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## EFFECT OF CERTAIN OXIDES ON THE RECRYSTALLIZATION OF MOLYBDENUM

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In view of its inherent properties, molybdenum is suitable for use at high temperatures. Molybdenum is ordinarily strengthened by alloying followed by a thermomechanical treatment. Alloys which are strengthened by dispersed particles of a second, hard phase have attracted much attention in recent years [1-3]. For instance, a sintered aluminum alloy containing  $Al_2O_3$  has a much higher long-time rupture strength than other heat-resistant aluminum alloys [4, 5].

This work is concerned with the effect of the oxides  $TiO_2$ ,  $ZrO_2$ ,  $ThO_2$ , as well as a complex addition containing titanium with  $ZrO_2$ , on the recrystallization of molybdenum. Not more than 0.5% of the oxides  $ZrO_2$  and  $TiO_2$  or 2% of  $ThO_2$  were added to the molybdenum.

All the alloys were prepared by powder metallurgy methods. Molybdenum powder Mch (99.97%) was used as raw material. Particles of  $ZrO_2$  and  $ThO_2$  were added to the molybdenum chemically, by saturating the molybdenum powder with an aqueous solutions of zirconium nitrate and thorium nitrate; the appropriate Zr and Th oxides were

formed during subsequent sintering. Alloys with  $TiO_2$  additions were prepared by mechanical mixing of molybdenum with titanium oxide powders in an alc. suspension. Alloys of molybdenum with additions of Zr and Th oxides were sintered by passing electric current through the appropriate compacted mixtures. The sintering temperature was about 2400°C. Alloys with additions of  $TiO_2$  were sintered at 1700°C in a tubular electric furnace, in wet hydrogen. The oxide contents of the various molybdenum alloys are shown in the Table.

The sintered specimens were forged at 1400-1300°C to 2.5 mm dia. rods and drawn at 800-700°C to 0.8 mm dia. (92% reduction).

In the recrystallization studies, all specimens were held for 30 minutes in a salt bath at temperatures from 900 to 1300°C. Microhardness tests, microscopy and X-rays were used. As a symptom of recrystallization, we regarded the fall of microhardness or the appearance of interference spots on the lines of the X-raygrams obtained with Cr radiation. For microhardness measurements and observations

TABLE I\*

Alloy No.	Oxide Content	Recrystallization Threshold °C	Alloy No.	Oxide Content	Recrystallization Threshold °C
1	0,176% $ZrO_2$	1000	6	0,45% $TiO_2$	1150
2	0,402% $ZrO_2$	1150	7	0,57% $ThO_2$	1100
3	0,483% $ZrO_2$	1210	8	0,53% $ThO_2$	1150
4	0,084% $TiO_2$	1200	9	1,72% $ThO_2$	920
5	0,217% $TiO_2$	1190	10	0,706% $ZrO_2$ +0,475% Ti	1260

\*All commas are equivalent to a decimal point.

of microstructure, the surface was polished using a solution of 50 g potassium ferricyanide, 3 g sodium hydroxide and 20 g of  $\text{Al}_2\text{O}_3$  powder in 1000 ml  $\text{H}_2\text{O}$ . Polishing and etching was repeated several times to remove the work-hardened layer.

The effect of the annealing temperature on microhardness of molybdenum and its alloys is seen in Figs. 1-4. Recrystallization of pure molybdenum starts at  $900^\circ\text{C}$ .

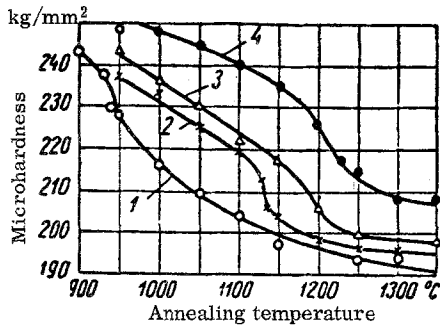


Fig. 1. Effect of annealing temperature on microhardness of Mo +  $\text{ZrO}_2$  wire: 1 - Mo; 2 - Mo + 0.1%  $\text{ZrO}_2$ ; 3 - Mo + 0.3%  $\text{ZrO}_2$ ; 4 - Mo + 0.5%  $\text{ZrO}_2$ .

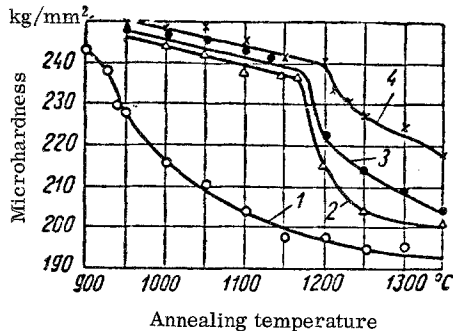


Fig. 2. Effect of annealing temperature on microhardness of Mo +  $\text{TiO}_2$  wire: 1 - Mo; 2 - Mo + 0.5%  $\text{TiO}_2$ ; 3 - Mo + 0.3%  $\text{TiO}_2$ ; 4 - Mo + 0.1%  $\text{TiO}_2$ .

Figure 1 shows that the best composition of the three molybdeMo-alloys with zirconium oxide additions is an alloy with 0.5%  $\text{ZrO}_2$ . The loss of microhardness started in this case at  $1200^\circ\text{C}$ . With a decreasing proportion of oxide, the microhardness of the alloys was impaired.

Figure 2 refers to the effect of titanium oxide additions. The highest recrystallization temperature was obtained at 0.1%  $\text{TiO}_2$ , the microhardness decreasing when the percent of oxide increased to 0.5%.

Thorium oxide was less effective in increasing the recrystallization temperature. The best alloy with 1%  $\text{ThO}_2$ , Figure 3, had a recrystallization threshold of about  $1150^\circ\text{C}$ . More or less  $\text{ThO}_2$  lowered the recrystallization temperature.

The most interesting the alloy of Mo with 0.5% Ti and 0.5%  $\text{ZrO}_2$ : It retained a high hardness up to the annealing temperature ( $1260^\circ\text{C}$ ) which is  $350^\circ\text{C}$  above the recrystallization temperature of pure Mo, Figure 4.

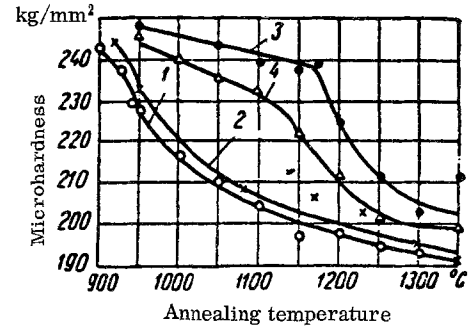


Fig. 3. Effect of annealing temperature on microhardness of Mo +  $\text{ThO}_2$  wire: 1 - Mo; 2 - Mo + 2%  $\text{ThO}_2$ ; 3 - Mo + 1%  $\text{ThO}_2$ ; 4 - Mo + 0.5%  $\text{ThO}_2$ .

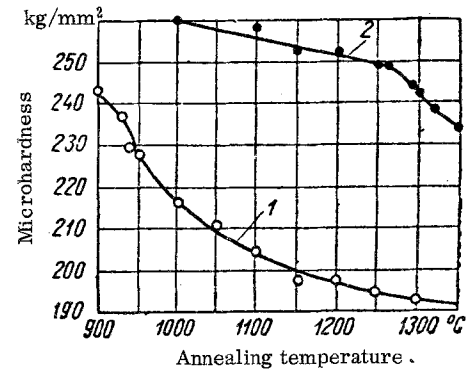


Fig. 4. Effect of annealing temperature on microhardness of Mo (1) and Mo + 0.5%  $\text{ZrO}_2$  + 0.5% Ti (2) alloy wire.

The X-ray results are included in the Table.

Addition of oxides hampered the recrystallization and grain growth in most of the alloys. Figure 5 depicts the relation between composition and grain size after annealing at  $1300^\circ\text{C}/30$  min. The grain size was determined on a longitudinal section. For each of the systems studied there was an optimum oxide content which was the most effective in raising the recrystallization temperature, Figure 6. It is interesting that alloys with the highest recrystallization temperatures had almost identical oxide contents on a volume basis, especially in the case of  $\text{ZrO}_2$  and  $\text{ThO}_2$ . Apparently the slowing-down of the recrystallization and grain growth processes after an addition of a definite amount of a second phase can be explained by the formation of thin films by oxides located along the grain boundaries.

The alloy with 0.5%  $\text{ZrO}_2$  and 0.5% Ti had the highest recrystallization temperature since recrystallization was hampered both by the action of the zirconium oxide particles and by alloying with titanium.

## CONCLUSION

1. Recrystallization and grain growth in molybdenum is obstructed by additions of titanium, zirconium and thorium oxides. For each of the Mo-oxide systems there is a definite optimum oxide content which had the most pronounced effect on recrystallization.

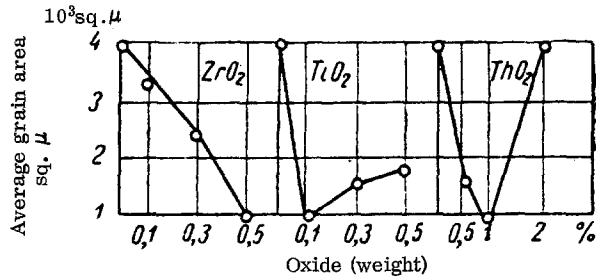


Fig. 5. Effect of oxide content on grain size of Mo after annealing at 1300°C/30 min.

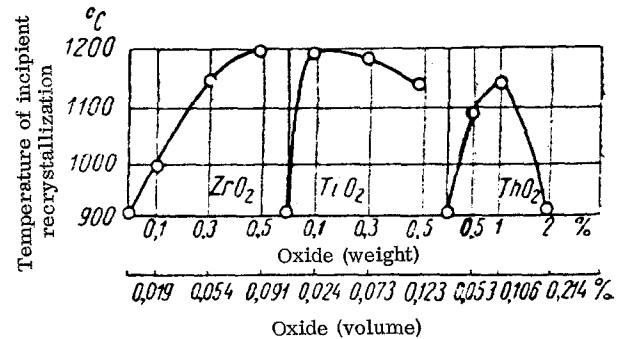


Fig. 6. Effect of oxide content on recrystallization threshold.

2. The most effective were additions of 0.1% TiO<sub>2</sub>, 0.5% ZrO<sub>2</sub> and 0.5% ZrO<sub>2</sub> + 0.5% Ti. The recrystallization temperature in the first two alloys exceeded that of molybdenum by 300°C and of the third, by 350°C.

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## MECHANISM OF RECRYSTALLIZATION AFTER SMALL DEFORMATIONS

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There are two basic viewpoints about the mechanism of structure formation during recrystallization following small strains. S. S. Shteinberg, E. Houdremont, D. M. Nakhimov, R. Mehl and others consider that the mechanisms of recrystallization immediately after a critical deformation and after large strains are identical, recrystallization taking place by formation of nuclei of new, undistorted grains. The coarse grain found after a critical deformation is attributable to the small number of such nuclei. E. M. Savitskii, A. P. Gulyaev, Ya. R. Rauzin and this author consider that the large grain is formed during growth of some of the initial grains at the expense of their neighbors.

It was shown in [1-3] that deformation, beginning from small values, essentially occurs by intracrystalline shear and not by intergranular displacements. There is no qualitative difference between the character of the subcritical and the critical deformations. Heating after a subcritical deformation is accompanied by polygonization while after a critical, by growth of some of the initial grains at the expense of others. At critical strains, there is a formation and growth of nuclei of undistorted grains. Heating

after intermediate deformation involves both these processes.

In the same publications, a suggestion was made and partially supported by experiments, that the main driving force for grain growth after critical deformation is the inhomogeneous strain and differences between the levels of the strain energy of neighboring grains. A definite gradient of such elastic strains in coating grains is necessary for critical growth. The magnitude of such a gradient depends on heating conditions.

According to other views, principal importance is attributed to the establishment of contact among adjacent grains during critical deformation [4].

This work contains experimental data on the mechanism of structural changes during heating after small deformations. X-ray photography and metallographic methods were employed.

Figure 1 displays the X-raygrams of compacted