Lattice Constants, Thermal Expansion Coefficients and Densities of Molybdenum and the Solubility of Sulphur, Selenium and Tellurium in it at 1100 °C*)

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Although there is an extensive literature on the compounds of molybdenum with selenium, tellurium and especially with sulphur, no published studies on the solid solubility of these elements in molybdenum could be found.

Nevertheless, some investigations, e. g. the thermodynamic study of S. C. Schaefer[1], showed that there is a certain solid solubility of sulphur in molybdenum, up to ~ 1.5 at.-% at 1100 °C. It seemed to be interesting to know whether this solid solubility could also be verified by other methods, for instance by measuring the lattice parameters, and to extend the investigation using the similar elements selenium and tellurium. At the same time the changes in the thermal expansivities could also be explored.

The Materials and the Preparation of the Alloys

Very fine powder, obtained from the Hilger Co. (nominally 99.9935 % Mo) and Sylvania Electric (99.95 % Mo) was used. The first preparation contained as impurities about 0.0015 wt.-% Fe, 0.005 Si and traces of other elements. The second contained chromium, iron, nickel, silicon, tin and carbon (50 p. p. m. of each) and aluminium, calcium, copper, lead, magnesium and manganese (10 p. p. m. of each). However, the samples could have contained about 0.01 % of oxygen in form of a surface oxide. Sulphur, selenium and tellurium were very pure (99.999 % for the last two, ordered from ASARCO).

Calculated amounts of the Hilger molybdenum and the alloying element (S, Se or Te) powders were weighed with an accuracy of ± 0.00005 g. and ground intimately in a mortar. Then the mixtures were shed into clean, dry fused quartz tubes closed at one end, evacuated and sealed off. For heat treatment the tubes were placed horizontally into a furnace, heated at 1100 °C for 144 hours, and the tubes were then quenched in ice water. Thereby it was assumed that the chalcogenides formed would dissolve within the range of their solubility in the molybdenum at 1100 °C and would not segregate at room temperature or during quenching. The samples were still in form of a fine powder after heating and there was no attack or reduction of the inside walls of the quartz tubes.

Lattice Parameter Determinations

Since the radii S^{2-}, Se^{2-} and Te^{2-} are much larger than the radius of even a molybdenum-atom, an increase of the lattice parameter of the solid solutions should occur. However, as the amounts dissolved in

molybdenum may be quite small, only a small increase in the parameter should be expected.

Therefore, the lattice parameters of molybdenum and the solid solutions have to be known with u t - m o s t   p r e c i s i o n . For such determinations the asymmetric film method is appropriate[2]. The fine powders which passed the tightest bolting cloth were dusted onto a lithium-boron-glass fiber (about 0.08 mm in diameter) fastened to the sample holder of the cylindrical precision X-ray camera, 64 mm in diameter. Such thin sample mounts do not require absorption corrections and extrapolation procedures are unnecessary[3]. CuK$_s$ radiation of the wavelength 1.389350 kX was used as it produced in 30 min. the (420) line having the high Bragg angle of about 81.6°. From the latter the lattice constant was calculated and converted into Å-units by multipling by 1.00202. The final constant for each preparation was obtained as an average of at least 12 films, which all were measured with a comparator. From the deviations from the average, the standard deviation S of the constants was calculated in the usual way. The probable error, $S_{50\%}$, at 50 % confidence limit (as given in the Tables) was found from

$$S_{50\%} = 0.675\,S \qquad (1)$$

If it is desired to have the error with confidence limits of 95 %, the error $S_{50\%}$ has to be multiplied by 3, ore more correctly

$$S_{95\%} = 2.96\,S_{50\%} \qquad (2)$$

The precise measurements would not help at all, if the temperature of the samples were not exactly known and kept constant during the exposure. Therefore, the whole camera with the sample and film in it was placed in a special thermostat[2]) and the exposures were made after the constancy of temperature (within ± 0.05 °C) was attained. To calculate the expansion coefficients, the exposures were made at 15, 25, 35, 45, 55, and 65 °C, and from the constants a at the respective temperatures t the thermal expansion coefficients α were obtained from

$$\alpha = \Delta a / \Delta t \cdot a_{25} \qquad (3)$$

were a_{25} is the constant at 25 °C, and Δ is the change in a and t.

The lattice constants were corrected for refraction by adding 0.00009 Å to them[3][4].

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[2]) M. E. Straumanis, Encyclopedia of X-rays and Gamma Rays, G. L. Clark, ed., p. 700, Reinhold Publ. Corp., New York, 1963; J. Appl. Phys. 20 (1949) 726. Analytical Chem. 25 (1953) 700; M. E. Straumanis and A. Ievinš, Präzisionsbestimmung von Gitterkonstanten nach der asymmetrischen Methode, J. Springer, Berlin (1940).

[3]) M. E. Straumanis, J. Appl. Phys. 30 (1959) 1965; Acta Cryst. 13 (1960) 818.

[4]) M. E. Straumanis, Acta Cryst. 8 (1955) 654.