УДК 669-1

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INTERACTION OF AG, PB, IN AND THEIR ALLOYS WITH SINGLE CRYSTALS OF NIOBIUM AND IRON

By the method of sessile drop the interphase properties of the systems Pb, Ag, In, Pb-14%Ag and Ag-28%Cu — monocrystal of niobium and Pb — monocrystal of iron have been studied. For the investigation an improved technique for measuring the interfacial characteristics of liquids in sessile drop configuration was used. The results of influence of the temperature on surface properties and contact wetting angles of monocrystal of niobium with pure silver, lead and indium and binary alloys lead-silver and silver-copper and monocrystal of iron with lead are presented.

Keywords: *sessile drop; contact wetting angle; nterfacial properties; argentum, plumbum, indium alloys; monocrystals of niobium and iron.*

Методом лежащей капли были исследованы межфазные свойства систем Pb, Ag, In, Pb-14%Ag и Ag-28%Cu — монокристалл ниобия и Pb — монокристалл железа. Для исследования была использована усовершенствованная методика измерения межфазных характеристик жидкости в конфигурации лежащей капли. Показаны результаты влияния температуры на поверхностные свойства и величины угла смачивания контакта монокристалла ниобия с чистым серебром, свинцом и индием и бинарных сплавов свинец-серебро и серебро-медь и монокристалла железа со свинцом.

Ключевые слова: *лежащая капля, угол смачивания контакта, межфазные свойства, сплавы свинца, серебра, индия, монокристаллы ниобия и железа.*

Методом лежачої каплі було досліджено міжфазові властивості систем Pb, Ag, In, Pb-14%Ag та Ag-28%Cu — **монокристал ніобію та Pb — монокристал заліза. Для дослідження було ви**-*користано удосконалену методику виміру міжфазових характеристик рідини в конфігурації лежачої каплі. Показано результати впливу температури на поверхневі властивості та величини кута змочування контакту монокристалу ніобію з чистим сріблом, свинцем та індієм і бінарних сплавів свинець-срібло й срібло-мідь та монокристалу заліза із свинцем.*

Ключові слова: *лежача капля, кут змочування контакту, міжфазові властивості, сплави свинцю, срібла, індію, монокристали ніобію та заліза.*

1. Introduction. Monocrystalline materials are widely used at different branches of science and engineering. In connection with this nowadays the interest for more detailed studying of their properties, including their interaction with liquid metals and alloys, has increased. Our analysis of the literature shows that data for interphase properties of the system monocrystal of niobium – liquid metal are very scarce. In the works [1-2] only the wetting of polycrystals and thin films of niobium with low-melt-point metals such as Pb, Sn and In and some alloys on their base was studied. It is shown that pure liquid copper wets poly crystalline niobium slightly, which was connected with comparatively low purity of niobium and presence of oxide films on its surface [2]. It is determined, that in process of wetting of niobium thin film coatings of selenide of zinc with liquid lead, tin and indium the value of contact wetting angle increases with decreasing of thickness of the film and increasing of the temperature. For niobium film with thickness 15 nm the contact wetting angle is about 90-100 grad within the temperature interval from 400 to 500 °C [1]. In the work [3] the comparison of calculated and experimental values of surface tension of niobium in solid state (cts-i) at temperature near melting point is presented. These values are equal to 2210±54 and 2010±37 mJ/m^2, respectively. Most reliable data for surface tension of metals and alloys are presented in reviews [4-5].

There is a comparatively large disagreement between data for metallic systems in comparison with ceramic materials. It is explained with presence in metallic systems of surface-active impurities. These impurities concentrating on interfaces is able to change surface characteristics and thus essentially changes a lot of properties of the matter. Therefore, it is very important to control the content of impurities and try to delete them from interphase boundaries for fulfillment of investigation on interphase interaction. Authors [2, 6, 7] suppose, that the main difficulty for studying of wetting of solid metals with metallic melts is presence of oxide films on both solid and liquid matters. Thickness and stability of these pellicles are high differed for majority of metals and their destruction arises under different temperature and pressure conditions. To take into account the mention conditions the investigation of composition and properties of surface film on the monocrystal of niobium was performed. The specimen annealed in vacuum 2-10-2 Pa during three hours at temperature 1250 °C was studied using OG-spectrometer. It is determined, that surface of monocrystal of niobium is covered with entire film consisting of carbon and oxygen and has the following chemical composition (in at %): 54.0%C, 36.0%O, 10.0%Nb. To estimate the thickness of surface film the etching of the specimen was performed with ions of nitrogen. It was estimated that thickness of the oxide films on the surface of the monocrystal of niobium is about 15-16 nm. Full removal of oxygen was observed under etching during 15 minutes. At the same time the quantity of carbon decreases only to 40.1 %. Character of OG-curves shows, that the carbon on the surface of monocrystal is at free state. Thereto, the experiments have shown that to purity the surface from carbon practically impossible.

2. Experimental materials and procedure. In the present work interfacial properties were studied in the niobium monocrystal – melt and iron monocrystal – melt systems. The monocrystals were obtained by special method described in the work [8]. Metals and binary alloys, which according to phase diagrams [9] do not form chemical compounds with niobium, were chosen for investigation. As the initial materials lead with purity 99.999 %, copper (purity 99.99 %) and silver (purity 99.99 %), which previously were refused in vacuum were used. Alloys Pb-14.0%Ag and Ag-28.0%Cu were molten in vacuum in alumina crucible.

Surface properties of the melts were determined by a method of sessile drop, using a device, which consists of the resistance furnace with the heater made from platinum wire, power supply and the optical system (Fig.1). The temperature was measured with a platinum thermocouple and controlled with accuracy ±1 °C by a regulator. Before fulfilment all necessary rigs were subjected of prolonged vacuuming at temperature 1250 °C. Working surface of investigated material was polished with diamond paste, and then flushed with ethyl alcohol. Specimens from iron or niobium with investigated alloy were put to the device, and vacuumed after pressurization of the device. For experiments mutual heating of studied solid material and alloy was applied. For stabilization of measurement of the contact wetting

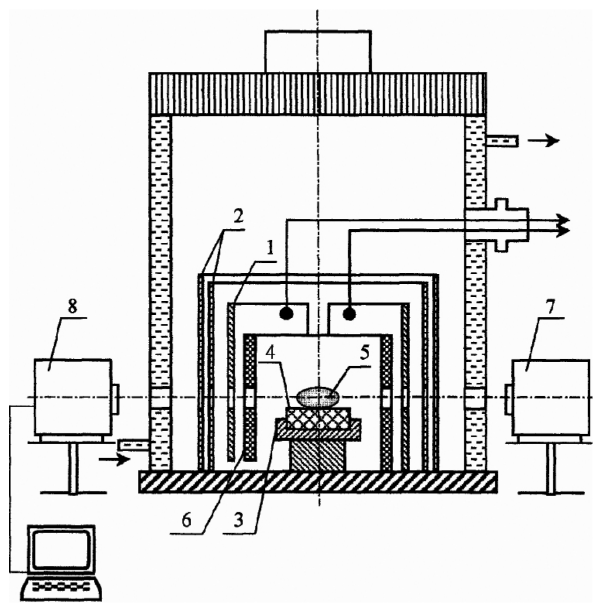

Fig. 1. Scheme of the device for investigation of interphase properties by the method f sessile drop: *1* – heater; *2* – metallic screen; *3* – table; *4* – specimen; *5* – drop of the melt; *6* – ceramic screen; *7* – lighter; *8* – video camera

angles of monocrystals of niobium and iron with liquid metals they were held during five minutes under each temperature. For choosing of optimal conditions of fulfilment of experiments they were carried out in vacuum, helium and argon. Considerable evaporation of the melt was observed in vacuum, which resulted in big discrepancies of surface tension measurement, although contact wetting angles were essentially smaller than in other surroundings. Convergence of results in surroundings of argon was unsatisfactory and some oxidation on the planes of investigated monocrystals was observed. For these reasons the experiments were fulfilled in surroundings of high-purity helium under excess pressure 1.5-10-4 Pa within temperature interval from melting point up to 1200 °C.

An improved technique for measuring the interfacial characteristics of liquids in the sessile drop configuration was used [11]. The procedure is based on grabbing of the observed shape of the sessile drop by digital camera followed by computer analysis. Accuracy of the system was checked by measuring the sizes of small steel balls and comparing them with values obtained using measurement microscope. It was found that a relative error of measurement system for objects with sizes 2-10 mm is about 0.7 %. The advantages of this technique in comparison with classical procedures (photography with subsequent measurement on a microscope and calculation of surface tension by one of known method, e. g., Porter or Dorsay [12]) has been discussed in [11].

For evaluation of capillary constant of the method of sessile drop the equation of Laplass was used [12]:

$$\frac{Z''}{(1+Z'^2)^{3/2}} + \frac{Z'}{X(1+Z'^2)^{1/2}} = \frac{Z}{a^2} + \frac{2}{h}, \quad (1)$$

where Z and X are the coordinates of the drop profile, a^2 is the capillary constant and h is the radius of the contour the top of the drop. The method of solution of this differential equation is previously described in [11].

Surface tension between liquid and gaseous phases ($\sigma_{1\text{-}g}$) was evaluated as:

$$\sigma_{1-g} = a^2 g\,\Delta\rho, \quad (2)$$

where g is the acceleration of gravity and $\Delta\rho$ is the difference between densities of liquid and gaseous phases. Interphase energy between solid and liquid phases ($\sigma_{s\text{-}1}$) was determined using Young's equation [12]:

$$\sigma_{s-1} = \sigma_{s-g} - \sigma_{1-g}\cos\theta, \quad (3)$$

where $\sigma_{s\text{-}g}$ is interphase tension between solid and gaseous phases and θ is the contact wetting angle.

3. Results and discussion. In the present work the influence of the temperature on to surface tension of pure liquid metals silver, indium and lead and binary alloys silver-lead and silver-copper was studied (Fig. 2). Temperature dependence of contact wetting angles between these melts and monocrystal of niobium (plane 110) has been obtained as well (Fig. 3). The surface tension of all investigated alloys is independent from temperature in studied temperature interval. The temperature variation of contact wetting angles in these systems, as a rule, indicates an improvement of wetting under rising of the temperature (Fig. 3).

The contact wetting angles for liquid indium, lead and lead-silver alloy are about 30-40 grad less than for liquid silver and its alloy with copper (Table).

Isothermal holding of liquid indium and lead on the monocrystal of niobium at temperature 1100 °C changes wetting essentially. Thus, after ten minutes the contact wetting angle decreases down to 40 grad for the system In-Nb and down to 30 grad for the

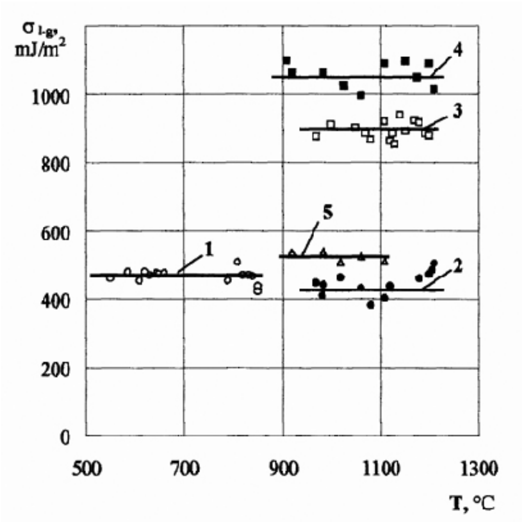

Fig. 2. Temperature dependence of surface tension of liquids: *1* – lead; *2* – lead-silver (14.0%Ag) alloy; *3* – silver; *4* – silver-copper (28.0%Cu) alloy; *5* – indium

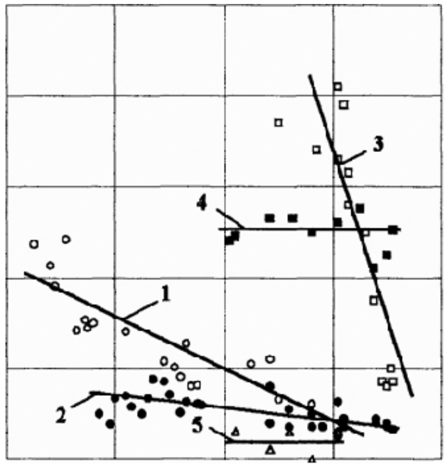

Fig. 3. Influence of the temperature on to contact wetting angles of monocrystal of niobium with liquids: *1* – lead; *2* – lead-silver (14.0%Ag) alloy; *3* – silver; *4* – silver-copper (28.0%Cu) alloy; *5* – indium

Table. Interfacial characteristics of the system liquid metal – monocrystal of niobium (1-1100 °C)

Melt	θ, grad	$\sigma_{1\text{-}g}$, mJ/m²	$\sigma_{s\text{-}1}$, mJ/m²
Pb	94+5	465±19	2242±37
Pb-14.0%Ag	94±5	442±36	2241±45
In	92±5	534±27	2228±41
Ag	125±5	882±30	2713±42
Ag-28.0%Cu	115±5	1051±47	2655±51

system lead-niobium. Strong decreasing of the contact wetting angles in these systems is probable connected with destruction of surface film on the monocrystal of niobium as the result of its interaction with the melt. Analogous effect is observed for the liquid binary Pb-Ag alloy. It was not observed the destruction of surface film at the systems Nb-Ag and Nb-(AgCu) at temperature 1200 °C in atmosphere of helium. However, isothermal holding during forty minutes of liquid silver drop on the monocrystal at 1150 °C in vacuum leads to decreasing of contact wetting angle down to 40 grad (Fig. 4).

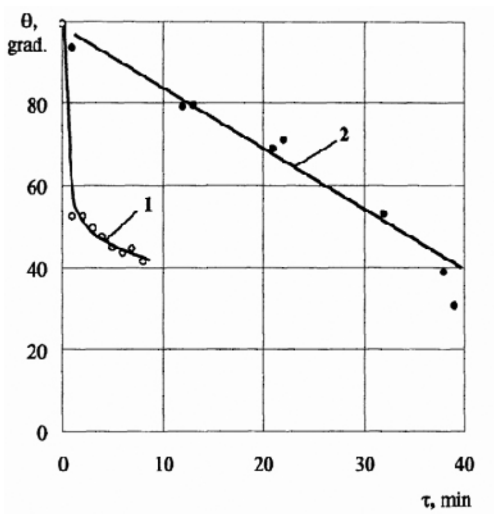

Fig. 4. Time variation of contact wetting angles of monocrystal of niobium with liquid: *1* – Pb-Ag (14.0 %Ag) (helium, T = 1 200 °C); *2* – silver (vacuum, T = 1200 °C)

Isothermal holding during 35 minutes of liquid lead drop on the monocrystal of iron at temperature 720 °C leads to the decreasing of contact wetting angle from 100 grad down to 75 grad. Increasing of the temperature of the

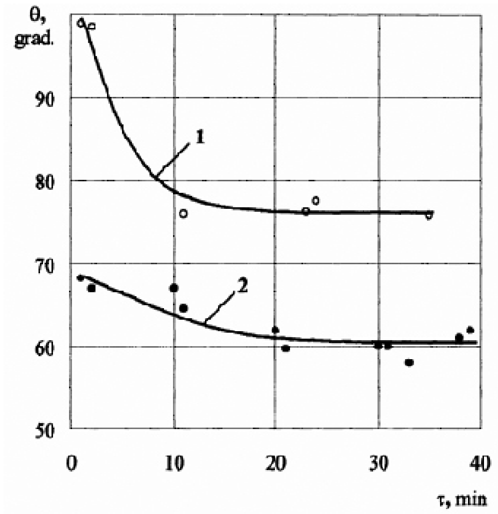

Fig. 5. Time variation of contact wetting angles of monocrystal of iron with liquid lead during isothermal holding at: *1* – 720 °C; *2* – 850 °C

isothermal holding up to 850 °C conduces to decreasing of contact wetting angle down to 60 grad (Fig. 5).

Supposing, that interphase tension on the solid-liquid boundary (σ_{s-1}) is independent from temperature and using literature data of σ_{s-1} for niobium, values of surface tension aj.g and above presented values of contact wetting angle, the interphase tension on the boundary niobium-melt was evaluated applying the Young's equation [12] (Table).

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Поступила 01.09.2015