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Wettability and contact interaction of gallium-containing melts with non-metallic solids

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The wettability of sapphire, quartz and graphite by gallium, gallium-based binary alloys with indium, tin, copper, silver, nickel, manganese, chromium, vanadium and titanium and by ternary Cu–Ga–Ti, Cu–Ga–Cr and Cu–Ga–Mn alloys has been studied by sessile drop, plate weight and meniscus form methods. The character and intensity of contact reactions and the composition of transition layers at the solid–melt boundary have been investigated by X-ray analysis and profilographic measurements and the correlation between the wettability and the contact reaction intensity has been established. The condition for high wettability of non-metallic solids by multicomponent melts is shown to be a combination of high affinity of a component for solid phase atoms with high thermodynamical activity of this component in the melt.

1. Introduction

There exists a number of systems of interest for modern technology where the liquid Ga-containing melts are in contact with solids [1–5]. Gallium and Ga-based alloys are used as heat-transfer media, sliding electrocontacts, thermometric liquids in high-temperature thermometers etc. Gallium alloys find their most important application as a basic component of diffusively-solidifying solders for soldering different materials, including non-metallic ones.

Properties and operational parameters of such contact systems and assemblies as well as the quality and strength of the soldered joints are determined largely by the capillary characteristics of the liquid phase, its ability to wet solids, by melt–solid interaction features and by adhesion within the system.

Data that have been published on the wettability of some non-metallic solids from Ga-containing melts are very scarce [6–12]. Therefore, a systematic study of capillary and adhesion effects in Ga-containing melt contacts with different non-metallic solids and also an elucidation of the interaction mechanism at the interphase boundary are of great importance. This is the subject of the present work.

2. Materials and experimental technique

The solids selected for experiments included oxidic and carbonic materials. The oxides were single crystals of alumina (leucosapphire) and silica (quartz glass). The carbon was in the form of solid graphite and vitreous carbon.

Pure gallium, its binary alloys with indium, tin, silver, copper, nickel, manganese, chromium, vanadium and titanium and also Cu–Ga–Ti, Cu–Ga–Cr and Cu–Ga–Mn ternary alloys were examined. The purities of the constituent metals were: Ga (99.9999%), Sn and Ag (99.999%), Cu (99.997%), In (99.99%), Ti, V and Cr (99.985%), Ni (99.98%) and Mn (99.97%).

Prior to measurements, oxidic and graphitic substrates were polished, washed in acetone and alcohol and heated in vacuum. The metals, gallium, indium, tin, silver and copper, were remelted in a graphite crucible in the vacuum resistor furnace (1 to 2×10^{-3} Pa) at temperatures 1100, 900, 1150, 1000 and 1300° C, respectively. The refractory metals, nickel, manganese, chromium, vanadium and titanium, were remelted in the vacuum electron-beam furnace.

The substrates were in the form of 20 to 25 mm diameter discs approximately 2 mm thick. The mass of drops was 0.5 to 0.6 g.

The wettability was investigated by sessile drop, plate weight and meniscus form methods using a universal vacuum installation [13, 14]. The vacua employed were always better than 3×10^{-5} Pa. The alloying additions were made to the melt by the introduction of solid [15] or liquid [16] elements into the molten drop during the experiment.

In the first case the gallium or Ga–Cu alloy sample was placed on the substrate studied. Samples of titanium, vanadium, chromium, manganese or nickel were placed in a special dispenser located inside the vacuum chamber, and were introduced into the melt drop by a special device at the temperature of the experimental conditions.

To introduce additives in the form of a liquid melt, special dropping bottles made of solid graphite, a material non-interacting with gallium and its indium, tin, silver and copper alloys, were used. The use of dropping bottles made it possible, by separately heating the melt and substrate, to carry out vacuum–thermal and capillary purification of the melt, to remove the oxide film and the oxygen dissolved in metal (through its reaction with carbon), and to deposit measured drops of the melt on the substrates at the experimental temperature.

The measurements were made before and after introduction of the additive, on the elapse of a time interval necessary for the dissolution of the alloying component and for alloy homogenization.

The drop profile was photographed after the contact angles had reached the stable values ($\tau = 30$ to 60 min). The contact angles were microscopically measured on photographs.

The evaluation of the degree of wettability and the adhesion tension ($\sigma_{\text{lg}} \cos \theta$) by the plate weight technique consisted in measuring the force acting on a hollow thin-walled cylinder or a plate, and in recording and measuring the form of the meniscus produced at the contact between the solid and the melt studied. The form of the meniscus was observed optically and recorded photographically, and the magnitude of the force was determined by cathetometer-measured deformation of an elastic member on which the examined sample was suspended on a thin filament. The depth of immersion of the solid into the melt was also measured to account for a buoyancy force.

The contact interaction was examined by X-ray analysis and by profilography. The phase analysis of the transition layers was made on rods about 1 mm diameter and 10 to 15 mm long coated with a layer of reaction products, obtained from immersing the rods into the melt, holding them at a definite temperature and subsequent withdrawal. The photographs were made with a sample rotating in a Debye-type chamber with Cu- and Cr-radiations [17]. The surface topography of solids that had been in contact with the melt was studied with a diamond-needle profilograph with sensitivity better than 10^{-5} mm and also by a rod diameter change (thinning or thickening) after contacting the melt. The solidified melt residual was removed by etching in a mixture of hydrochloric and nitric acids.

3. Results

Pure gallium and its alloys with indium, tin, copper, silver and nickel do not wet sapphire, quartz glass, graphite and vitreous carbon over a wide temperature interval (Figs. 1 and 2). The contact angle in Ga-solid systems diminishes as the experimental temperature rises. Similar dependencies are typical for systems examined. On introduction up to 64.5 at % In and 37 at % Sn into gallium, an insignificant tendency is observed to improve the wettability of sapphire and quartz glass. Introduction of up to 47.9 at % Ag, 9.2 at % Ni and 68 at % Cu into gallium result in the degradation of quartz glass wettability. The work of adhesion values of gallium to above solids are small and lie within 160 to $350 \times 10^{-3}\,\text{J}\,\text{m}^{-2}$. Introduction of indium, tin, silver, copper and nickel into gallium only slightly changes the work of adhesion values.

The introduction of titanium, vanadium, chromium and manganese into gallium improves the wettability of non-metallic solids (Figs. 3 to 5) especially for greater and higher temperature and concentration values of the transition metal. In so doing, the titanium shows the highest interphase activity. An improvement to wettability is observed when passing from sapphire to quartz glass and graphite.

Wettabilities of sapphire, quartz glass and graphite by ternary melts are shown in Figs. 6 and 7.

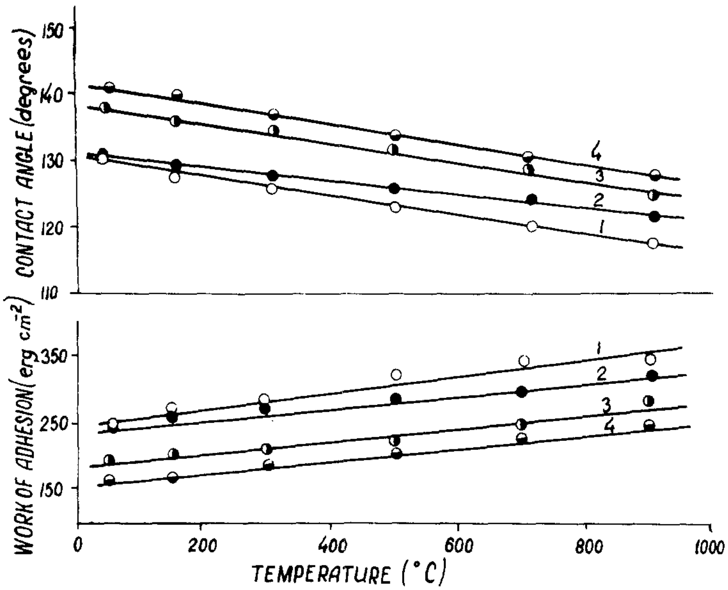

Figure 1 Wettability and work of adhesion of gallium to sapphire (curve 1) to quartz glass (curve 2), to vitreous carbon (curve 3) and to graphite (curve 4).

The comparison of wettabilities by ternary melts with those by binary ones and with the literature data [12] shows that the ternary Cu–Ga–Ti melts are wetting the non-metallic solids either better than both the binary Ga–Ti and Cu–Ti melts (in the case of quartz glass), or better than one of the binary alloys (in the case of sapphire and graphite). Here the wettability of non-metallic solids by Cu–Ga–Ti melts preserves its tendency to improve when passing from sapphire to quartz glass and graphite.

The Cu–Ga–Mn-graphite system is characterized by the presence of a "concentrational" threshold of wetting, i.e. by such a concentration of the active additive, at which a sharp improvement of wettability begins. For the ternary melts such a critical concentration is 20 at % Mn whereas for the binary Ga–Mn melt it is 39 at % Mn.

The increase of copper content in Ga–Cr melt from 0 to 69 at % leads to an improvement of the graphite wettability (Fig. 7). It is also improved with the growth of chromium concentration in the melt. The interphase activity of chromium in ternary melts, containing over 35 at % Cu, is greater than in binary Ga–Cr and Cu–Cr melts.

To understand the interphase boundary processes better and to clarify their effects upon the wettability it is essential to know the composition of transition layers, direction of their growth and the surface state of non-metallic solids in the region of the wetting perimeter after their contact with the melts. These were examined by X-ray analysis and profilography.

The X-ray phase investigations have shown that in the case of titanium being used as an interphase-active element, a transition layer consisting of titanium carbide with a composition close to stoichiometric is formed on the graphite, while on

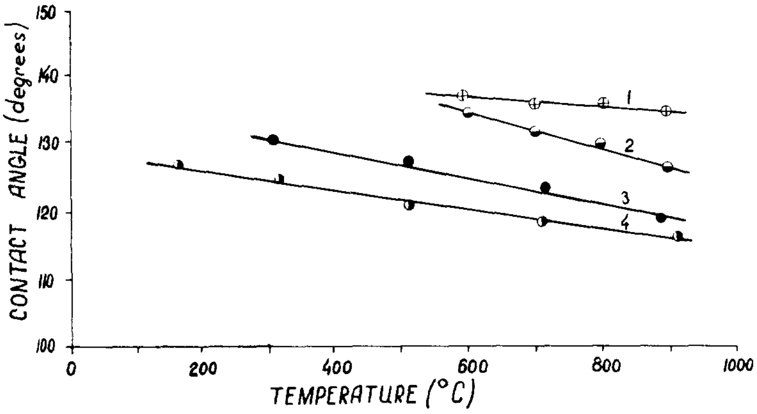

Figure 2 Quartz glass wettability by Ga + 9.2 at % Ni (curve 1), Ga + 27.9 at % Ag (curve 2), Ga + 37.0 at % Sn (curve 3), Ga + 64.7 at % In (curve 4) melts.

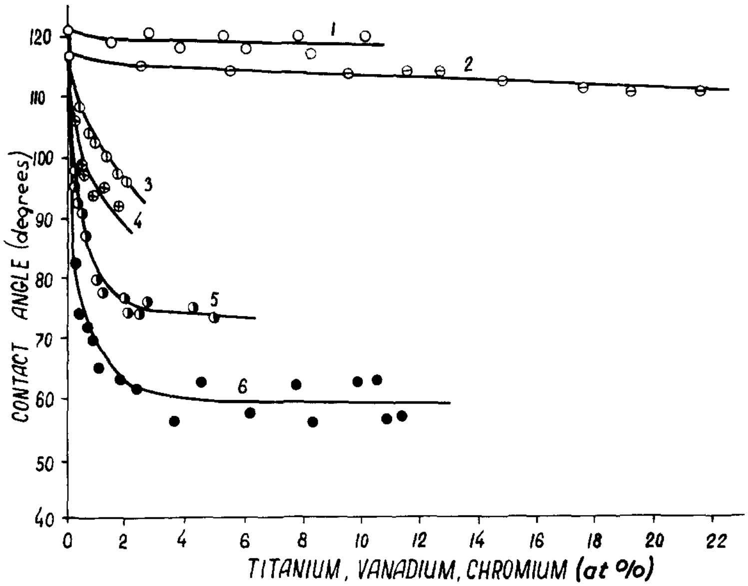

Figure 3 Sapphire wettability by Ga–Cr (curves 1 and 2), Ga–V (curves 3 and 4) and Ga–Ti (curves 5 and 6) melts. Curves 1, 3 and 5 at 900° C and curves 2, 4 and 6 at 1050° C.

the quartz a transition layer, composed of TiO and Ti_2O_3 oxides, is formed.

In the case of the Ga–V melt–graphite interaction at the liquid–solid interphase boundary, a transition layer is formed, consisting of VC, V_2C and of a solution of carbon in vanadium. A very thin grey-coloured translucent transition layer is formed on quartz. Identification of this layer failed. The layer is supposed to be the vanadium oxides.

The carbide formation process in the Ga–Cr–graphite system begins only when chromium concentration in the melt exceeds 2 to 3 at % starting from the lowest $Cr_{23}C_6$ carbide. As the holding time, chromium concentration and temperature rise, higher carbides Cr_7C_3 and Cr_3C_2 are formed, and the transition layer is composed of Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$. The most intense reaction is that with Cr_7C_3 formation.

The intensity of the chemical reaction between the (Cu + 17.5 at % Ga) + Cr-melts and graphite is high even with a chromium concentration as low as 0.25 to 0.5 at %, and the carbide phase interlayer consisting of Cr_7C_3 and Cr_3C_2 carbides is formed at the interphase boundary.

No formation of the transition layers in the Ga–Cr–quartz glass system was found by X-ray and visual inspection.

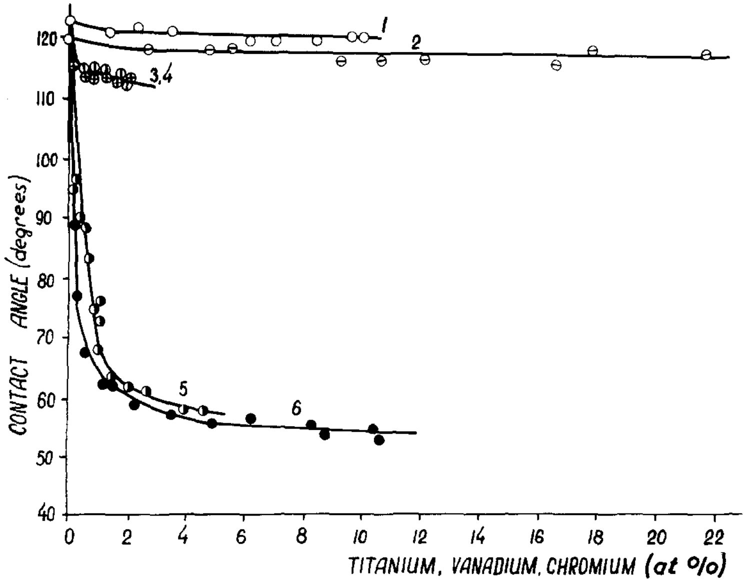

Figure 4 Quartz glass wettability by Ga–Cr (curves 1 and 2), Ga–V (curves 3 and 4) and Ga–Ti (curves 5 and 6) melts. Curves 1, 3 and 5 at 900° C and curves 2, 4 and 6 at 1050° C.

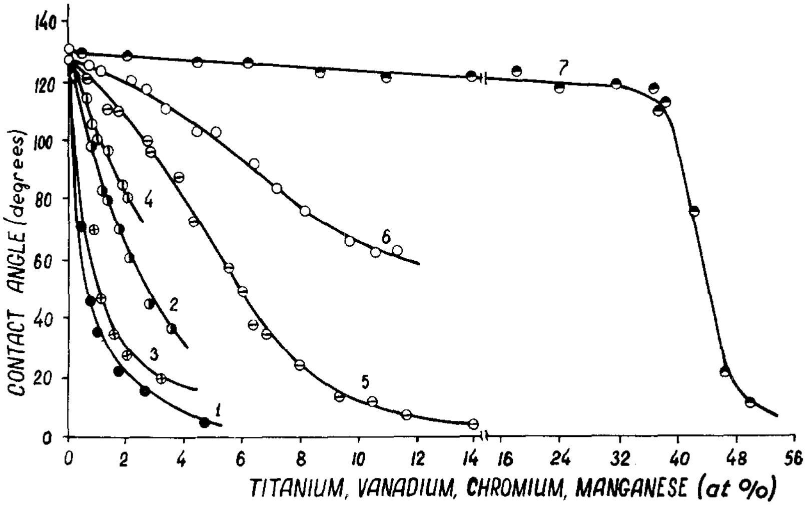

Figure 5 Graphite wettability by Ga–Ti (curves 1 and 2), Ga–V (curves 3 and 4), Ga–Cr (curves 5 and 6) and Ga–Mn (curve 7) melts. Curves 1, 3 and 5 at 1050° C and curves 2, 4, 6 and 7 at 900° C.

Pure thermal-vacuum processed gallium was deposited by a graphite dropper onto sapphire and quartz glass in high vacuum at 1050° C and held at this temperature for 15 min. The profilographic examinations show no change of the solid substrate surface profile under the drop. The interaction between binary Ga–Me (In, Sn, Ag, Cu and Ni) melts and sapphire, quartz and graphite also did not lead to a change in the surface state of the solids under the drop.

The introduction of titanium into gallium resulted in sapphire surface pitting (Fig. 8). A depression was formed under the drop, mainly within the wetting zone. On the other hand, for the quartz–Ga–Ti system at the interface boundary a build-up was observed of a transition layer, elevated over the quartz glass free surface level (Fig. 9). These effects strengthened with the titanium concentration in the melt.

The interaction between Ga–V melts and sapphire led to an insignificant pitting of the sapphire surface and the interaction between a Ga–Cr melt and quartz glass increased the roughness of the substrate surface under the drop.

In graphite–Ga–Me (Ti, V and Cr) systems the interaction process resulted in the formation of a carbide layer, slightly elevated over the free surface of the graphite, and at the same time in the pitting of the graphite surface under the melt.

For a ternary Ga–Cu–Cr melt the increase of copper content in the melt led to a change of interphase interaction character (Fig. 10). For instance,

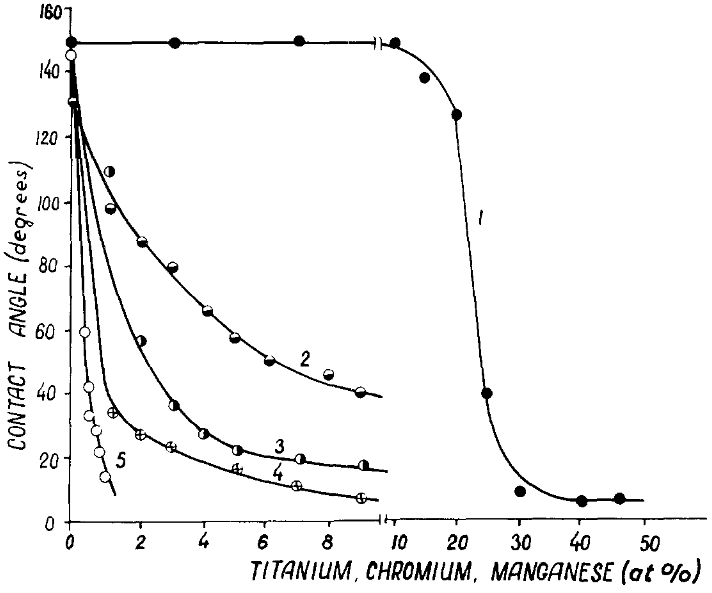

Figure 6 Wettabilities at 1050° C: of graphite by (Cu + 17.5 at % Ga)–Mn melt (curve 1); of sapphire (curve 2), quartz glass (curve 3) and graphite (curve 4) by (Cu + 17.5 at % Ga)–Ti melt; of graphite by (Cu + 17.5 at % Ga)–Cr melt (curve 5).

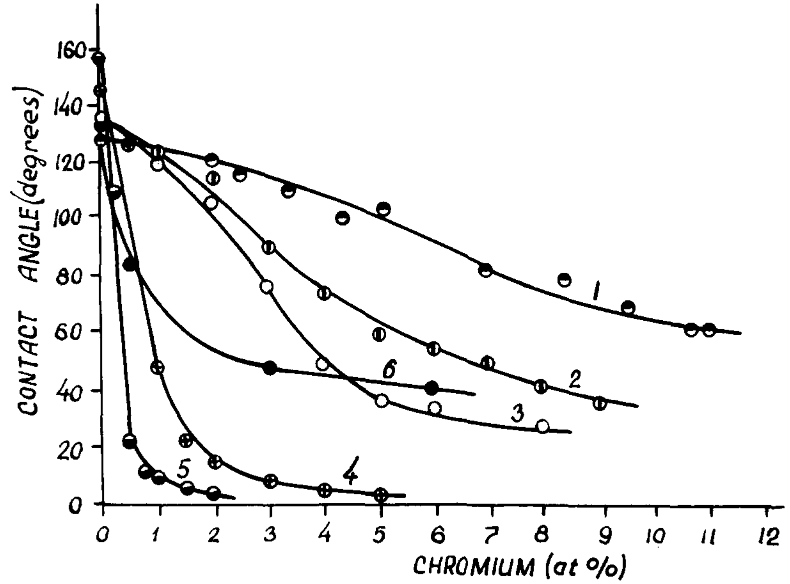

Figure 7 Graphite wettability at 900° C by Ga–Cu–Cr melts: curve 1, (Ga–Cr); curve 2 (Ga + 17.5 at % Cu) + Cr; curve 3 (Ga + 35 at % Cu) + Cr; curve 4 (Ga + 50 at % Cu) + Cr; curve 5 (Ga + 69 at % Cu) + Cr; curve 6 (Cu + Cr) according to [12] at 1150° C.

while in a graphite–Ga + 5 at % Cr system a thinning of the carbon rod was observed along with the formation, at the interface boundary, of a very thin (presumably discontinuous) $Cr_{23}C_6$ layer; at a higher copper content in the melt the degree of thinning lowered, and at concentrations of 35 at % Cu a build-up of the carbide layer, consisting of $Cr_{23}C_6$ and Cr_7C_3, took place.

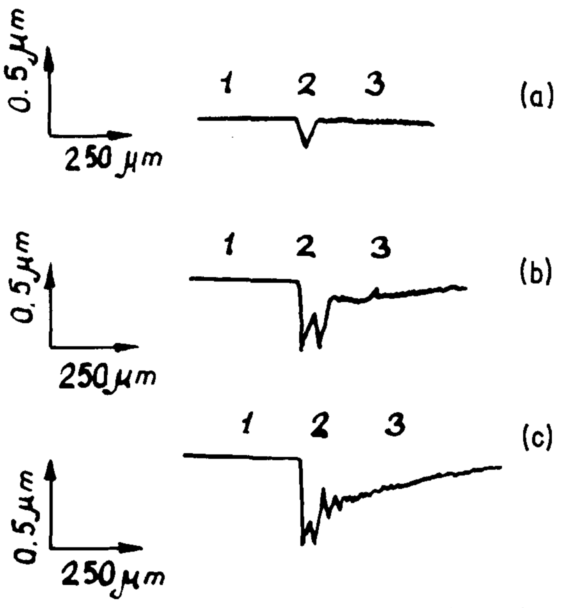

Figure 8 Profilograms of sapphire surface after interaction with Ga–Ti melts ($T = 1050°C$, $\tau = 15$ min, $p = 3 \times 10^{-3}$ Pa). Curve 1, the surface in front of the drop; curve 2, the profile of perimeter of wetting in radial direction and curve 3, the surface under the drop. Charge concentration of titanium in alloy (a) 0.70 at %, (b) 7.77 at %, (c) 11.33 at %.

4. Discussion

The comparison of intensity, type and character of the interphase interaction and capillary and adhesion properties of binary Ga-containing melts is given in Table I.

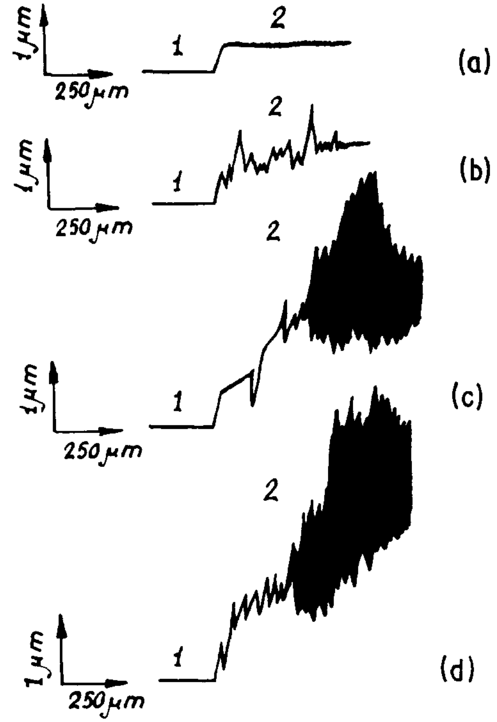

Figure 9 Profilograms of quartz glass surface after interaction with Ga–Ti melts ($T = 1050°$ C, $\tau = 15$ min, $p = 2 \times 10^{-3}$ Pa). Curve 1, the surface in front of the drop and curve 2, the surface under the drop. Charge concentration of titanium in alloy (a) 0.29 at %, (b) 0.86 at %, (c) 1.52 at %, (d) 10.37 at %.

TABLE I Comparison of wettabilities and adhesion properties with interphase interaction character and the composition of transition layers

System	T (°C)	θ (degrees)	$\sigma_{lg} \cos\theta$ ($\times 10^{-3}$ J m^{-2})	W_A ($\times 10^{-3}$ J m^{-2})	ΔG (kcal (g at O_2(C))$^{-1}$)	Shape of profilograms of s–l and s–g surfaces near wetting perimeter	Phase composition of transition layer	Condition of interphase boundary under drop
Al_2O_3–Ga	1050	117	−294	353	+37		–	no change
Al_2O_3–Ga–In(Sn)	900	115	−266	364	+49(63)		–	no change
Al_2O_3–Ga–Cr	1050	114	−264	384	+36		–	no change
Al_2O_3–Ga–V	1050	91	−11	643	+29		–	slight pitting of solid phase
Al_2O_3–Ga–Ti	1050	60	+324	972	+6		–	pitting of solid phase
SiO_2–Ga	1050	119	−314	333	+14		–	no change
SiO_2–Ga–In(Sn, Ni, Cu, Ag)	900	119–135	−(467–305)	193–325	+25(39–80)		–	no change
SiO_2–Ga–Cr	1050	118	−304	344	+13		–	increase of roughness
SiO_2–Ga–V	1050	114	−266	388	+6		vanadium oxides	–
SiO_2–Ga–Ti	1050	57	+353	1001	−17		Ti_2O_3–TiO	transition layer growth in melt direction
C–Ga	1050	127	−389	258	–		–	no change
C–Ga–In	900	126	−370	260	–		–	no change
C–Ga–Mn	900	126	−389	274	−3		–	–
C–Ga–Cr	1050	65	+274	922	−19		$Cr_{23}C_6$, Cr_7C_3, Cr_3C_2	carbide layers formation and graphite surface pitting
C–Ga–V	1050	15	+632	1286	−26		VC, V_2C, V(C)	
C–Ga–Ti	1050	5	+646	1294	−40		TiC	

θ, $\sigma_{lg} \cos\theta$ and W_A values are given for compositions of Ga + 5 at % of the second component.

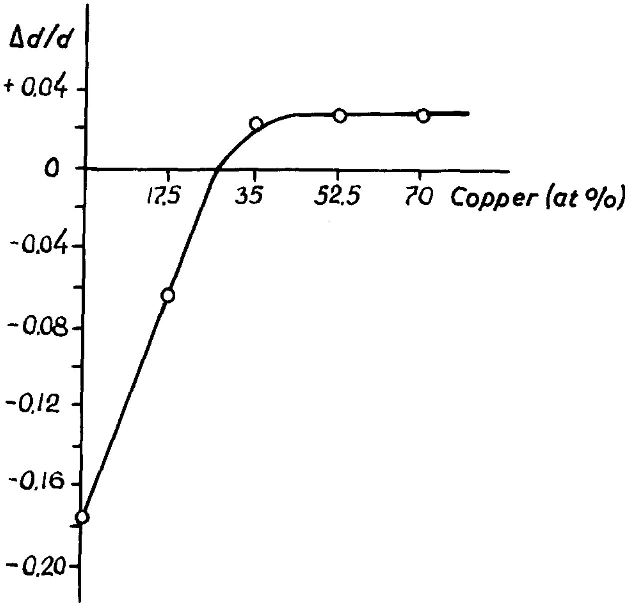

Figure 10 Relative variation of graphite rod diameter against copper concentration in melt.

On the basis of the chemical theory of wetting [12, 18], the high values of the wettability and of the work of adhesion to non-metallic solids are possible for the case of an intense chemical reaction taking place at the interphase boundary. Its intensity is determined by the free energy loss (ΔG) at the liquid metal-wetted body interaction and, for the case of oxide or graphite, wetting is determined by the interaction of the liquid phase metal with oxygen or carbon, respectively.

The metals examined fall into two groups by their affinity for oxygen and carbon [19–21]. The first group contains the elements whose affinities for oxygen and carbon are equal or lower than those of Ga–In, tin, silver, copper and nickel*; the second one contains those with higher affinities, manganese, chromium, vanadium and titanium.

Pure gallium does not wet the examined oxide and carbon solids. The isobaric–isothermic potential (ΔG) of the interaction reaction

$$\mathrm{Ga} + \mathrm{Me}_x\mathrm{O}_y \rightleftarrows \mathrm{Ga}_x\mathrm{O}_y + \mathrm{Me}$$

arising from the contact of gallium with Al_2O_3 and SiO_2 oxides with the formation, for instance, of Ga_2O_3, acquires a high positive value, i.e. practically no reaction occurs. As regards to graphite, gallium is chemically inert. The interaction at the liquid–solid interphase boundary in these systems is determined by weak physical (dispersion) binding forces which are unable to provide a high degree of wettability.

Metals (indium, tin, copper, silver and nickel) introduced into gallium do not decrease the contact angle of wetting and do not change the interphase bond type. Their affinity for oxygen (in the case of oxide wetting) is lower than that of gallium and (in the case of graphite wetting) all of them (except nickel) are carbon-inert, like gallium.

The chemical reaction occurring at the solid–melt boundary due to the introduction of metals, titanium, vanadium, chromium and manganese, into gallium, which have a higher affinity for oxygen and carbon as compared to gallium, provides an increase in wettability, a transition from negative adhesion tensions to positive ones and an increase of adhesion work. These properties are improved with the increase in metal affinity for oxygen and carbon, i.e. by decreasing positive ΔG magnitude and its transition into the negative region.

The X-ray analysis and profilographic examinations show that the intensity of the melt–oxide interphase chemical reaction (thickness of intermediate phases, corrosion depth of solid phase) increases following the sequence (Ga–Cr) → (Ga–V) → (Ga–Ti), and, in the case of melt–graphite, increases following the sequence (Ga–Mn) → (Ga–Cr) → (Ga–V) → (Ga–Ti). The wettability increases along the same sequences.

The interphase activity of additives in inert melts, i.e. solvents, apart from their chemical affinity for the solid phase elements, essentially

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*Only for systems with oxides.

depends upon the strength of the interatomic melt-active additive bond, i.e. upon the thermodynamical activity of the additive in the melt.

Typical concentrational dependences the degree of wettability for Ga–Mn and Ga–Cr melts (high values of contact angle at low concentrations, presence of a peculiar concentrational wettability threshold) may be explained by a low thermodynamical activity of the additive in the melt. The values of the binding energies of the gallium and manganese atoms, on the basis on constitution diagrams [22–25] (the presence of intermetallics in the systems), must be comparable to the manganese affinity for carbon (approximately $-3\,\text{kcal}\,(\text{g at C})^{-1}$).

The existence of strong bonds between gallium and manganese atoms, the affinity of the latter for carbon being small, results in that manganese begins to appear as an interphase-active element, only at high concentrations. The greater affinity of chromium for carbon ($-19\,\text{kcal}\,(\text{g at C})^{-1}$) as compared with manganese, leads to a shift of the concentrational wettability threshold into the region of lower chromium concentrations in the melt.

The high wettability of ternary melts can be explained by a greater thermodynamical activity of adhesion-active additives in the ternary melt as compared with those in the binary ones.

The latter statement for Cu–Ga–Cr and Cu–Ga–Mn melts stems from the following. For Cu–Ga, Ga–Cr and Ga–Mn systems the presence of intermetallics is characteristic while in Cu–Cr and Cu–Mn systems no chemical composition are present [22–26]. One may conclude that the binding energy between copper and chromium or copper and manganese atoms is very slight and is smaller than that for Cu–Ga, Ga–Cr and Ga–Mn systems. Therefore, the introduction of copper into gallium must weaken the chromium or manganese atom bonds with melt–solute Ga–Cu atoms (substitution of gallium for copper and binding the gallium atoms left with copper), which determines an increase in the thermodynamical activity coefficient of chromium or manganese and an augmentation of their interphase activity in the ternary melt. For Cu–Ga–Ti alloys the pattern is somewhat more complicated due to the presence of intermetallics in the Cu–Ti systems.

Moreover, the increase of copper content in the Ga–Cr melt led to the change of the interphase interaction character, namely, the change from graphite surface corrosion (pit depth about 10^1 to $10^2\,\mu$m) accompanied by the simultaneous formation of a very thin (obviously discontinuous) carbide layer at the melt–solid interphase boundary, to the formation of a thick carbide interlayer elevated over the graphite surface level. The latter favours the wettability since, at the contact boundary, an interlayer is formed of chromium carbides with metal-like properties, which are better for melt-wetted graphite.

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