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Journal of Alloys and Compounds 224 (1995) 148–152

Journal of
ALLOYS
AND COMPOUNDS

Rhenium effect on bend properties at liquid nitrogen temperature in single-crystal molybdenum

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Received 10 November 1994

Abstract

With the aim of improving the low temperature strength and ductility of single-crystal molybdenum, single-crystal molybdenum–rhenium alloys were prepared by means of secondary recrystallization. Then the bend properties of these crystals were evaluated at liquid nitrogen temperature.

The results can be summarized as follows.

(1) The yield strength decreased gradually as the rhenium content increased to 10 mass%.

(2) The fracture strength of as-heated crystals increased and showed a maximum at a rhenium content of 3–7 mass%. In contrast, the fracture strength of carburized crystals did not clearly show a maximum, though the absolute value of the strength of carburized crystals was generally higher than that of as-heated crystals.

(3) The bend angle showed a maximum at a rhenium content of 5–7 mass% irrespective of carbon content. The ductility of the crystals was generally improved by adding carbon.

(4) The fractography of crystals containing 3–7 mass% rhenium was similar to that of pure Mo, whilst a crack generated at one of the massive island grains in the crystal with 10 mass% rhenium.

Keywords: Rhenium effect; Bend properties; Molybdenum; Liquid nitrogen temperature

1. Introduction

Fujii et al. [1,2] reported that large-scale sheets of single-crystal molybdenum can be prepared by adding a proper amount of dopants such as CaO and/or MgO, by controlling the working process so as to maintain the reduction in area over a critical value of about 60% and lastly by heating the sample at high temperatures typically above 2373 K. The low temperature fracture behaviour of these crystals was also investigated [3–5] and the results can be summarized as follows. Firstly, the crack(s) always generated at one of the island grains and the fracture strength of the crystal apparently depended on the size of the island grain at which the crack generated. Secondly, the fracture strength of the crystal was generally enhanced by adding a small amount of carbon and the carburized crystals indicated no size dependence.

In order to improve the strength and ductility of single-crystal molybdenum, the addition of a specific alloying element is one of the prospective ways. Therefore in this study four molybdenum–rhenium alloys were heated at 2573 K for 18 ks in vacuum. Then bend tests were carried out at liquid nitrogen temperature and the rhenium effect on the strength and ductility were investigated. In a previous paper [6] we reported that rhenium alloying enhances both the intergranular and transgranular fracture strengths of polycrystalline molybdenum, with the maximum effect occurring at a rhenium content of 10 mass%. Additionally, the low temperature ductility increased as the rhenium content increased to 10–13 mass%. More recently it was reported [7] that hardening of single-crystal molybdenum can be achieved by surface alloying with rhenium using an electron beam of high power density.

2. Experimental

The starting materials were powder metallurgy molybdenum–rhenium (3, 5, 7 and 10 mass%) alloys of about 1 mm thickness supplied by Tokyo Tungsten Co., Ltd. These materials are designated “Mo–3Re”, “Mo–5Re”, Mo–7Re” and “Mo–10Re” alloys in this paper. Rectangular samples of dimensions 50 mm × 30 mm were cut out from the sheets and then subjected

SSDI 0925-8388(95)01515-9

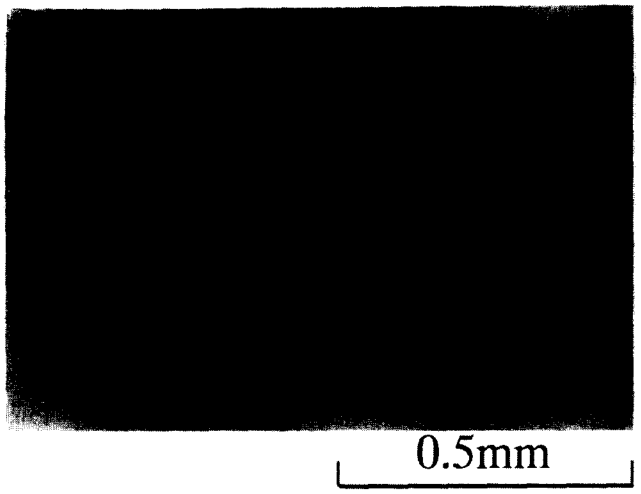

Fig. 1. Sketch of the typical grain structure in the as-heated Mo–10Re alloy.

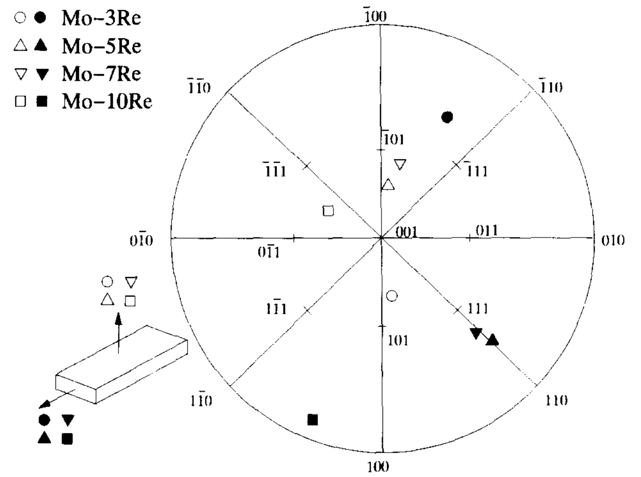

Fig. 2. Crystallographic orientations of as-heated crystals of Mo–Re alloys.

to the following heat treatment. The samples were heated at 2573 K for 18 ks in a vacuum of about 1.3×10^{-4} Pa (designated "as-heated"). The grain structures of the alloy samples after heating were observed using an optical microscope. The Mo–3Re, Mo–5Re and Mo–7Re alloys showed a single-crystal grain structure, apparently the same as that of pure molybdenum (designated "pure Mo") prepared by means of secondary recrystallization. However, in the Mo–10Re alloy a number of massive island grains were observed at the specimen surface as sketched in Fig. 1. Half of the as-heated samples were then subjected to a carburizing treatment (designated "carburized"). The surface of the as-heated sample was carbon vaporized and then heated in vacuum at 1773 K for 1.2 ks. This treatment was carried out in order to enhance the interface strength between the island grains and the matrix.

From the as-heated and carburized samples, bend test specimens 4 mm wide and 30 mm long were cut out and subjected to mechanical and electrolytical polishing. Three-point bend tests were carried out at liquid nitrogen temperature at a cross-head speed of 0.017 mm s^{-1}. The surface and axial orientations of the as-heated crystals are plotted in a (001) stereographic projection in Fig. 2. It is noted that the crystallographic orientations of the single-crystal Mo–3Re, Mo–5Re and Mo–7Re alloys were very similar to each other.

The fracture surfaces of failed specimens were observed using a scanning electron microscope and the crack generation and propagation characteristics were investigated. Then the size of the crack generation site was measured.

3. Results

The yield and fracture strengths of the as-heated and carburized crystals are plotted against the rhenium content in Figs. 3 and 4 respectively. The tensile test data [6] obtained for recrystallized and carburized polycrystals of molybdenum–rhenium alloys are also plotted in these figures for comparison. It is noted that

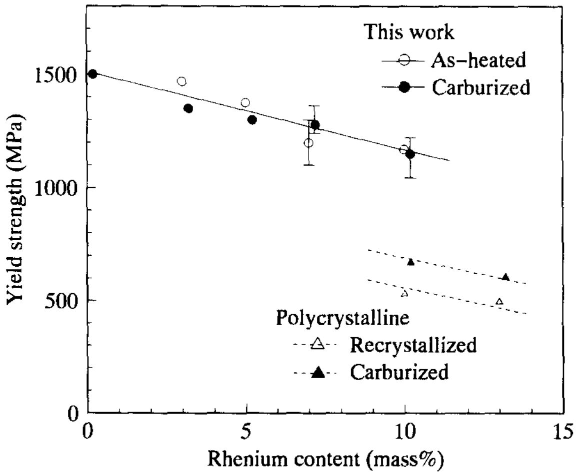

Fig. 3. Plots of yield strength against rhenium content.

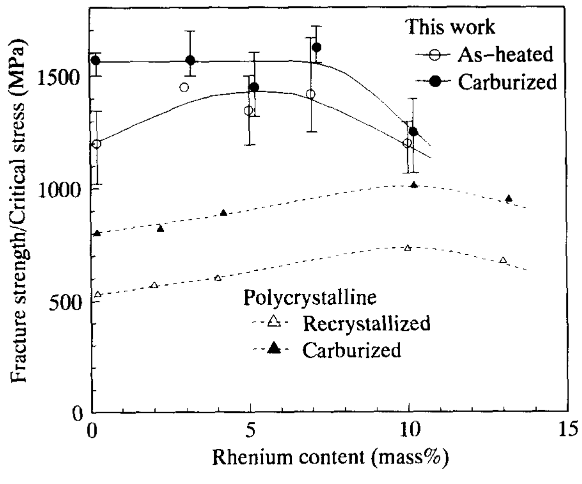

Fig. 4. Plots of fracture strength against rhenium content.

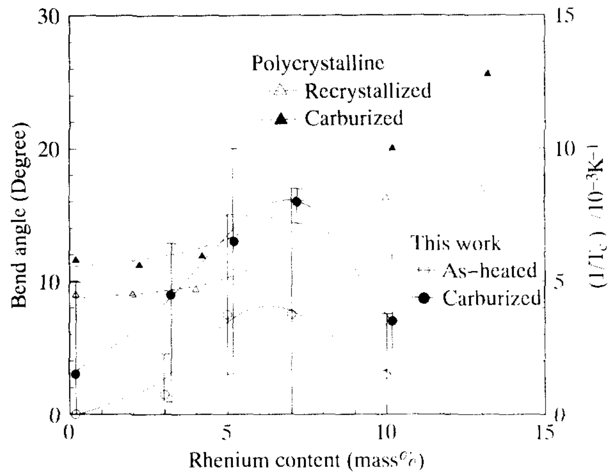

Fig. 5. Plots of bend angle against rhenium content.

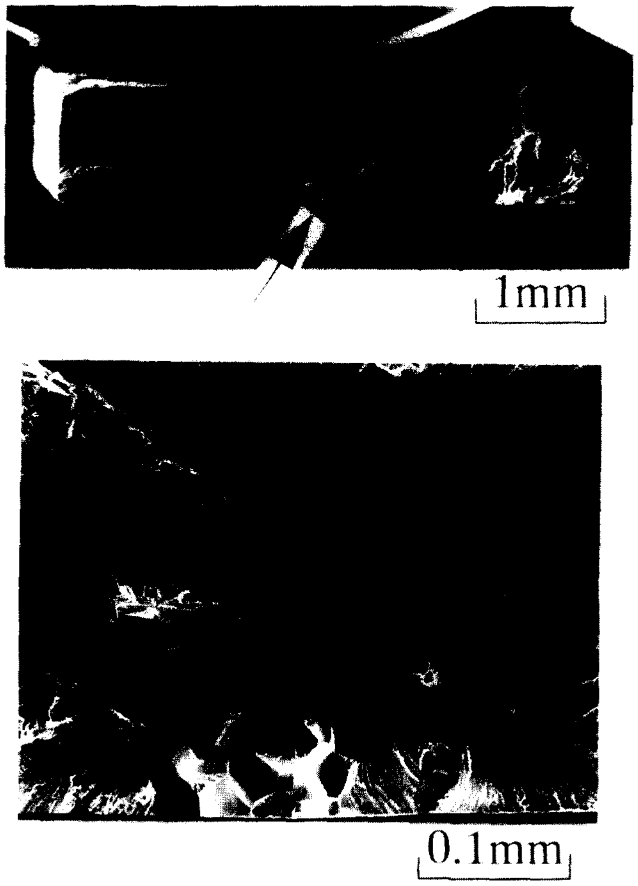

Fig. 6. Typical fractograph of the as-heated Mo–10Re alloy.

the low temperature fracture strength and ductility in the tensile tests are represented by the critical stress and $1/T_c$ (T_c is the critical temperature) [8] respectively. The critical stress is the stress that propagates microcracks intergranularly and/or transgranularly at and around T_c. T_c is an expression of the ductile-to-brittle transition temperature. The yield strength of the crystals decreased gradually as the rhenium content increased, notwithstanding carbon addition. This result is qualitatively consistent with that of the polycrystals, though the applicable data are limited. On the other hand, the change in fracture strength in the single crystals as a function of rhenium content was not simple, since there was a scattering of the data. The fracture strength of the as-heated crystals showed a maximum at a rhenium content of 3–7 mass%. In contrast, the fracture strength of the carburized crystals did not show a maximum for a rhenium content of 3–7 mass% and was almost as high as that of the carburized single crystal of pure Mo. However, the fracture strength began to decrease with a further increase in rhenium content. These results are qualitatively inconsistent with those for the polycrystalline molybdenum–rhenium alloys. In the polycrystalline alloys the critical stress tended to show a maximum at a rhenium content of 10 mass% notwithstanding carbon addition. In any case the fracture strength of the carburized crystals was generally higher than that of the as-heated crystals.

The bend angle prior to fracture of the crystals is plotted against the rhenium content in Fig. 5. The bend angle showed a maximum at a rhenium content of 5–7 mass% notwithstanding carbon addition, though there was again a scattering of the data. Additionally, the bend angle of the carburized crystals was generally larger than that of the as-heated crystals.

The fracture surfaces of the crystals were examined in detail using the scanning electron microscope. The fractography of the as-heated single crystals of Mo–3Re, Mo–5Re and Mo–7Re alloys was similar to that of the single crystal of pure Mo. The crack always generated at one of the island grains existing at or near the specimen surface where maximum fibrous tensile stress was applied. Then the crack propagated along specific crystal planes. In the Mo–10Re alloy the crack generated at one of the massive island grains and/or at a polycrystalline layer as shown in Fig. 6. The fractography of the carburized crystals was generally similar to that of the as-heated crystals. The only differences were that, first, a number of carbides were recognized on the interfaces between the island grains and the matrix and, secondly, the crack generated at other site(s) besides the island grain(s) in some cases.

4. Discussion

As already reported in our previous papers, the fracture strength of single-crystal molybdenum [3,4] and tungsten [9] produced by means of secondary recrystallization is closely related to the size of island grains. According to Griffith's criterion [10] for a surface crack in a semifinite plate,

$$F^* = k\left(\frac{E\gamma}{c}\right)^{1/2} \tag{1}$$

where F^* is the resolved normal component of the applied stress (F). Thus F^* is equal to $F\cos\theta$, where θ is the angle between the axis of fibrous stress and the axis normal to the cleavage fracture plane. The value of θ was estimated in terms of the crystallographic orientations of the specimen by considering that the cleavage planes are {110} in this study. E is the Young modulus in the direction normal to the specific plane, γ is the surface energy of the plane, c is the crack depth and k is a constant depending on the specimen and crack geometries. Eq. (1) is then transformed into

$$E_{110}^{-1/2}F\cos\theta = k\gamma^{1/2}c^{-1/2} \qquad (2)$$

where $E_{110} = 3.64\times10^5$ MPa [11].

In Fig. 7 the value of $E_{110}^{-1/2}F\cos\theta$ is plotted against $c^{-1/2}$, where c is the size of the island grain at which the crack generated. One datum for the as-heated Mo–10Re alloy is also plotted in the figure for reference, by assuming that c is the size of the massive island grain at which the crack generated. The data [4] for single-crystal pure Mo whose fracture planes are {110} are indicated by the hatched zone including the scattering of data in the figure. It is obvious that the data for the as-heated crystals are approximately in agreement with the data for single-crystal pure Mo. It may therefore be concluded that the large difference in the fracture strength between specimens and alloys is attributable primarily to the difference in the size of island grains and somewhat to the difference in crystallographic orientations. The data for the carburized crystals seem to support such an explanation, since the fracture strength was generally enhanced by adding carbon and was independent of the size of island grains in a similar manner to that reported for single-crystal pure Mo [3,4]. The substantial reduction in the strength at a rhenium content of 10 mass% is therefore due to the grain structure in the vicinity of the specimen surface where massive island grains exist.

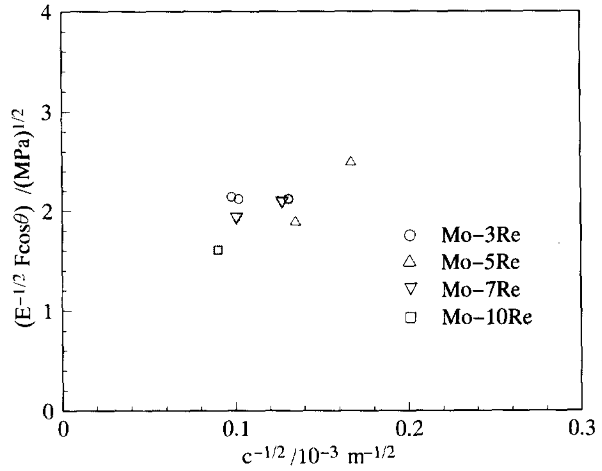

Fig. 7. Plots of $E_{110}^{-1/2}F\cos\theta$ against $c^{-1/2}$.

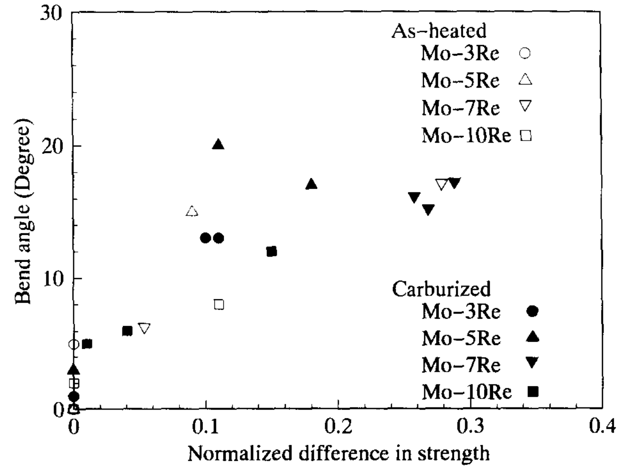

Fig. 8. Plots of bend angle against normalized difference in strength.

We showed in Ref. [6] that the apparent transgranular fracture strength increases as the rhenium content increases. The increase in the transgranular fracture strength upon adding 7 mass% rhenium is about 15% and such an increase in the strength should reflect directly on the increase in the slope of the linear relationship. However, the scatter in the data was large and it was impossible to recognize the difference between single-crystal pure Mo and the alloys in this study.

The change in the bend angle as a function of rhenium content is interpreted as follows. The ductility of a material is determined by both the yield and fracture strengths (or tensile strength) by assuming that the work-hardening characteristics are similar [12]. In Fig. 8 the bend angle is plotted against the difference between the yield and fracture strengths. Here the difference in strength was normalized by the yield strength of each specimen. There was a tendency for the bend angle to increase as the difference in strength increased. Thus the maximum appearing in the bend angle at a rhenium content of 5–7 mass% was only a result of two factors, i.e. the yield strength depending on the rhenium content and the fracture strength depending on the size of island grains. Additionally, the higher ductility of the carburized crystals compared with the as-heated crystals was attributed to the enhancement of the interface strength between the island grains and the matrix due to carbon addition, with the yield strength being unchanged.

5. Conclusions

(1) The yield strength decreased gradually as the rhenium content increased, notwithstanding carbon addition.

(2) The fracture strength of the as-heated crystals increased with increasing rhenium content and showed a maximum at a rhenium content of 3–7 mass%.

(3) The fracture strength of the carburized crystals was generally higher than that of the as-heated crystals. The fracture strength of the carburized crystals with a rhenium content of 3–7 mass% was as high as that of pure Mo and no maximum was observed. A further increase in rhenium content led to a decrease in the fracture strength.

(4) The bend angle showed a maximum at a rhenium content of 5–7 mass% notwithstanding carbon addition. The ductility of the carburized crystals was generally higher than that of the as-heated crystals.

Acknowledgment

The author would like to express his appreciation to Dr. Tadayuki Fujii of the National Research Institute for Metals for his fruitful discussion.

References

[1] T. Fujii, R. Watanabe, Y. Hiraoka and M. Okada, *J. Less-Common Met., 96* (1984) 297.

[2] T. Fujii, R. Watanabe, Y. Hiraoka and M. Okada, *J. Less-Common Met., 97* (1984) 163.

[3] Y. Hiraoka, M. Okada, T. Fujii and R. Watanabe, *J. Less-Common Met., 97* (1984) 99.

[4] Y. Hiraoka, M. Okada, T. Fujii and R. Watanabe, *J. Less-Common Met., 97* (1984) 117.

[5] Y. Hiraoka, T. Fujii, M. Okada and R. Watanabe, *Trans. Jpn. Inst. Met., 26* (1985) 332.

[6] Y. Hiraoka, *J. Jpn. Inst. Met., 56* (1992) 161.

[7] Y. Hiraoka, *J. Alloys Comp., 177* (1991) L1.

[8] Y. Hiraoka, *Mater. Trans., JIM, 31* (1990) 861.

[9] Y. Hiraoka and T. Fujii, *Z. Metallkd., 84* (1990) 275.

[10] A.A. Griffith, *Philos. Trans. R. Soc. Lond. A, 221* (1921) 163.

[11] R. Ayre and D.F. Stein, *Acta Metall., 19* (1971) 789.

[12] J.H. Bechtold and E.T. Wessel, in J.J. Harwood (ed.), *The Metal Molybdenum,* ASM, Cleveland, OH, 1958, p. 241.