

Kinetics of oxygen and carbon removal from liquid molybdenum in the process of high-frequency levitation in vacuum

V. G. Glebovsky, B. M. Shipilevsky, I. V. Kapchenko and V. V. Kireiko
Institute of Solid State Physics, 142432, Chernogolovka, Moscow (Russia)

(Received January 8, 1990; in final form December 7, 1991)

Abstract

The kinetics of removing oxygen and carbon from liquid molybdenum in the process of high-frequency levitation in vacuum has been studied. The range of the concentrations of both impurities was 10^{-4} – 5×10^{-6} %. It has been shown that samples of molybdenum with predetermined low contents of oxygen and carbon can be obtained. The effective rate constant of oxygen release from liquid molybdenum has been determined.

1. Introduction

New applications of refractory metals impose specific demands on their impurity contents. Such impurities as carbon, oxygen and other interstitials have a decisive effect on the physical and mechanical properties of refractory metals (of molybdenum and tungsten particularly). This generated a need for a sharp decrease in the interstitial impurity concentration. As a rule, the content of nitrogen in ingots of molybdenum and tungsten obtained from vacuum melt does not practically exceed 1 p.p.m; therefore the problem can be reduced to removing both oxygen and carbon. Since oxygen desorbs from the surface of refractory metals in the form of oxides or in the atomic state, a decrease in the concentrations of oxygen and carbon occurs due to two competing fluxes of desorption. It is evident that the densities of these fluxes and their dependence on the initial and actual oxygen and carbon concentrations, temperature, sample geometry and on the residual CO pressure in the vacuum chamber should define the probabilities of preparing highly oxygen- and carbon-free refractory metals.

The theoretical aspects of interaction of impurities of different natures (oxygen and carbon) in the process of their desorption from the surface of refractory metals at high temperatures in vacuum have been considered in detail in refs. 1 and 2. The validity of the model representations developed has been proved on an example of liquid niobium levitated in vacuum and doped precisely with oxygen and carbon. However, no systematic study of kinetic singularities of the oxygen and carbon release from molybdenum and

tungsten has been carried out so far, which is mostly due to insufficient reliability of experimental and analytical methods.

One of the basic criteria determining the possible decrease in the oxygen and carbon content in refractory metals is the equilibrium constant K_p for the $C+O\rightarrow CO$ reaction. Having the data on K_p for molybdenum in mind one expects to observe very low concentrations of oxygen and carbon in molybdenum even at very high partial pressures of CO. It has been assumed that, when one of the two impurity elements is introduced in excess, the content of the other in the process of vacuum melting should be extremely low. However, the attempts made to establish a correlation between the initial ratios of the concentrations of oxygen and carbon and minimal concentrations of these impurities, which can be achieved in the process of high-temperature treatment of liquid metal in vacuum, resulted in essential discrepancies between the estimates and the experimental results.

There are two reasons for these discrepancies. First, the diffusion deceleration of the impurity transport to the metal–vacuum interface surface and a small specific surface of the liquid metal may cause a decrease in the rate of impurity release and, accordingly, to the extended duration of the process [3, 4]. In contrast, increase in the number of paths of diffusion may lead to a decrease of the impurity flow to the interface in the square-law variation. The authors of ref. 5 have proposed different versions of optimal initial concentrations of the surplus carbon for the effective removal of carbon or both impurities during vacuum melting. Second, marked discrepancies between the experimental results and those derived thermodynamically under certain vacuum conditions may be due to insufficient sensitivity of the analytical methods employed. For instance, the results of earlier studies, in which it was supposed that the $C+O\rightarrow CO$ reaction slows down drastically with diminishing actual concentrations of oxygen and carbon down to the values corresponding to some critical product $[C]\times [O]$, were not supported in the related experiments, when different methods of vacuum melting and advance analytical methods of impurity control were used [6, 7].

In this paper some results of investigations on the kinetics of the oxygen and carbon release from liquid molybdenum in high vacuum using highly sensitive activation analyses are presented.

2. Experimental procedure

2.1. Samples

In order to obtain samples with the given contents of oxygen and carbon the following technique was used. It involved the process of preparing a mixture of powder components with no more than 5% deviation from the given content and pressing the powders to tablets of 28 ± 0.25 g. The compacted samples had 80% of the theoretical density. Twelve series of samples were prepared for three concentration levels of oxygen and carbon (Table 1). The

TABLE 1

The initial oxygen and carbon contents (%) in samples of molybdenum for vacuum levitation

Series	Oxygen content	Carbon content	O:C ratio
1	3	0.04	75.00
2	3	1.48	2.02
3	3	1.84	1.63
4	3	2.24	1.34
5	3	2.64	1.14
6	3	2.36	1.27
7	3.0	2.48	1.21
8	0.3	0.22	1.36
9	0.3	0.24	1.25
10	0.3	0.27	1.11
11	0.03	0.024	1.25
12	0.03	0.032	0.94

samples of series 11 and 12 were prepared from commercial molybdenum with the same deviation from the standard chemical composition.

All samples were subjected to preliminary annealing at 1900 ± 25 °C for 45 s, and then melted. The time of melting is counted from the moment of complete melting and forming a stable drop. As a result of obeying exactly the given electric regime the period of complete melting of the samples ranged from 25 ± 0.5 s (series 5) to 32 ± 0.5 s (series 3, 8–12), depending on the carbon content in the samples. This helped the samples to be chosen according to the time of their melting, which is extremely important since the transition through the solid–liquid state strongly affects the position of the initial point of counting off the concentration.

2.2. Levitation system

The high-frequency levitation melting system consisted of a vacuum chamber with a double-coil inductor and generator with 100 kW power and 220 kHz frequency. The residual pressure in the chamber during levitation of the drop was $(6-9) \times 10^{-3}$ Pa. The chemical composition of gases released in the process of melting was analysed periodically by means of a mass spectrometer. The temperature of the liquid metal was measured by an optical micropyrometer which was within the experimental error in the range 2635 ± 15 °C. After a given period of time, a drop of liquid molybdenum was thrown into a water-cooled copper crystallizer.

The liquid drop in the process of levitation and pouring into the crystallizer may touch the coils of the inductor for a short time. This source of errors can be eliminated only by solidification directly in the electromagnetic field and by increasing the stability of the drop levitated. A technique of dividing the drop has been worked out. It consists in realizing fast solidification (0.5–1 s) of the melt in the electromagnetic field and in applying the electric

regime providing stable levitation of the drop and ruling out any contact with inductor coils. As the voltage decreased in the oscillatory contour of the generator at the preset rate, the melt started pouring out of the inductor. At the moment when the drop of the melt was crossing the plane of the lower coil of the inductor, the voltage was increased drastically. The metal stopped pouring out of the inductor and the greater part of the melt rose above the lower coil and crystallized in a levitated state. The smaller part of the melted sample was poured into a crystallizer located coaxially to the inductor. The rest of the melt crystallized due to the strong dependence of the liquid metal temperature (for the given type and shape of the inductor) on the mass of the drop levitated. Therefore, after dividing the sample, the maximum possible temperature of the metal under the given electric parameter turns out to be considerably lower than its melting point.

2.3. Elemental analysis

The carbon content in the samples in the range from 5×10^{-1} to $1 \times 10^{-3}\%$ was determined by the combustion in the oxygen flow with a coulomb-metric registration. To record lower carbon concentrations (down to $3 \times 10^{-6}\%$) we used the deuteron activation by $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ reaction with chemical separation of ^{13}N radionuclide with the half-life period $T_{1/2}$ of 10 min. A cyclotron was the source of deuterons with a maximum energy of 13.6 MeV and a current up to 50 μA . The samples were exposed to radiation for 10 min by an extracted-to-air deuteron beam with an initial energy of 6.5 MeV and a beam current to 2 μA . A set of aluminium collimators with an aperture diameter of 8–25 mm was used to collimate the deuteron beam up to the transverse dimensions of the sample. Copper and iron–nickel foils 20 μm thick served as monitors. Standard iron with a carbon content of 0.15% was applied for comparing the samples.

The oxygen content up to $5 \times 10^{-5}\%$ was checked by the fast neutron activation method (14 MeV) by the $^{16}\text{O}(\text{n},\text{p})^{16}\text{N}$ reaction, and as a result a ^{16}N radionuclide was formed, the half-life period being 7.14 s and the energy of emitted γ quanta 6–7 MeV. A neutron generator with maximum flux 2.5×10^{12} neutrons s^{-1} served as a neutron source. A pneumatic transport system was used for delivering the sample to the neutron source. The system provided a “soft landing” for the transport capsule with the sample at the generator’s target, its delivery to the device for 1.5 s, discharging of the sample from the capsule and its transport to the region of etching ($\text{HF}:\text{HNO}_3 = 1:1$ in the regime of removal of surface impurities) and further delivery of the sample to the region for measuring radioactivity. The sample under analysis and that used for comparison were successively exposed to radiation and their activities measured. The induced activity was measured by means of three spectrometric channels; two of them served for measuring the sample activity in the regime of summation, and the third was used for measuring the activity of the neutron flux monitor sample. Titanium disks with a certain oxygen content served as comparison samples. The oxygen content was computed according to the numerical values of activities after

three or four successive measurements. The method of activation by protons by the $^{18}\text{O}(\text{p},\alpha)^{13}\text{N}$ reaction was applied to record the oxygen content in molybdenum up to $1 \times 10^{-5}\%$ and to check the homogeneity of its distribution within the thickness of the sample.

The solution of the problem related to the kinetics of the carbon–oxygen interaction made it necessary to improve the accuracy of the activating methods of the analysis by removing possible sources of errors. The estimation of the limits of discovery by activation analysis may be represented by the dependence $\eta = A_{\text{min}}/S$; here A_{min} is the minimum activity which can be measured as the excess of the background; S is the analysis sensitivity or specific activity, *i.e.* the activity of a radionuclide, induced under the given conditions of the analysis and its accuracy. For instance, while determining the carbon content, the increase in the sensitivity of the analysis due to the growing energy of particles results, as a rule, in additional errors caused by interference from other elements. An increase in the current of the beam on the sample leads to an increase in the effect of surface impurities on the result of the volume determination.

The errors in determining the carbon content in molybdenum may have any of the following possible origins: interference due to other impurities, insufficient purity of radiochemical separation, the non-reproducible value of the radiochemical yield of the ^{13}N isotope, monitoring of the deuteron flux, errors of the afterirradiation, or an inhomogeneous distribution of carbon in the sample examined.

When the oxygen content is analysed in molybdenum the following sources of errors may exist: difference in the geometrical sizes of the sample under analysis and that used for comparison, inhomogeneity of the oxygen distribution within the analysed sample, its structural factor (porosity, cavities, surface impurities), nuclear characteristics of the matrix and its impurity composition, features the irradiation regime and the statistical error of measurement.

3. Results and discussion

Figure 1 illustrates the kinetics of decreasing the actual oxygen concentrations for the samples of series 1, and here dependences 1 and 2 correspond to different conditions of solidification after dividing of the drop: the first in the crystallizer, and the other in the electromagnetic field of the inductor. The difference in the oxygen concentrations of two parts of the same sample after dividing of the melt and solidification in different conditions grows gradually and reaches more than two orders of magnitude. This indicates the reasons for the severe deviation of the experimental results observed in a number of papers devoted to the preparation and study of pure metals, particularly, of molybdenum.

Figure 2 presents the data on changes in the actual oxygen content for the samples of series 1–4 and 6. We did not manage to construct analogous

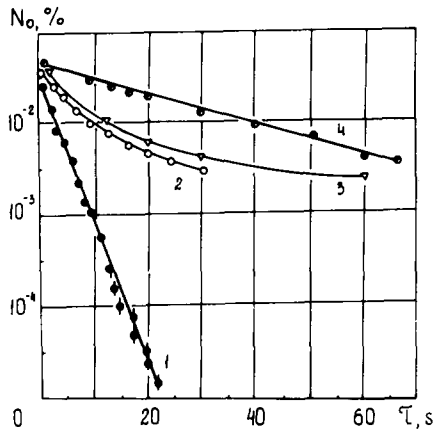


Fig. 1. Kinetics of oxygen release during levitation of liquid molybdenum: curve 1, solidification in electromagnetic field; curve 2, solidification in a water-cooled crystallizer, present work; curves 3 and 4, solidification in a water-cooled crystallizer (see ref. 8 and ref. 9 respectively).

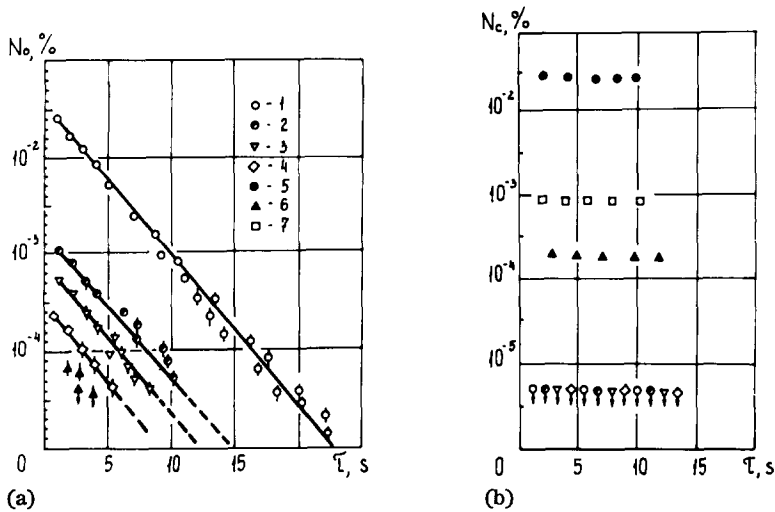


Fig. 2. Kinetics of (a) oxygen and (b) carbon release during melting and solidification of levitated molybdenum drops: \circ , series 1; \bullet , series 2; ∇ , series 3; \diamond , series 4; \bullet , series 5; \blacktriangle , series 6; \square , series 7.

dependences for the samples of series 5 and 7, since even in the first moments of vacuum levitation the actual oxygen concentrations in the samples could not be detected by the activation method. The linear dependence in the $\log N_o - \tau$ coordinates shows that the rate of the oxygen release from molybdenum into vacuum obeys a first-order equation. The samples of all five series exhibit equal inclination of straight lines to the time axis. This is due to the fact that oxygen is removed in the form of CO in the process of sample melting. Indeed, from Fig. 2(b) one may see that for the samples

of series 1–4 the oxygen content was at the limit of sensitivity of the deuteron activation analysis immediately after the sample was melted, and for the samples of series 6, 7 and 5 at levels of $10^{-4}\%$, $10^{-3}\%$ and $10^{-2}\%$ respectively. The reaction rate constant determined with respect to the slope of the experimental curve for the samples of series 1 with the carbon content of $5 \times 10^{-3}\%$ is 0.37 s^{-1} . The effective rate constant of the oxygen release is $\omega = K/v_a\alpha$; here $K = 0.37 \text{ s}^{-1}$, $v_a = 9.5 \text{ cm}^3 (\text{g at.})^{-1}$; $\alpha = 3.8 \pm 0.2 \text{ mol cm}^{-2} \text{ s}^{-1} \text{ at.}\%^{-1}$ is the specific surface of the melt. As a result, we have $\omega = 1.025 \times 10^{-4} \text{ mol cm}^{-2} \text{ s}^{-1} \text{ at.}\%^{-1}$.

The data given in Fig. 2(a) suggest the following remarkable conclusion: at a sufficient intensity of the convective oxygen diffusion to the melt–vacuum interface it is possible to provide its effective removal from molybdenum, without introducing carbon or other deoxidizers. Comparing the kinetic dependences of the oxygen behaviour in the process of maintaining liquid molybdenum in vacuum with estimates of the time required to decrease the oxygen concentration by three orders of magnitude in the process of desorption in an atomic state, one may observe much higher rates of the real process of oxygen release.

It is also evident that limiting the oxygen content strongly depends on the initial O:C ratio: with decreasing initial level of both impurity concentrations, even a slight change in the initial carbon contents changes the limiting oxygen content by several orders of magnitude (Figs. 2 and 3). For instance, for the samples of series 5 and 6 a change in initial carbon concentration by $3.5 \times 10^{-3}\%$ leads to a decrease in its content in the metal by more than two orders of magnitude, whereas for the samples of series 11 and 12 a similar result is achieved by changing the initial carbon concentration by only $1 \times 10^{-3}\%$.

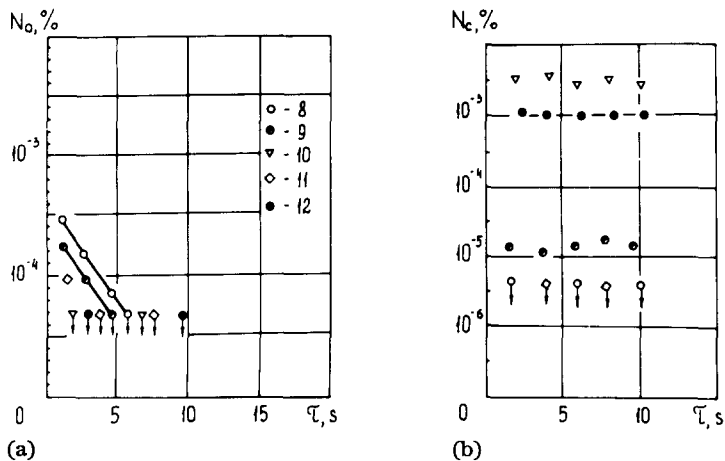


Fig. 3. Kinetics of (a) oxygen and (b) carbon release during melting and solidification of levitated molybdenum drops: \circ , series 8; \bullet , series 9; ∇ series 10; \diamond , series 11; \bullet , series 12.

Since the probabilities of changing the levitated metal mass are limited (20–35 g) and it is hard to measure the velocities of hydrodynamical flows in liquid metal, one cannot draw any definite conclusion concerning the region (kinetic or diffusive) where the processes of carbon and oxygen release from liquid molybdenum take place. However, comparing the results of the present paper with those of refs. 5, 8 and 9, one may see a real potential for a considerable increase in the rate of oxygen release from molybdenum in the process with intensive convective diffusion of impurity to the melt–vacuum interface.

4. Conclusions

The difference in the oxygen content in the solidified samples after dividing of the melt and solidification in different conditions (in the crystallizer and in the electromagnetic field) can reach more than an order of magnitude during 30 s. This elucidates deviations of the experimental results of different studies on liquid molybdenum.

The rate of the oxygen release from molybdenum into vacuum obeys a first-order equation. At a sufficiently high intensity of the oxygen convective diffusion to the melt–vacuum interface it is possible to remove oxygen from molybdenum without introducing carbon.

Limiting the oxygen content strongly depends on the initial O:C ratio. With decreasing initial level of both impurity contents even a slight change in the initial carbon content changes the limiting oxygen content by several orders of magnitude.

References

- 1 B. M. Shipilevsky and V. G. Glebovsky, in J. Morgenthal and H. Oppermann (eds.), *High Purity Materials in Science and Technology*, Akademie Verlag, Dresden, 1980, p. 211.
- 2 B. M. Shipilevsky and V. G. Glebovsky, *Surf. Sci.*, **216** (1989) 509.
- 3 M. Semcheshen and R. O. Barr, *J. Less-Common Met.*, **1** (1966) 1.
- 4 R. J. Browne, *Vacuum*, **21** (1971) 37.
- 5 K. Ono and J. Moriyama, *Metall. Trans. B*, **13** (1982) 241.
- 6 S. W. H. Yih and C. T. Wang, *Tungsten*, Plenum, New York, 1979, p. 500.
- 7 V. G. Glebovsky and B. M. Shipilevsky, *J. Cryst. Growth*, **60** (1982) 369.
- 8 A. V. Revyakin, V. E. Efimov and L. N. Kozina, in V. I. Kashin (ed.), *Physikochimicheskie osnovy vsaimodeystviya zhidkikh metallov s gasami*, Nauka, Moscow, 1978, p. 26 (in Russian).
- 9 K. Narita, T. Matsumura and N. Nagata, *Tetsu To Hagane*, **59** (1973) 500.