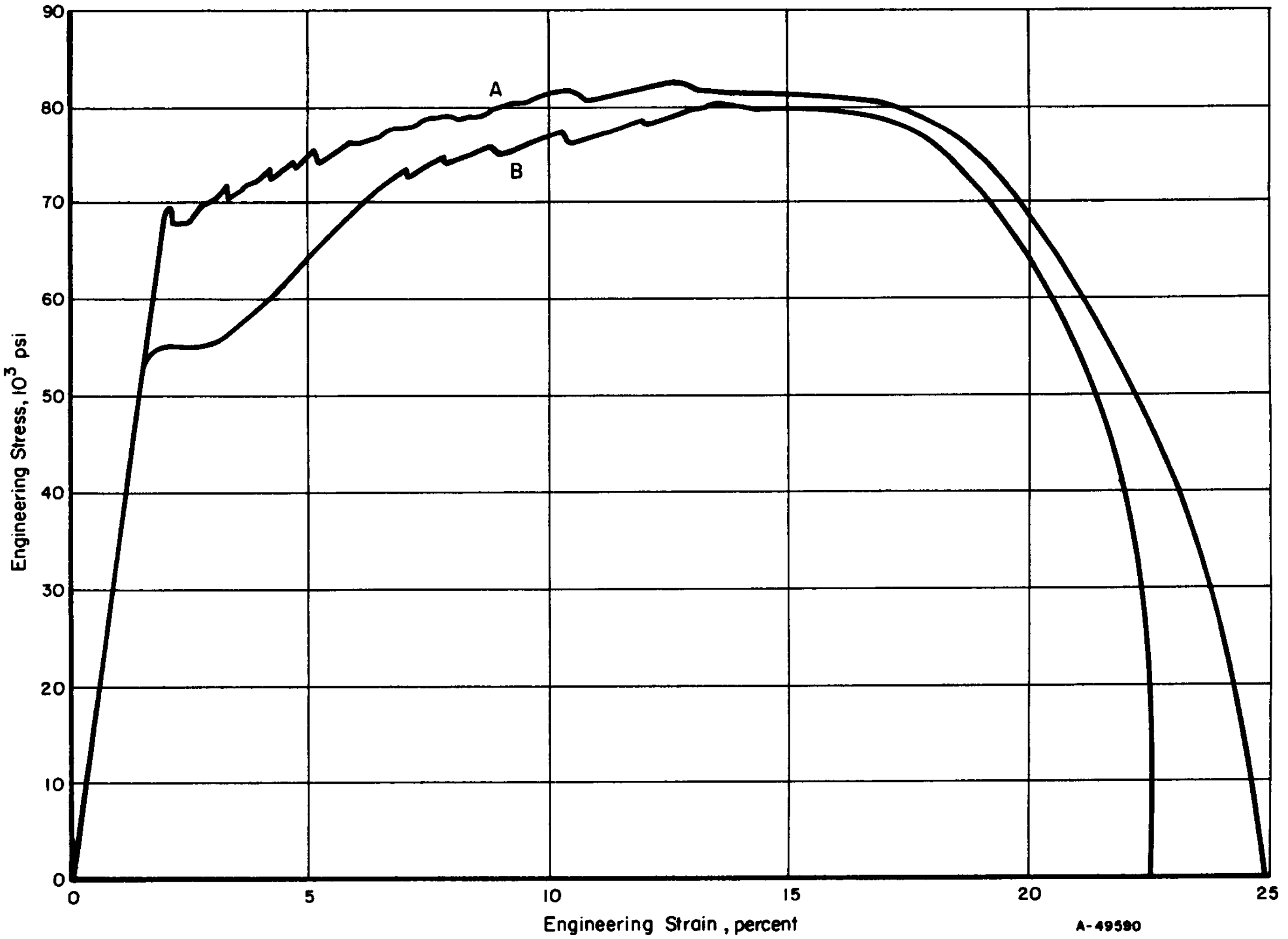
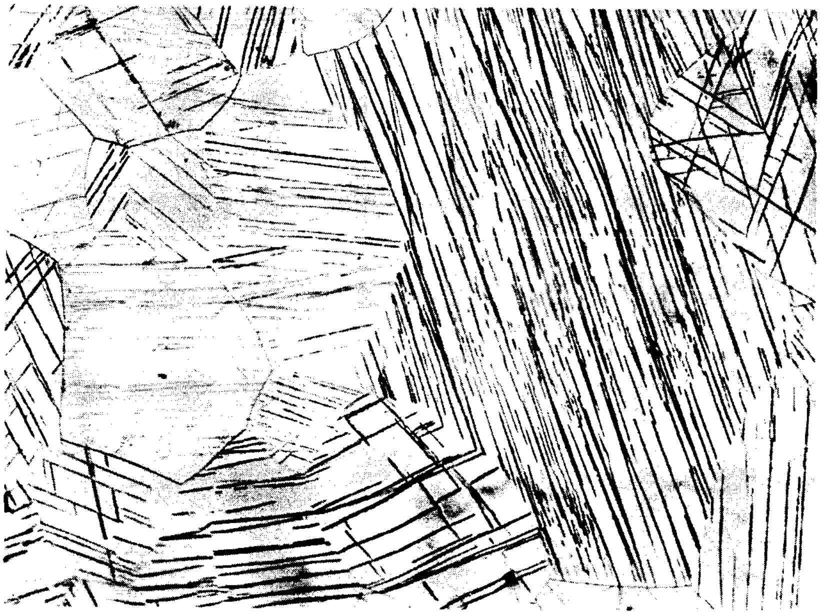


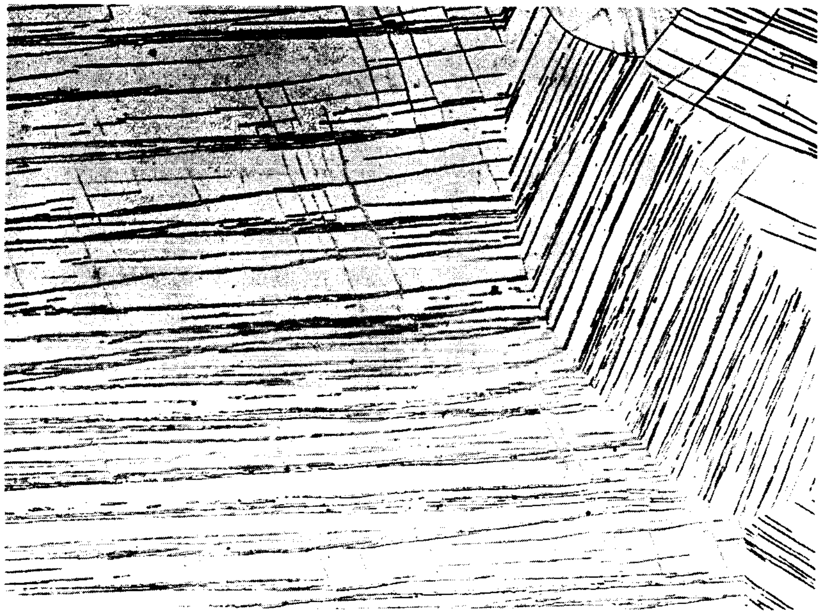
FIGURE 2. STRESS-STRAIN CURVES OF MOLYBDENUM-35 AT. % RHENIUM TESTED AT 600 C

Specimen A – prestrained to 1 percent elongation at 30 C
Specimen B – as annealed



100X 16633

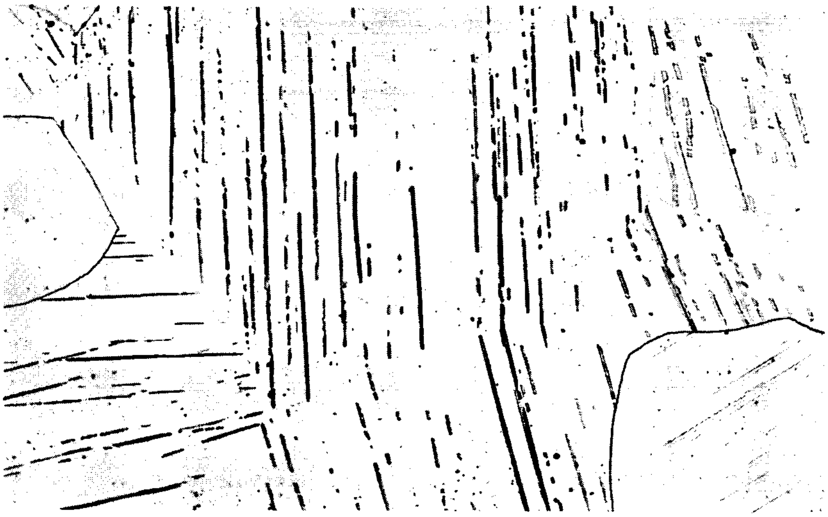
a. As Rolled



100X 16634

b. Annealed 1000 C

FIGURE 3. PHOTOMICROGRAPHS SHOWING THE EFFECT OF ANNEALING TEMPERATURE ON THE MICROSTRUCTURE OF NIOBIUM-40 WT% VANADIUM ALLOY PREVIOUSLY ROLLED TO 5 PERCENT REDUCTION IN THICKNESS AT 30 C



c. Annealed at 1100 C

100X 16636

d. Annealed at 1200 C

100X 16637

e. Annealed at 1300 C

100X 16638

FIGURE 3. (CONTINUED)

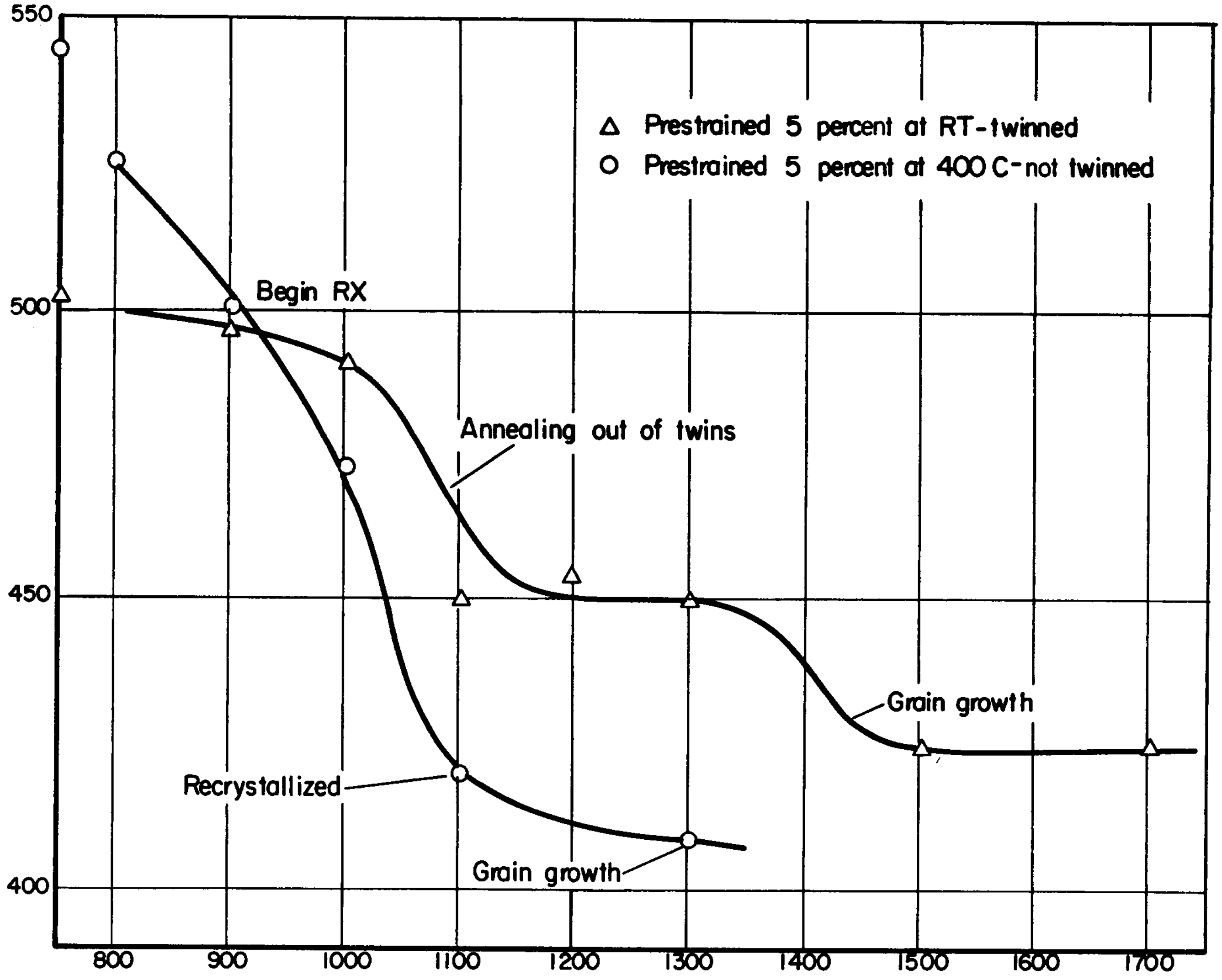
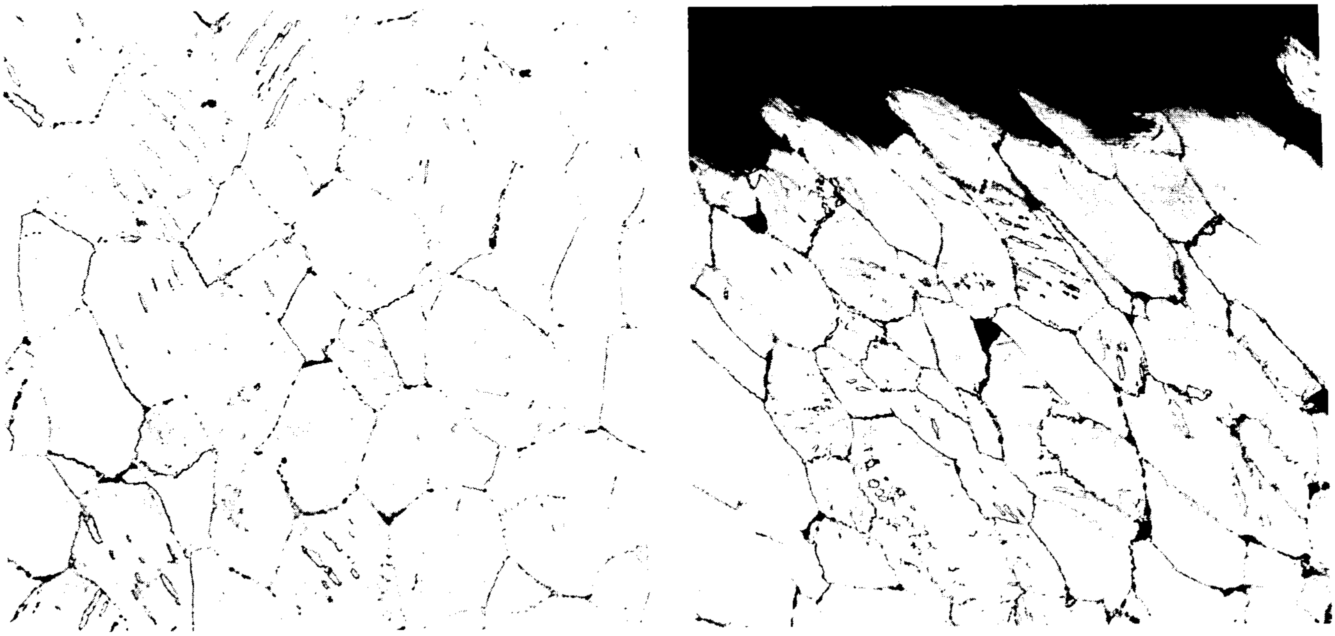


FIGURE 4. THE RELATIONSHIP BETWEEN MICROHARDNESS AND ANNEALING TEMPERATURE FOR THE NIOBIUM-40 WT % VANADIUM ALLOY

133X

FIGURE 5. A PHOTOMICROGRAPH SHOWING A TYPICAL AREA OF AN FS 85 ALLOY SHOCKED AT A PRESSURE OF 400 KILOBARS AT 30 C



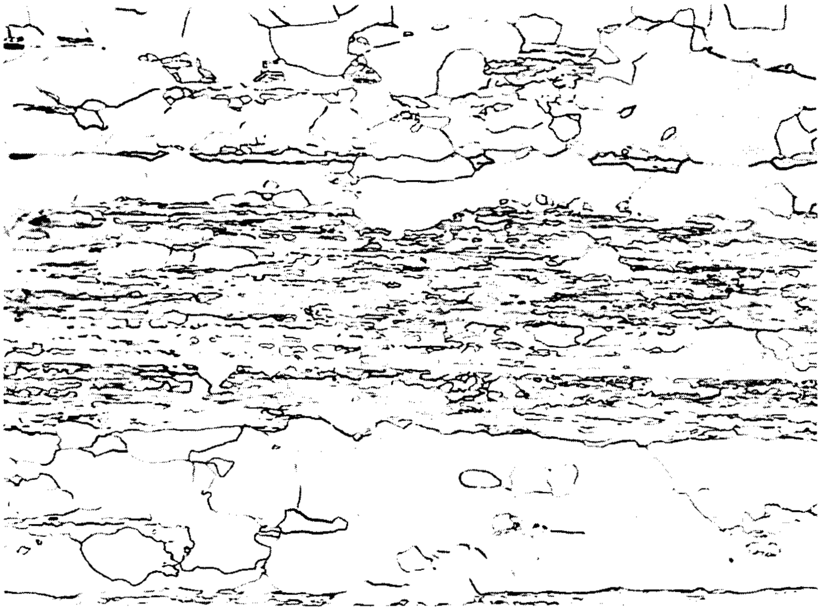
100X

a. Gage Length

100X

b. Fracture

FIGURE 6. PHOTOMICROGRAPHS SHOWING A TYPICAL AREA OF THE GAGE LENGTH AND FRACTURE OF A SHOCKED SPECIMEN AFTER A CREEP RUPTURE TEST AT 1100 C



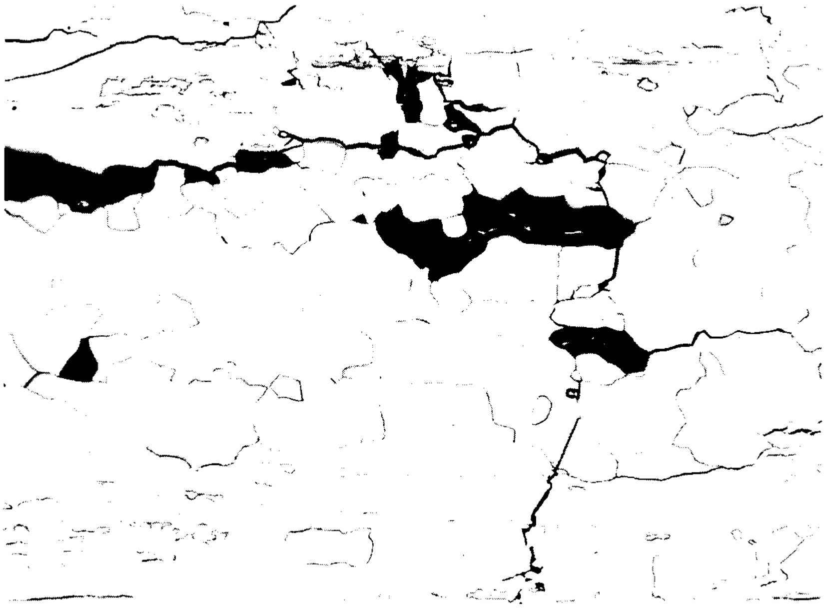
100X 15080

a. Recrystallized Tungsten

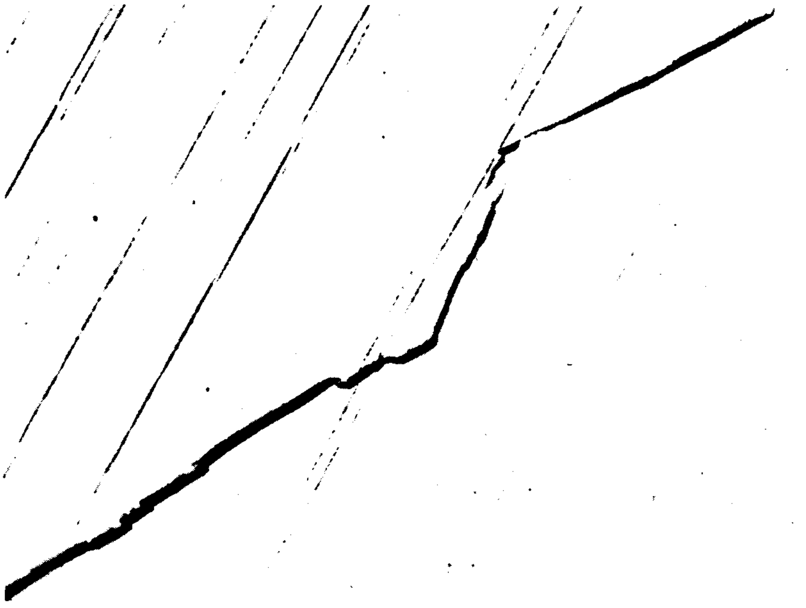
100X 15081

b. Fully Recrystallized Niobium

FIGURE 7. PHOTOMICROGRAPHS SHOWING EFFECT OF COMPRESSIVE SHOCK LOADING ON TUNGSTEN AND NIOBIUM



c. Tungsten Specimen in a. After Explosive Loading to 100 Kilobars, Note Grain-Boundary Cracks and Absence of Deformation Twins



d. Niobium Specimen in b. After Explosive Loading to 90 Kilobars, Note Cleavage Cracks A and Deformation Twins B

FIGURE 7. (CONTINUED)

REFERENCES

(1) Tardiff, H. P., Claisse, F., and Chollet, P., Response of Metals to High Velocity Deformation, Interscience Publishers (1961), p 389.

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(3) Jaffee, R. I., Sims, C. T., and Harwood, J. J., "Proceedings of the Third Plansee Seminar", Reutte, Tyrol (1958).

(4) Schnitzel, R. H., and Keith, G. H., J. of Less-Common Metals, 4, 98 (1962).

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(7) Sleeswyk, A. W., and Helle, J. N., Acta Met., 9, 344 (1961).