ISSN 0543-5846
METABK 46 (4) 233-236 (2007)
UDC - UDK 539.4:669.28–138=111

THE EFFECT OF HEAT TREATMENT ON MECHANICAL CHARACTERISTICS AND NATURE OF FAILURE OF SHEET MOLYBDENUM ALLOYS

Received - Primljeno: 2006-08-20
Accepted - Prihvaćeno: 2007-03-25
Original Scientific Paper - Izvorni znanstveni rad

The annealing temperature within the range of 1223 - 2273 K has been studied for its effect on the grain size, mechanical properties, cold brittleness temperature, and nature of failure of sheets molybdenum alloys TsM-6 and TsM-10. The method of Auger-electron microscopy has been used to study the change of carbon and oxygen content on grain boundaries of the alloy TsM-10 and the change of mechanical properties associated with it as dependent on the annealing temperature.

Key words: *molybdenum alloys, heat treatment, the method of Auger-electron microscopy, grain size, nature of failure*

Učinak toplinske obradbe na mehanička svojstva i karakter loma traka molibdenskih legura. Istraživan je utjecaj temperaturnog žarenja u dijapazonu 1223 - 2273 K na veličinu zrna, mehanička svojstva, temperaturu hladnog loma i karakter razaranja traka molibdenskih legura TsM-6 i TsM-10. Auger-metodom elektronske mikroskopije istraživana je promjena sadržaja ugljika i kisika na granici zrna legure Tsm-10 i povezano s tim promjene mehaničkih karakteristika u zavisnosti od temperature žarenja.

Ključne riječi: *molibdenske legure, toplinska obradba, metoda Auger-elektronske mikroskopije, veličina zrna, karakter loma*

INTRODUCTION

Of the industrial molybdenum alloys there is extensive use of TsM-6 and TsM-10 as structural high-temperature materials. They relate to low-alloy aging materials in which after specific heat treatment it is possible to form dispersed precipitates of a second phase. The mechanical properties of these alloys are to a considerable degree due to their structural state.

In the literature consideration has been given to the effect of heat treatment on the aging process in molybdenum alloys [1, 2], and also on the wide range mechanical properties of these alloys [3 - 11].

Results are presented in the present communication for a study of the effect of annealing temperature for rolled molybdenum alloys TsM-6 and TsM-10 on their mechanical properties and nature of failure at room temperature.

MATERIAL, TREATMENT AND TESTING

The chemical composition of the test alloys is given in Table 1. Mechanical tests were carried out in a VTU-2V device on five proportional specimens in the worked condition and after 1 h of annealing in the temperature range 1223 - 2273 K [12]. Specimens were cut from sheets 1,0 mm thick along the rolling direction. The deformation rate was 2 mm/min, which corresponds to a relative deformation rate $2,2 \cdot 10^{-3}\ s^{-1}$. As a result of testing tensile strength R_m, proof strength $R_{p0,2}$, the percentage elongation after fracture A, and the percentage reduction of area Z were found [13].

The cold brittleness temperature T_c was determined in specimens cut along the rolling direction in bending tests by a three-point loading scheme and a deformation rate of

Table 1. **Chemical composition of molybdenum alloys, wt. %**
Tablica 1. **Kemijski sastav molibdenskih legura, tež. %**

Alloy	Zr	Al	B	C	O_2	N_2	H_2
TsM-6	0,12	-	0,0022	0,003	0,003	0,005	0,0004
TsM-10	-	0,01	0,0018	0,007	0,002	0,001	0,0005

V. V. Buchanovsky, Pisarenko Institute of Problems of Strength National Academy of Sciences of Ukraine, Kiev, Ukraine, I. Mamuzić, Faculty of Metallurgy University of Zagreb, Sisak, Croatia, E. P. Polishuk, Paton Welding Institute National Academy of Sciences of Ukraine, Kiev, Ukraine

2 mm/min. The cold brittleness temperature was taken as the minimum temperature at which the test specimen held a bend by 90° without failure or occurrence of cracks.

Heat treatment (annealing) was carried out in a vacuum furnace at a pressure of $2{,}6\cdot10^{-3}$ Pa. After soaking for 1 h at the prescribed annealing temperature specimens were cooled in the furnace.

RESULTS AND DISCUSSION

It was established that an increase in annealing temperature to 2273 K causes grain growth and leads to steady weakening of the test alloys (Figures 1. and 2.). This weakening indicates that during cooling the strengthening phase either does not precipitate altogether, or it precipitates in a small amount. The cold brittleness temperature for alloy TsM-10 increases uniformly with an increase in annealing temperature, but percentage elongation changes by a curve with a maximum corresponding to the treatment temperature T_{an} in the range 1423 - 1523 K. The change in cold brittleness temperature T_c for alloy TsM-6 is more complex in nature. Up to T_{ann} = 1573 K it increases, in the range 1573 - 1873 K it decreases to the original value, and subsequent increase in annealing temperature promotes an increase in cold brittleness temperature. The dependence of percentage elongation for alloy TsM-6 on annealing temperature is reverse in nature to the relationship T_c - T_{ann}.

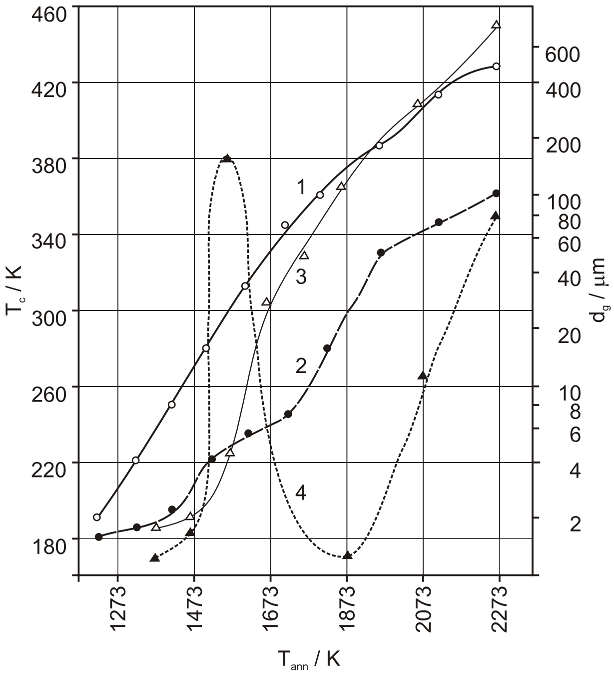

Figure 1. **Effect of annealing temperature on grain size (solid line) and cold brittleness temperature (broken lines) for alloys TsM-10 (1, 2) and TsM-6 (3, 4)**

Slika 1. **Učinak temperature žarenja na granici zrna i temperatura hladnog loma (isprekidane crte) za legure TsM-10 (1, 2) i TsM-6 (3, 4)**

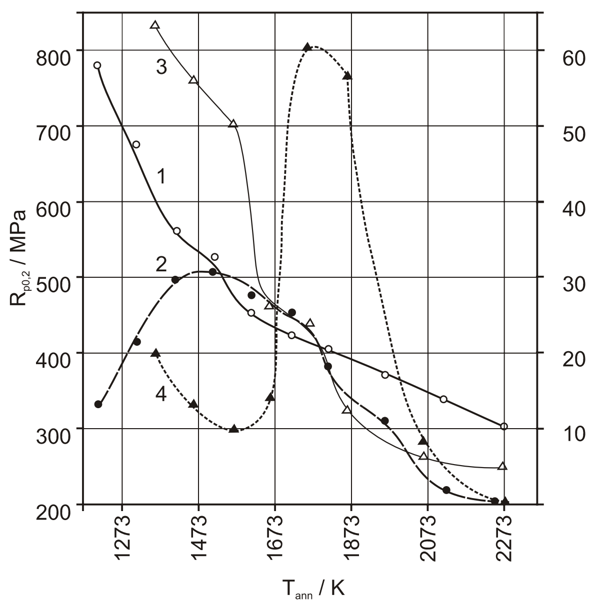

Figure 2. **Effect of annealing temperature on proof strength (solid line) and percentage elongation (broken lines) for alloys TsM-10 (1, 2) and TsM-6 (3, 4)**

Slika 2. **Učinak temperture žarenja na granicu razvlačenja i relativno izduženje (isprekidane crte) za legure TsM-10 (1, 2) i TsM-6 (3, 4)**

The microstructure of molybdenum alloy TsM-10 (Figure 3.a, b) in the as-supplied condition is fibrous, and the dislocation structure is quite equiaxed cells with a size of about 2 μm and a low dislocation density. Annealing the alloy at 1223 K is accompanied by a marked coarsening of the cells as a result of the disappearance of some of their boundaries. A further increase in temperature intensifies cell growth, and with T_{ann} = 1423 K the process of primary recrystallization is almost complete (Figure 3.c). In the temperature range 1423 - 1623 K in alloy TsM-10 sheet

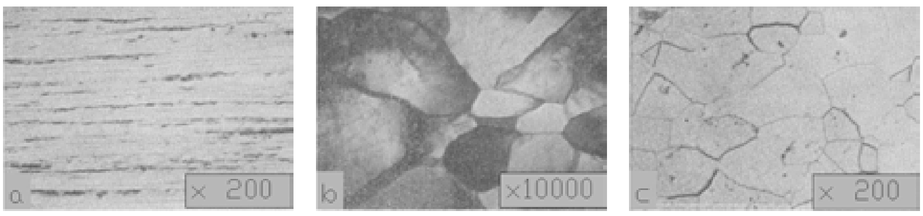

Figure 3. **Effect of annealing temperature on alloy TsM-6 microstructure: a), b) T_{ann} = 1223 K; c) T_{ann} = 1423 K**

Slika 3. **Učinak temperature žarenja na mikrostrukturu leguru TsM-6: a), b) $T_{žarenja}$ = 1223 K; c) $T_{žarenja}$ = 1423 K** there is selective recrystallization which at higher temperatures changes into secondary recrystallization. Recrystallization processes in alloy TsM-6 proceed in a similar way, only shifted into the higher temperature regions.

Content of carbon in alloy TsM-10 is greater than in alloy TsM-6, although in the latter the recrystallization temperature is higher. This indicates that carbon in the free state or in the form of molybdenum carbides has little effect from the point of view of delaying recovery and recrystallization processes. However, the rate of grain growth after recrystallization in alloy TsM-6 is much greater than for alloy TsM-10, and after annealing at a temperature exceeding 2123 K the grain size of alloy TsM-10 becomes less than in alloy TsM-6. Thus, the nature of grain growth at temperatures above the recrystallization temperature clearly indicates that transfer of zirconium into solid solution is less effective for delaying grain boundary migration at high temperature compared with precipitation of highly dispersed carbide phase.

The relationship T_c - T_{ann} for alloy TsM-6 is in good agreement with results obtained in studying the effect of rolling temperature on the mechanical properties of this alloy [14, 15]. Annealing of the basic metal at 1573 K, as for rolled product at the same temperature, is accompanied by an increase in T_c. In all probability processes occurring in alloy TsM-6 during rolling and annealing at this temperature are mainly identical. Rolling at 1573 K leads to dynamic strain aging, and annealing at this temperature also promotes strain aging. By causing blocking of mobile dislocations with impurity atom atmospheres [16, 17] the latter promotes a reduction in the deformation capacity of individual zones of rolled sheet, which causes an increase in T_c.

With an increase annealing temperature to 1773 - 1873 K there is formation of zirconium oxycarbide. The number of second phase particles is small, and it cannot cause marked alloy strengthening, although their precipitation promotes a reduction in the concentration of oxygen and carbon impurities at the boundaries and within the body of grains. This situation also leads to a reduction in T_c.

With a higher annealing temperature zirconium oxycarbides dissolve in the matrix with subsequent precipitation during cooling of molybdenum carbide mainly along grain boundaries. Grain growth reduces the surface area of their boundaries and it increases the specific impurity content at boundaries. According to data in [2, 4, 18] this and other data cause an increase in T_c for alloy TsM-6.

A direct relationship is observed between cold brittleness temperature and grain size for molybdenum alloy TsM-10. Since carbon and oxygen content in this alloy considerably exceed their solubility in molybdenum, it is entirely possible to assume that in fact the distribution of these elements governs the level of T_c.

A study was made by the Auger-electron microscopy method of the change in carbon and oxygen content at grain boundaries of alloy TsM-10 in relation to annealing temperature (Figure 4.). An increase in temperature from 1423 to 1823 K corresponds to a continuous increase in carbon and oxygen content at grain boundaries. Probable reasons for this phenomenon may be two factors operating in one direction: an increase in solubility of these elements at boundaries and a reduction in the surface area of boundaries. Analysis of the ratio of grain boundary surface area and amount of oxygen contained in them indicates that up to T_{ann} = 1623 K the increase in specific concentration of oxygen corresponds entirely with reduction in grain boundary surface area.

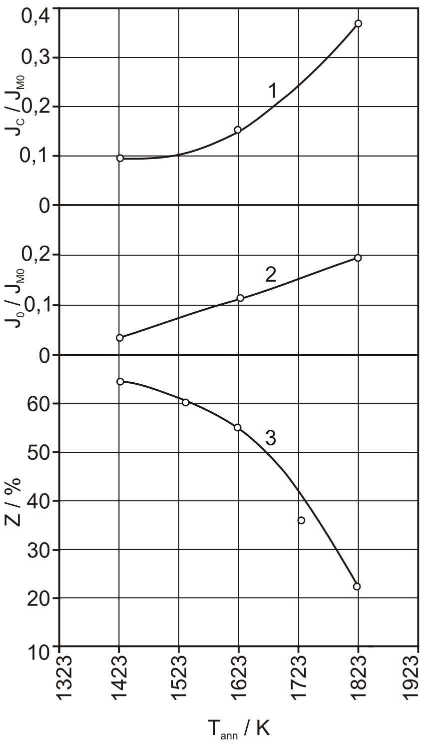

Figure 4. **Effect of annealing temperature on some alloy TsM-10 characteristics: 1, 2 – relative intensity of carbon and oxy-gen peaks at the surface of grain boundaries respectively; 3 – percentage reduction of area**

Slika 4. **Učinak temperature žarenja na neke karakteristike legure TsM-10: 1, 2 – odgovarajući relativni intenzitet pikova ugljika i kisika na površini granice zrna; 3 – relativno suženje poprečnog presjeka**

After annealing at above 1623 K the total content of oxygen at grain boundaries decreases, which may be a result first of “loss” from boundaries of oxygen atoms during heating as a result of sharp increase in their mobility, and second, a marked increase in the diffusion path of oxygen atoms toward grain boundaries and insufficient soaking at the annealing temperatures. The latter assumption is based on experimental and calculated data according to which an increase in annealing temperature from 1423 to 1823 K is accompanied by an increase in average grain diameter by almost a factor of thirteen, whereas the distance covered by oxygen atoms diffusing in molybdenum increases in all by only a factor of 1,5.

A similar picture is observed for carbon distribution in alloy TsM-10 in relation to annealing temperature.

Thus, redistribution of carbon and oxygen between the body of grain and its boundaries is one of the decisive factors governing the level of mechanical properties for the alloy, in particular its low-temperature ductility.

Analysis of the fracture surface of specimens tested in tension at room temperature indicates that the nature of their failure is governed by annealing temperature, i. e., almost by grain size. After annealing at a temperature below that for primary recrystallization (for alloy TsM-10, $T < 1423$ K, for alloy TsM-6, $T < 1573$ K) specimen failure occurs by macrolamination, and within each layer there is a pitted character (Figure 5.a).

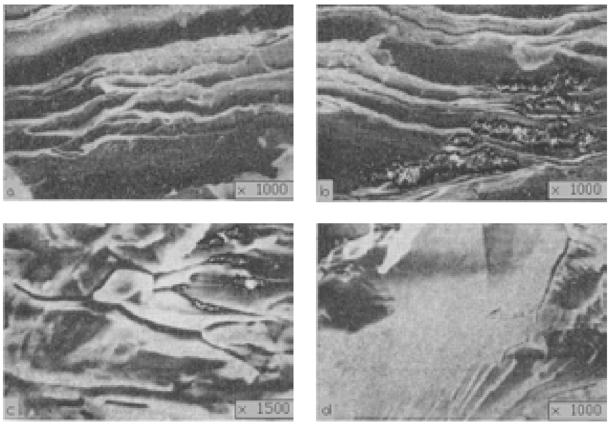

Figure 5. **Effect of annealing temperature on the nature of failure for molybdenum alloy TsM-10: a) T_{ann} = 1223 K; b) T_{ann} = 1423 K; c) T_{ann} = 1523 K; d) T_{ann} = 1823 K**

Slika 5. **Učinak temperature žarenja na prirodu loma za molibdensku leguru TsM-10: a) $T_{žarenja}$ = 1223 K; b) $T_{žarenja}$ = 1423 K; c) $T_{žarenja}$ = 1523 K; d) $T_{žarenja}$ = 1823 K**

After completing primary recrystallization lamination is still retained. This indicates that the grain structure formed in this way retains a laminated character (Figure 5.b), and only an increase in grain size to 15 - 20 μm (for alloy TsM-10 it is reached by annealing at 1523 K, and for alloy TsM-6 at 1673 K) is macrolamination completely avoided and a changeover is provided to microlamination combined with shear (Figure 5.c). An increase in annealing temperature for alloy TsM-10 to 1823 K, and for alloy TsM-6 to 1973 K leads to development of transcrystalline failure combined with brittle intercrystalline failure (Figure 5.d). A further increase in annealing temperature promotes an increase in the proportion of intercrystalline component in the fracture of specimens.

CONCLUSIONS

1. An increase in annealing temperature for worked molybdenum alloys is accompanied by a uniform reduction in proof strength. The most marked reduction in $R_{p0,2}$ is observed with an annealing temperature corresponding to that for the primary recrystallization range.
2. Maximum values of relative elongation are noted after annealing at temperature corresponding to that of the selective recrystallization range.
3. Redistribution of oxygen and carbon between boundaries and the body of grains has a marked effect on molybdenum alloy ductility.

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