

# EFFECT OF CARBON ON THE SURFACE TENSION AND DENSITY OF LIQUID VANADIUM, NIOBIUM, AND MOLYBDENUM

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In all cases of liquid chemically active metals spreading over the surface of graphite, where the flow of a metal is accompanied by its simultaneous carburization, it is particularly important to know how carbon affects the physicochemical properties of the liquid metal. Yet this phenomenon appears to have been studied by only one author [1], who examined the influence of carbon on the surface tension of liquid molybdenum and tantalum within a narrow range of carbon concentrations. No experimental data are available in the literature on the density of liquid refractory metals of groups V-VI and on the effect of carbon on these properties.

For the present investigation, an apparatus was constructed in which metals being tested are heated by electron bombardment (Fig. 1). The axially-symmetrical electron-optical system incorporated a spiral cathode (instead of the usual single ring), which substantially increased the stability of test results by extending the heating zone and giving a closer approximation to a state of equilibrium in the system.

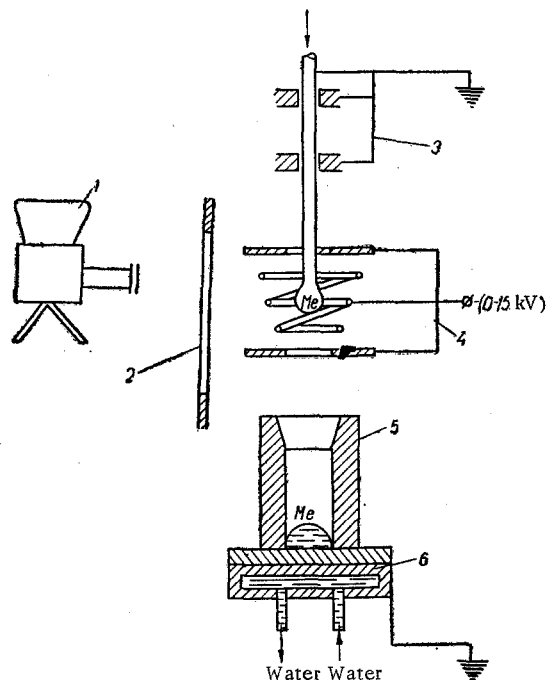


Fig. 1. Diagram of test apparatus: 1) motion-picture camera; 2) inspection window; 3) specimen suspension and travel system; 4) cathode unit; 5) copper mold; 6) water-cooled copper base plate.

The density of liquid chemically active refractory metals of groups V-VI with and without carbon was experimentally determined by calculating the volume of a falling drop of each liquid metal being tested in a vacuum and weighing the drop after the experiment. Under the action of electron bombardment, a drop of liquid metal formed on the tip of a rod of the metal being tested. At the instant of separation of the drop from the rod, a motion picture camera was switched on, recording the whole flight of the drop until it fell into a collecting crucible. After solidification, the drop was weighed on an analytical balance. The density of the test metal was calculated from the weight of the drop and its volume in the liquid state.

Liquid metal drops were collected either in a water-cooled copper crucible or in a crucible made of molybdenum sheet and provided with deflectors designed to minimize the extent of splashing of metal. The drop formation and flight processes were photographed with a 16-mm Pentaflex 16 motion picture camera at a speed of 96 frames per second. To reduce the size of the drop image obtained, long-focus objectives with  $F = 135$  and  $210$  mm were employed. Since the drop was photographed at right angles to the direction of its flight, the volume could be calculated by assuming the drop to be symmetrical about

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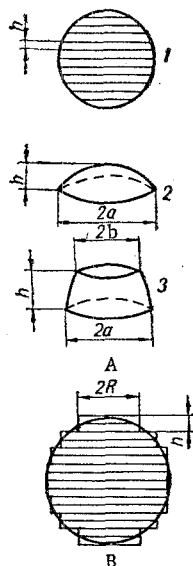


Fig. 2. Procedure for calculating drop volume. Equations are given in text.

TABLE 1

Metal	Calc. $\rho$ , g/cm <sup>3</sup>	Lit. exp. $\rho$ , g/cm <sup>3</sup>	Source	Exp. $\rho$ , g/cm <sup>3</sup>
Nickel	7,85	7,75	[2]	7,65
Titanium	4,15	4,12	[3]	4,10
Zirconium	5,80	6,08	[4]	5,60

literature data are available. The results of these measurements, together with calculated and literature density values, are presented in Table 1. An examination of the data in this table leads to the conclusion that the proposed contactless method of density determination gives satisfactory results and may be employed for measuring the density of refractory metals.

To study the effect of carbon on the density and surface tension of vanadium, niobium, and molybdenum use was made of alloys with carbon contents close to the eutectic concentrations shown in the Me-C constitution diagrams of these metals. The choice of these concentrations was dictated by the fact that, when liquid chemically active metals are in contact with carbon, their carbon content rapidly reaches the eutectic concentration as a result of carburization. Subsequently, the rate of carburization as a rule sharply falls off.

Experiments were performed in the following manner. To a specimen of a test metal was applied a thin layer of carbon black mixed with latex, care being taken to ensure that the whole of this layer was completely fused during the experiment and that the weight of the resulting metal drop did not exceed a critical value (i.e., that the drop did not detach itself prematurely from the metal rod). Each liquid metal drop was held for not less than 60 sec in a molten condition to secure thorough mixing and dissolution of the carbon. During this time, steady-state conditions of melting were established and the boiling of the drop ceased. The drop then detached itself from the metal rod and at the same time its flight began to be filmed. The solidified drops were analyzed for carbon. The measurements were performed by a gas-volumetric method, using a Strollein apparatus, at a sample combustion temperature of 1400-1450°C. Electrolytic copper, tin, and lead with NaF additions were used as fluxes.

The results of density measurements on liquid vanadium, niobium, molybdenum, and their alloys with carbon at temperatures close to  $T_{\text{melt}}$  of the alloys are presented in Fig. 3. It can be seen that the presence of carbon in amounts close to the eutectic concentrations appreciably reduces the density of the melts. Thus, the decrease in density compared with pure metal is in the range 6-7.5% for molybdenum, 2.5-4.5%

its axis. The assumption was experimentally verified by filming drops in a vertical direction, as a result of which it was established that drop shape deviation from a solid of revolution for vanadium, niobium, and molybdenum was 3-5%.

For the volume calculations, use was made of drops having a shape approximating as closely as possible to spherical. The drop volume determination procedure is illustrated diagrammatically in Fig. 2A.

$$\text{Here for } 1: V_d = \sum_1^n V_i;$$

$$\text{for } 2: V_1 \text{ and } V_n = \frac{1}{6} \pi h (3a^2 + h^2);$$

$$\text{for } 3: \text{from } V_2 \text{ to } V_{n-1} = \frac{1}{6} \pi h (3a^2 + 3b^2 + h^2).$$

With a sufficiently large number of sections, the calculation may be simplified by regarding each layer as a cylinder having a height  $h$  and a diameter equal to the width of the sphere layer at the height  $h$  [2] (Fig. 2B):

$$V_d = \sum_1^n V_i; \quad V_i = \pi R^2 h.$$

To determine true dimensions, a reference standard was filmed. All measurements on films were made using a UIM-21 measuring microscope.

The procedure was tested by measuring the density of liquid nickel, titanium, and zirconium, for which

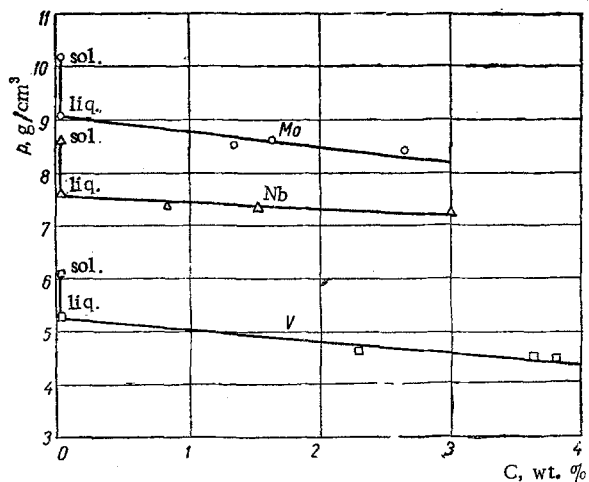


Fig. 3. Effect of carbon on density of liquid metals.

TABLE 2

Metal	C, wt. %	Exp. $\rho$ , g/cm <sup>3</sup>	$\sigma_{L-G}$ , ergs/cm <sup>2</sup> (mean)
Vanadium	0	5,3	1760
	2,0-2,3	4,6	1800
	3,0	—	1780
	3,6	4,5	1770
	3,8	4,45	1780
Niobium	0	7,6	2020
	0,8	7,4	1900
	1,5	7,35	1960
	3,0	7,25	1970
Molybdenum	0	9,1	2130
	1,3-1,4	8,5	2050
	1,6	8,6	2200
	2,6	8,4	2080
	3,9	—	2180

Comparing our data on the density of V-C, Nb-C, and Mo-C melts with the results discussed above, and also bearing in mind that the maximum solubility of carbon in solid vanadium, niobium, and molybdenum is extremely low, we may conclude that the density changes observed in the melts of these systems and, consequently, the structural changes occurring in these liquid metals, are linked with the presence of free carbon.

It should be noted that the density decreases found in Mo-C and, particularly, Nb-C melts are smaller than the density jumps found in Fe-C, Co-C, and Ni-C melts at carbon contents exceeding the solid-state solubility limit of carbon in these metals. This seems to indicate that raising the melting point of a solvent metal substantially increases the dissolution rate of carbon in the melt. The behavior of carbon is anomalous in molten V-C alloys, for which an appreciable decrease in density (of up to 15%) was recorded. Since the metals investigated (V, Nb, and Mo) undergo no solid-state polymorphic transformations, in a molten state they can be expected to exhibit only a density jump linked with solidification phenomena; this is confirmed by the linear decrease in the density of the melts with rise in their carbon content.

To assess the effect of carbon on the surface tension of liquid vanadium, niobium, and molybdenum, "contactless" - drop-weighing and drop-shape - methods of surface tension determination [7, 8] were employed. All experiments were performed using a spiral cathode and stationary rods of the test metals. The melting process and the drop shape were filmed. The method of introduction of carbon into the metals and the analysis of the resulting alloys for carbon were the same as in the above-described determinations of the density of Me-C melts.

for niobium, and 12-15% for vanadium. The greatest reduction in density is observed for vanadium and the least for niobium, which is probably attributable to the difference in the affinities of carbon for these metals.

It is, of course, of interest to compare the data obtained with results of density determinations for the systems Fe-C, Co-C, and Ni-C, particularly since the constitution diagrams of the systems V-C, Nb-C, and Mo-C are similar to the Fe-C constitution diagram. Densities in these systems were investigated by Filippov [5], who postulates the existence of two types of structural changes in liquid metal - one taking place near the solidification temperatures (a change in the short-range order arrangement of atoms in accordance with the short-range order in the crystal) and another, which is apparently a polymorphic transformation involving a change in the coordination number in short-range order at temperatures remote from the crystallization point. Experimental data enabled Filippov [5] to arrive at certain conclusions regarding the mutual effect of solvents and solutes in Me-C systems on the structural state of molten metal. Thus, when the Me-C systems investigated contain carbon in amounts smaller than their solid-state solubility limit, after melting all of the carbon is in combined form and all changes in density with temperature strictly correspond to the liquidus and solidus lines. Above the solubility limit, discrepancies were found between test results and the constitution diagrams for all the melts investigated, which could only be eliminated by prolonged heating, i.e., by causing the carbon to dissolve fully in the melt. In the systems Co-C and Ni-C, dissolution processes leading to equilibrium take place rapidly, but in the system Fe-C, owing to the difference in the structure of the  $\delta$ -region, full dissolution of graphite requires a long time. In his investigation into the density of Fe-C melts, Lucas [6] also noted a sharp change in density at a C content of 2%.

One of the causes of error in surface tension measurements on molten metals is the possibility of formation of gas blisters in metal drops. According to Flint [9], this may occur even in pure metals. No pores were detected by us in sections of the alloy drops examined, but this, of course, is no guarantee that the drops were in fact completely free from porosity.

Experimental data on the effect of carbon on the surface tension of liquid vanadium, niobium, and molybdenum are listed in Table 2. It will be seen that, within the concentration ranges investigated, the surface tension of the alloys does not appear to be affected by their carbon content. It may be concluded that carbon in amounts of up to 3-4 wt.% is an inactive component in molten vanadium, niobium, and molybdenum. It is conceivable that the change induced in the surface tension of the molten metals investigated by carbon is less than the error involved in the measurement techniques employed, which is of the order of  $\pm 5\%$ .

#### LITERATURE CITED

1. B. C. Allen, *Trans. AMIE*, 227, 1175 (1963).
2. L. D. Lucas, *Compt. Rend.*, 250 (1960).
3. V. P. Elyutin and M. A. Maurakh, *Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk*, No. 4 (1956).
4. M. A. Maurakh (M. Maurach), *Trans. Indian Inst. Metals*, Sept. 14, 1961.
5. E. S. Filippov, *Dissertation [in Russian]*, Moscow (1965).
6. L. D. Lucas, *Mem. Sci. Rev. Mét.*, 61, No. 2 (1964).
7. I. M. Andress, E. A. Hauser, and W. B. Tucker, *J. Phys. Chem.*, 42, 1001 (1938).
8. W. P. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, 41, 499 (1919).
9. O. Flint, *AERE Mem.*, 1479 (1964).