Academician of the Academy of Sciences of the Ukrainian SSR V. N. Svechnikov, G. F. Kobzenko

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Abstract

Full Text

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Academician of the Academy of Sciences of the Ukrainian SSR V. N. Svechnikov, G. F. Kobzenko

THE PHASE DIAGRAM OF CHROMIUM–MOLYBDENUM

A number of data ([1–6, 13]) on the binary system Cr–Mo establish unlimited solubility of the components in the solid state. However, in a number of works results have been obtained that do not agree with these conclusions ([7–12]).

We have carried out an investigation of alloys of this system by thermal, X-ray structural, and dilatometric methods. Along with this, the change in the macrohardness of the alloys at different temperatures was studied.

Preparation of alloys and heat treatment

For the investigation, 15 alloys were melted and subjected to chemical analysis. The alloys were prepared from electrolytically refined Cr of 99.95% purity and Mo of 99.9% purity. Melting of the charge (flake Cr and powdered Mo) was carried out in a laboratory arc furnace ([14]). Ingots weighing 30-40 g were remelted 5-7 times in an argon atmosphere purified in a gas purifier ([16]), with subsequent gettering by molten titanium. The excess gas pressure was maintained from 29400 (0.3 atm) to 58800 N/m^2 (0.6 atm). Monolithic pieces of the alloys were annealed at temperatures of 1600° (97 h), 1550° (110 h), 1350° (55 h), 1275° (85 h), 1225° (100 h), 1115° (200 h), 1000° (417 h), and 800° (900 h).

Alloys annealed at 1350° and lower temperatures were first subjected to a homogenizing anneal at 1500-1550° for 100-110 h. Anneals at 1225° and higher temperatures were carried out in a TVV-2M furnace in an atmosphere of purified argon at an excess pressure from 9800 (0.1 atm) to 19600 N/m^2 (0.2 atm), followed by cooling together with the furnace at a rate of 2-2.5 deg/sec to 900-800°. Anneals at 1115, 1000, and 800° were carried out in double quartz ampoules.* After double evacuation and flushing, the ampoules were filled with purified argon to a pressure of 29400 (0.3 atm)-49000 N/m^2 (0.5 atm) at room temperature. In the working space of the ampoules, Ti–Zr chips (800°) and Zr chips (1000 and 1115°) were placed as getters. After the anneals had been carried out, the alloys were quenched in water. Alloys were also annealed at 1700° (holding time 15 min) and quenched in oil.

Research methods

X-ray structural analysis was carried out on powders (which had undergone recrystallization annealing) in chromium radiation, in RKD-57.3 cameras, by the asymmetric method. Dilatometric analysis was carried out according to the method ([14]), at a magnification of 4000 times. As refractories, instead of fused quartz, factory-supplied Al_2O_3 was used.

The rate of heating and cooling was from 0.05 to 0.08 deg/sec. The values of $\bar{\alpha}$ (the mean coefficient of linear expansion) for the alloys were calculated from the heating curves in the temperature interval 20–1300°. Pri-

* Annealing at 1000 and 800° was interrupted 10–15 times with intermediate cooling of the ampoules in air. At 800°, powders were subjected to annealing.

the set was graduated for Mo. The value of $\bar{\alpha}_{Mo}$ was taken equal to $5.74 \cdot 10^{-6}$ deg^{-1} according to [15]; $\bar{\alpha}_k$ (for Al_2O_3), according to our data, in the temperature interval $20 \div 1300°$ is $7.42 \cdot 10^{-6}$ deg^{-1}, and $\bar{\alpha}_{Cr} = 13.18 \cdot 10^{-6}$ deg^{-1}.

Differential thermal analysis was carried out by the method [16] on cast and annealed alloys. Heating and cooling thermograms were recorded no fewer than two times for each composition. Recording was performed from room temperature to temperatures exceeding complete melting of the alloys. The temperatures were determined only from the heating curves. The heating rate in determining the temperatures of the beginning and end of melting was $0.04 \div 0.05$ deg/sec.

The temperature was measured with a BP-5/20 thermocouple [17] with an accuracy of $\pm 10°$; the sensitivity of the differential method was 20900 (0.5) ÷ 16700 J/kg (0.4 cal/g).

The alloys were melted in crucibles of Al_2O_3, MgO, and ZrO_2. Hardness was measured on a VIM-1M apparatus at 20, 600, 800, and 1000°, using diamond indenters under a load of 9.8 N (1 kg). The loading duration was 30 sec. The final results were obtained as the average of five measurements for each temperature. For room temperatures, measurements were made before and after heating.

Results of the study

Figure 1 presents the curve of change in the lattice parameters of alloys annealed at 800° as a function of composition. The same dependence and the same parameter values were obtained for alloys annealed at other temperatures.

Fig. 1. Cr–Mo system. Change in the lattice parameters of alloys as a function of composition. X-ray diffraction patterns: *a* –Cr; *b* –alloy with 38% Mo; *v* – alloy with 50.46% Mo; *g* –Mo

In all X-ray diffraction patterns, systems of lines were found belonging to only one phase, having a body-centered cubic lattice. In none of the X-ray diffraction

Fig. 1. Cr–Mo system. Change in the lattice parameters of alloys as a function of composition. X-ray diffraction patterns: a –Cr; b –alloy with 38% Mo; v –alloy with 50.46% Mo; g –Mo

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Figure 2

Figure 2: Figure 2

patterns did we find two systems of lines that could have been assigned to phases having different lattices, or to one lattice with different parameters.

The parameter of the solid solution increases monotonically as the Mo content in it increases; moreover, a positive deviation from Vegard' s rule is observed. Figure 1 also presents X-ray diffraction patterns of Cr (a,

Mo (c) and alloys with a Mo content of 38% (b) and 50.46% (c)*. According to our data, $a_{\mathrm{Cr}} = 0.2882$ nm and $a_{\mathrm{Mo}} = 0.3139$ nm, with an accuracy of measurement of the parameters of 0.1%.

Figure 2 presents the changes in $\bar{\alpha}$ and in the ratio of $\bar{\alpha}$ to $\bar{\alpha}_K$ as a function of Mo content, as well as dilatograms of Cr (a) and of an alloy containing 30% Mo (b). On dilatometric curve (b), no volume effects were observed that would be associated with phase transformations. A similar picture is also observed for the other alloys. As can be seen from the dilatograms, the character of the thermal expansion of the alloys and of Cr does not differ fundamentally from one another.

For the curve of the change in $\bar{\alpha}$, a nonlinear dependence is observed. The values of $\bar{\alpha}$ for the alloys lie in the interval between the values of $\bar{\alpha}_{\mathrm{Cr}}$ and $\bar{\alpha}_{\mathrm{Mo}}$. Alloys containing 82-84% Mo have the same thermal expansion as Al_2O_3. The observed regularity in the change of $\bar{\alpha}$ of the alloys is in good agreement with the results of work [18] and, according to [19], is characteristic of solid solutions.

Figure 3 shows the phase diagram of the Cr–Mo system, constructed by us from the data of differential thermal, X-ray structural, and dilatometric analyses.

On all thermograms, only thermal effects associated with melting and crystallization of the alloys are found. (Thermograms of the alloy with 5% Mo (a) and Cr (b) are given in Fig. 3.)

On some cooling curves, taken from alloys containing 30, 35, and 50% Mo, thermal effects in the solid state were found in the temperature interval 1600-1650°, which in our work cannot be explained. The melting diagram belongs to type III according to Roozeboom' s classification, with a minimum

Fig. 2. Cr–Mo system. Change in the mean (20-1300°) coefficient of linear

Figure 3

Figure 3: Figure 3

expansion of the alloys as a function of composition. Dilatograms: a—Cr; b—alloy with 30% Mo

Fig. 3. Cr—Mo system. Phase diagram. Thermograms: a—alloy with 5% Mo; b—Cr

* Concentrations are in weight percent.

on the solidus and liquidus curves at a temperature of 1820° and a concentration of 20-22% Mo. The melting temperature of Cr was determined to be 1865°. The melting temperature of Mo, 2625°, was taken from the data of (20).

Alloys rich in Cr have a crystallization interval not exceeding 20-25°; in alloys rich in Mo it reaches 80-100°.

The change in macrohardness of Cr and Mo, as well as of Cr-Mo alloys, with temperature is shown in Fig. 4. Cr and Mo have a hardness at 20° of $1400 \cdot 10^6$ (142 kg/mm^2) and $1800 \cdot 10^6$ N/m^2 (188 kg/mm^2), respectively, and exhibit the greatest decrease in hardness with increasing temperature at 65-70%. Alloys containing 55-70% Mo are least affected by temperature. Their hardness at 1000° decreases by 18-25%. The alloys in the concentration range 35-65% Mo possess the highest hardness at room temperature, 4900 (500 kg/mm^2)-5900 N/m^2 (600 kg/mm^2).

Fig. 4. Cr-Mo system. Change in the hardness of alloys as a function of composition at constant temperatures: *a*—20°, *b*—600°, *v*—800°, *g*—1000°.

Thus, the data obtained by differential thermal, X-ray structural, and dilatometric methods give grounds to assume that the equilibrium phase diagram of the Cr-Mo system above 800° is a continuous series of solid solutions.

According to investigations of the ternary Cr-Nb-Mo system, in the Cr-Mo system it may be assumed that there exists a decomposition region (of the stratification type) with a critical point near 500° and a Mo concentration of 30%.

Institute of Metallophysics
Academy of Sciences of the Ukrainian SSR

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Note: Figure translations are in progress. See original paper for figures.