VISCOSITY OF RUBIDIUM NEAR ITS SOLIDIFICATION TEMPERATURE

V. N. Genrikh and A. B. Kaplun

We investigated the viscosity of high-purity (99.997%) rubidium by the vibration method. The viscosity was determined from the amplitude of forced vibrations of a thin plate immersed in molten rubidium. The measured viscosities were 15% below those given in the literature. The temperature trend of the viscosity of rubidium is described by an exponential function; no anomalies were observed in the temperature function to the solidification point. We also investigated the influence of air on the viscosity of rubidium. As the air concentration in the atmosphere over the melt was increased, the viscosity of the rubidium rose by several tens of percent, as a result of solution of atmospheric oxygen in the rubidium. An oxygen concentration of 0.15 wt. % in the ribidium corresponded to an increase of 20% in viscosity.

The viscosity of technical-grade rubidium was investigated at temperatures of from 250°C to the solidification point. At low temperatures (less than 50°C), there was an abrupt drop in vibration amplitude ("obstruction"), as a result of precipitation of impurities from the melt on the plate surface. A change in the impurity content of the melt caused a change in the temperature at which the drop began and in its depth.

We made a qualitative study of the influence of nitrogen, hydrogen, and oxygen on the viscosity of technical-grade rubidium.

Investigation of the behavior of various physical properties of a liquid near its solidification temperature is of great interest. Anomalous behavior of the temperature function of electric conductivity, viscosity, density, and other structure-sensitive properties in the crystallization region may indicate structural rearrangements in the liquid, i.e., so-called "precrystallization" and "postmelting" phenomena. The behavior of the structure-sensitive properties of liquid metals, particularly their viscosity, has been the subject of little research. Information on the existance of anomalies in the temperature function of viscosity is contradictory, and most experimental data on the viscosity of liquid metals are for temperatures 10-20°C above the melting point.

Use of the vibration method of measuring viscosity affords new opportunities for research on the viscosity of liquid metals. This method is continuous and automatic, affording a comparatively high measure of accuracy (1.5-3%). This permits thorough study of the viscosity of a liquid metal in the crystallization region and at the crystallization temperature itself.

The viscosity is determined from the amplitude of the forced vibrations of a thin plate placed on an elastic suspension device and immersed in the liquid to be investigated.

The formula used in the calculation has the form

$$\sqrt{\rho\eta} = C_1/A - C_2$$

Here η is the liquid viscosity, ρ is its density, A is the vibration amplitude, and C_1 and C_2 are the instrument constants determined during calibration.

The theory of the vibration method for viscosity measurements in liquids, the electrical measuring circuit, and the measurement method were described previously [1-3].

Investigation of the Viscosity of Pure Rubidium. We investigated rubidium with a base-metal content of no less than 99.997%. The main metallic impurities were less than 0.00018% Na, less than 0.0007% K, less than 0.0017% Cs, and less than 0.001% Ca.

Novosibirsk. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 6, pp. 122-126, November-December, 1970. Original article submitted January 6, 1970.

TABLE 1

	Regime	T_-, °C	T_{max}, °C	T^*, °C	T_*, °C
1	Cooling at 0.2°C/min	100	200	55	38
2	Heating at steady-state points, 15 min/point	100	200	70	—
3	Cooling at 0.2°C/min	43	100	43	37.8
4	Cooling at steady-state points, 20-60 min/point	100	200	54	37.8
5	Heating at 8-10°C/min	100	250	150	—
6	Cooling at 4°C/min	38.5	200	—	37.9

Here the numbers correspond to Fig. 2, and the following symbols are used: T_- is the batcher temperature, T_* is the temperature at which precipitation begins or solution of the solid phase in the melt ends, T^* is the solidification temperature (all in deg C), and T_{max} is the maximum melt temperature.

The working volume of the viscosimeter was filled with the metal to be investigated from a sylphon batcher, which was connected to the working volume by a system of capillaries and valves.

The batcher was filled with the test metal by vacuum distillation at a pressure of $5 \cdot 10^{-5}$ mm Hg from an auxiliary container. Rubidium-containing ampules were placed in the auxiliary container and then broken with a special device.

The visocity of the rubidium was measured in a high-purity helium atmosphere (with an impurity content of no more than 0.025%) at a pressure of 1.15 atm. In this experiment we measured 24 points under a steady-state regime over the temperature range from the melting point to 323°C. The temperatures from 323 to 90°C were established with a resistance furnace, while those from 90°C to the solidification point were established with a controlled-temperature vat. The holding time at each point was 10–20 min, and the total measurement time was 8 h. Measurements were made while the temperature was both rising and falling.

The solidification temperature of the liquid rubidium was determined from the point at which vibrations of the probe stopped. After solidification at a temperature of 38.5°C, we observed a rise in temperature to 39°C, which indicates supercooling of the liquid rubidium. The melting point of the rubidium, 39 ± 0.1°C, agreed with the data in the literature [4].

Figure 1 presents the results of our measurements of the viscosity of the rubidium (curve 1) and the data of other authors. The average discrepancy between the experimental viscosities and the average curve was ±0.4%. The viscosity was calculated with data on the density of rubidium from the literature [5].

The accuracy of the measurements, taking into account the calibration error and the corrections made, was ±3%. The experimental data are well described by the following exponential function (η is the cP and T is in deg K):

$$\mathrm{nl}\,\eta = -2.401 + 582.1/T$$

No anomalies were observed in the temperature function of viscosity over the entire temperature range investigated.

The results obtained for the viscosity of liquid rubidium over the temperature range investigated were ≈ 15% below those of other authors. Andrade and Dobbs [6] investigated 99.8% pure rubidium by the method of fading sphere vibrations. Weatherford et al. [7] investigated the viscosity of 99.9% rubidium with a capillary viscosimeter, while V. A. Fomin [5] investigated 98% pure rubidium by the method of torsional vibrations of a cylindrical beaker. The data of these authors agree with one another to within ±5%.

Analysis of the experimental methods used by these authors showed that it was possible for the test metal to be exposed to air during preparation for investigation and during the experiment itself.

The authors other than Weatherford [7] did not take special measures to purify the initial metal specimen of gaseous impurities and did not analyze it for such impurities. The presence of these impurities, particularly atmospheric oxygen, might have caused the difference between our data and those in the literature.

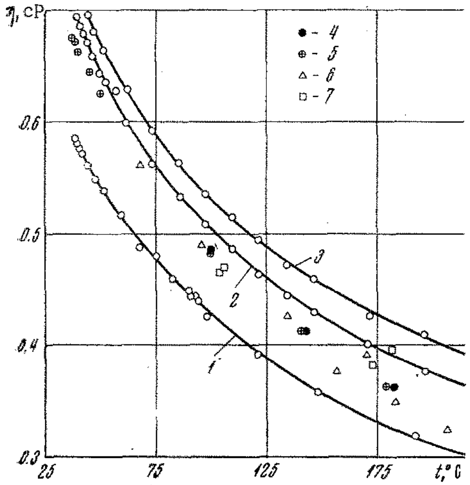

Fig. 1

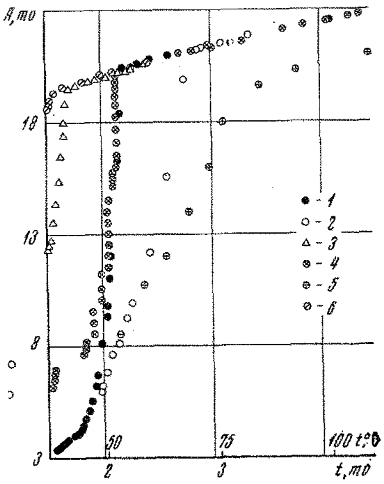

Fig. 2

Fig. 1. Viscosity of pure rubidium. 1) In helium atmosphere; 2) helium +0.05 atm air; 3) helium +0.1 atm air; 4) data from [5]; 5) data from [6]; 6) data from [7] (first series); 7) data from [7] (second series).

Fig. 2. Amplitude of probe vibration as a function of melt temperature. 1) First series (cooling); 2) second series (heating); 3) second series (cooling); 4) third series (cooling); 5) third series (heating); 6) fourth series (cooling).

In order to determine the influence of air on the viscosity of rubidium, air was introduced into the atmosphere over the metal (at 35°C) in an amount sufficient to cause an increase in pressure of 0.05 atm over the melt. Complete solution of the atmospheric oxygen in the rubidium corresponded to an oxygen concentration of 0.15 wt.%. The metal was then heated to 300°C for 2 h. The measurements were made during slow cooling from 220°C to the solidification temperature. We determined 21 points over a period of 1 h, 20 min. The solidification temperature decreased to 37.2°C in this series of measurements. The supercooling disappeared. The viscosity increased by 20%, and it coincided with the data in the literature (Fig. 1, curve 2).

Repeated admission of air to the apparatus, in an amount corresponding to an oxygen concentration of 0.3 wt.% in the rubidium, increased the viscosity of the latter by an additional 10% (curve 3), so that the results of the last series of experiments were higher than any known values. The solidification temperature decreased to 35°C, and no supercooling was observed.

Subsequent filling of the apparatus with air led to a further increase in viscosity and a decrease in solidification temperature. Subsequent experiments enabled us to establish that nitrogen has no effect on the viscosity of rubidium over the temperature range in question. The increase in the viscosity of the rubidium and the reduction in its solidification point were therefore due to the influence of atmospheric oxygen.

Viscosity of Technical-Grade Rubidium. We investigated the viscosity of impure rubidium with a base-material content of no less than 98.0% (pure grade). The metallic impurities included less than 0.1% Na, less than 1% K, less than 1% Cs, and less than 0.1% Ca (batch analysis).

As before, the crucible was filled with the molten metal whose viscosity was to be measured from a sylphon batcher. The batcher was filled from an auxiliary container through a porous stainless-steel filter.

Since the rubidium was not subjected to special purification before filling, it could contain nonmetallic impurities (nitrides, hydrides, oxides, etc.). The temperature during filling of the crucible with metal from the batcher was therefore held at 150-250°C, in order to dissolve as much of the impurities as possible and wet the probe.

Our investigations were conducted under different regimes involving fast and slow cooling and heating and at steady-state points. We also varied the maximum temperature of the test melt and the temperature of the batcher from which the metal was supplied before each series of measurements. The measurement regimes are given in Table 1.

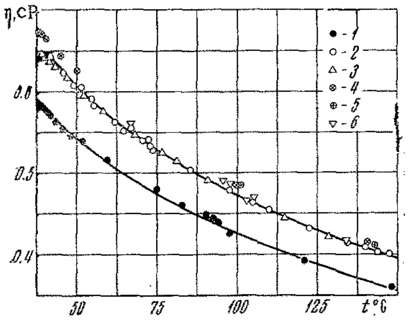

Fig. 3

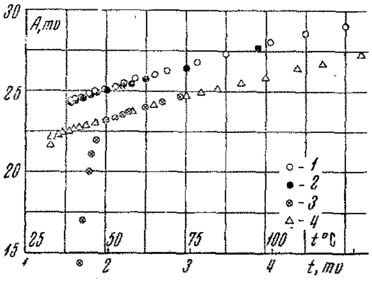

Fig. 4

Fig. 3. Viscosity of technical-grade rubidium. 1) Pure rubidium (present investigation); 2) technical-grade rubidium (first sample) 3) technical-grade rubidium (second sample); 4) data from [6]; 5) data from [5]; 6) data from [7].

Fig. 4. Probe-vibration amplitude as a function of temperature of liquid rubidium. 1) First series; 2) second series; 3) third series; 4) fourth series.

In the first series of measurements we observed an abrupt decrease in vibration amplitude at temperatures below 55°C (Fig. 2). This decrease may have been due either to an increase in viscosity by a factor of 20-30, which is improbable, or to precipitation of impurities in the form of a solid phase on the plate surface. In order to resolve this question, we conducted a special experiment in a crucible with inspection windows, in which we observed precipitation of a solid phase in the form of crystals on the surface of the crucible and melt; the amount of crystals precipitated increased as the vibration amplitude decreased.

The heating curve for the first series of measurements was plotted from steady-state points, with holding at each temperature for 10-15 min; the temperature was changed after the vibration amplitude had almost stopped rising.

The heating curve coincided with the cooling curve at temperatures above 70°C. Hysteresis occurred between the cooling and heating curve and was apparently due to concentrational supercooling. The hysteresis loop became larger when the heating rate was increased (third series of measurements), since the solid phase did not have time to dissolve in the melt.

We were able to vary the impurity concentration in the test volume in this experiment by precipitating the impurities in the batcher (second, third, and fourth series of measurements). In the last series the working volume was filled from a batcher cooled to 38.5°C, so that almost all of the impurities precipitated in the batcher.

Figure 3 gives the results obtained in measuring the viscosity of technical-grade rubidium with two different metal samples from the same batch.

After the experiment was completed, the metal was placed in a batcher, and the crystalline residue that precipitated was subjected to chemical analysis. The metallic-component content of the precipitate included less than 0.8% K, less than 0.5% Cs, less than 0.01% Na, less than 0.001% Ca, and no less than 98.7% rubidium, which corresponds to the initial composition of the metal tested.

Influence of Gaseous Impurities on Viscosity of Technical-Grade Rubidium. There are very few data on the solubility of gases and the formation of chemical compounds with alkali metals, particularly rubidium [8, 9]. The most probable gaseous impurities are compounds of rubidium or metallic impurities present in it with hydrogen, nitrogen, and oxygen. We investigated the influence of these gases on the viscosity of technical-grade rubidium.

The viscosity of the rubidium was studied in a crucible with inspection windows.

The metal was supplied from a batcher cooled to a temperature close to the solidification point of rubidium in order to precipitate the impurities present in it; the gas was introduced into the space above the melt. The amount of gas introduced was determined from the increase in pressure in this space, while the presence or absence of dissolved gas in the metal was established from the change in system pressure as a function of time. A decrease in pressure in the space above the melt indicated complete solubility of the gas in the metal when it reached its initial level.

Hydrogen. The hydrogen pressure in the space above the melt was 0.25 atm. The hydrogen was in-introduced at a melt temperature of 46°C, which was then raised to 200°C. Immediately after the hydrogen was admitted, formation of a compact film on the melt surface was observed; this apparently prevented further solution of hydrogen in the metal. After 30 h, we therefore removed the helium-hydrogen mixture from the space above the melt and substituted pure helium. After the melt was heated at 300°C for 2 h, the hydride film on its surface completely dissolved in the molten metal.

We made several series of measurements of the vibration amplitude of the plate as a function of melt temperature under different working regimes. These relationships were found to be identical to the curves shown in Fig. 2, which indicates that the main gaseous impurity in technical-grade rubidium is hydrogen.

Solution of hydrogen in rubidium does not cause an increase in viscosity and does not displace the solidification temperature of the melt.

Nitrogen. The melt was poured from the crucible into a batcher before introduction of the nitrogen. Precipitation of the impurities was conducted in the batcher, and the crucible was then again filled with the metal. The dependence of the vibration amplitude on the melt temperature after purification in this manner exhibited no anomalies down to the solidification point (Fig. 4, first series).

Nitrogen was introduced into the space above the melt at a metal temperature of 215°C. The entire curve (second series of measurements) from 215°C to the solidification point was determined over a 2 h period. During the entire experiment, the surface of the metal remained mirror-clean, and there were no changes in gas pressure in the apparatus over this period. As can be seen from Fig. 4, the second series of measurements yielded the same results as the first, i.e., the viscosity remained unchanged over the entire temperature range investigated when nitrogen was introduced into the atmosphere over the melt. This indicates that nitrogen has low solubility in rubidium at the temperatures in question and does not form chemical compounds with the rubidium or the alkali metals present as impurities.

Oxygen. Oxygen was introduced into the space over the melt at a metal temperature of 200°C. The oxygen pressure was 0.1 atm, which corresponds to 0.3 g. The oxygen completely dissolved in the metal after about 10 h. The oxygen concentration dissolved in the metal was 1 wt. %.

The vibration amplitude (Fig. 4, third series) was measured under a free-cooling regime with the temperature changing at 0.3-1 deg C/min. The vibration amplitude decreased by 8-10%, which corresponded to an increase in melt viscosity of 20%.

There was an abrupt drop in vibration amplitude at 50°C,and an oxide film appeared on the melt surface at this point. The vibration amplitude in this series of measurements decreased smoothly to 0 at complete solidification. The solidification temperature was reduced by 6°C and was 32°C.

The oxides did not have time to precipitate from the melt during rapid cooling, at rates of up to 3 deg C/min (fourth series), and no anomolies were observed in the dependence investigated.

LITERATURE CITED

1. A. N. Solov'ev and A. B. Kaplun, "A vibration method for measurement of liquid viscosity," Teplofiz. Vys. Temp., 3, No. 1 (1965).
2. A. N. Solov'ev, A. B. Kaplun, and V. N. Genrikh, "A vibration method for measurement of the viscosity of liquid metals at high temperatures," in: Research at High Temperatures [in Russian], Nauka, Novosibirsk (1966), pp. 89-100.
3. V. N. Genrikh, A. B. Kaplun, and A. N. Solov'ev, "Investigation of the viscosity of liquids by the vibration method," in: Research on the Thermophysical Properties of Materials [in Russian], Nauka, Novosibirsk (1967), pp. 112-136.
4. N. B. Vargaftik, Handbook of the Thermophysical Properties of Gases and Liquids [in Russian], Fizmatgiz, Moscow (1963).
5. É. É. Shpil'rain, Yu. A. Soldatenko, K. A. Yakimovich, V. A. Fomin, et al., "An experimental study of the thermophysical and electrophysical properties of molten alkali metals at high temperatures," Teplofiz. Vys. Temp., 3, No. 6 (1965).

6. E. N. Andrade and E. R. Dobbs, "The viscosities of liquid lithium, rubidium, and cesium," Proc. Roy. Soc., Ser. A, 211, No. 1104 (1952).
7. W. D. Weatherford, R. K. Johnston, and M. L. Valtierra, "Kinematic viscosity of liquid rubidium from 67 to 688°C," J. Chem. Engng. Data, 9, No. 4 (1964).
8. N. A. Galaktionova, Hydrogen in Metals [in Russian], Metallurgiya, Moscow (1967).
9. Rubidium [Russian translation], Izd. Inostr. Lit., Moscow (1959).