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# THE RELATION BETWEEN THE SURFACE TENSION AND THE SURFACE TEXTURE FORMATION

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***Abstract***
*Abstract. The temperature dependence of wetting angles Θ(T) of Ag-M based melts (M: Cu, Zn, Ga) on graphite substrates are compared. The slope of Θ(T) is negative, which follows from the spirit of Eötvös rule. The difference in the slope arises from the M alloying elements A texture formation was found in the substrate/drop interphase region after solidification. The enrichment (segregation) of Ag atoms in the interface layer was observed in the Ag-Ga alloy in the solidified structure. The action of the melt temperature was examined also on the degree of texture formation, which seems to be coupled with the magnitude of the contact angle.*

## 1 Introduction

The significance of Ag-based alloys is important in brazing and welding process [1]. The wetting phenomena between the filling alloy melt (brazing alloy) and the materials has of a central role in the formation of sufficient quality, which serve the formation of steady joint between the parts [2, 7, 8]. Alloying elements are also often used for this purpose partially because of the melting point lowering and, for the further increase of wettability between the parts outlined. Both property changes depend on the individual properties of alloying elements, including their surface activity in the Ag host and their interaction with the oxygen which cannot be fully eliminated from the ambient atmosphere. In earlier papers the role of Cd, Sn and Sb alloying elements on the wettability between graphite and $Al_2O_3$ substrates were reported [3]. It was found, that wettability of the same melt is better on $Al_2O_3$ surface. It was also detected, that electron density in the AgM (M = alloying element) may also have an influence on the surface energy of molten alloy drops [4]. Preferred orientation relationship between the interface layer of the solidified melt and the wetting angle in molten state was also discovered in certain alloys [5]. In this paper this structural investigation in the solidified interfacial layer will be continued.

## 2 Experimental

The detailed description of measuring principles systems as well as the equipment was reported in Refs. [3, 5].Alloys was prepared from high purity (4N) Ag, Cd, Sn and Sb respectively, using induction melting in cold crucible under inert (Ar) atmosphere. The graphite substrate was made from high purity, porosity free base material. Inert (Ar) atmosphere was applied during the alloy preparation and the wetting experiments. SEM investigations were carried out using a SEM type JEOL-JSM25-SIII, in secondary electron imaging mode. The constituent elements were analysed by a Bruker-Röntec EDS microanalyser system, attached to the SEM. The excitation parameters were 25keV beam energy and 50-200 pA beam current. The quantitative results were obtained from the measured spectra by a no-standard QUANTAX P/B ZAF correction program. The

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XRD measurements were performed with a Philips X'Pert diffractometer and the profile fitting of the detected XRD patterns were carried out using the Pro'Fitt commercial program.

## 3 Results and discussion

The wetting ability, represented by the wetting angle (Θ(T), increases with the increasing temperature in all samples as it is depicted in the Fig.1. This finding is in qualitative agreement with the earlier observations, supported also by the spirit of Eötvös rule [8]. Similar tendency is reported previously in $Al_2O_3$ substrate.

The effect of alloying elements on (Θ(T) is also visible in Fig.1. While Θ is slightly increased due to the Zn and Cu replacement (the wetting ability decreases), the influence of Cu and Ga is opposite: Θ is lowered, hence the wetting ability increases nearly in the whole temparature range investigated. Another important feature of the curves is the different slope of their T-dependence. The highest is for the AgGa alloy, while the lowest is for Zn and Cu.

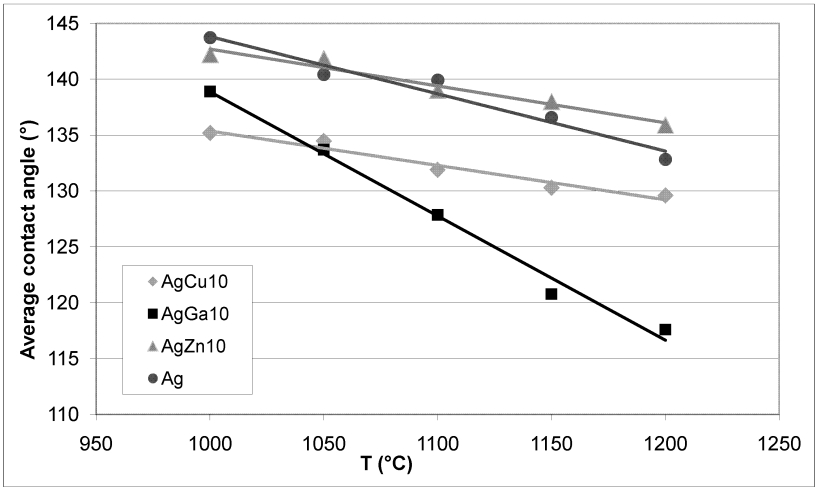


*Fig.1. The wetting angle for pure Ag, Ag(Cu10), Ag(Zn10) and Ag (Ga10) melt drops versus the temperature*

The existence of crossovers between Ag and Ag(Zn) as well as between Ag-Cu and Ag-Ga is also remarkable in the investigated systems. This means, that the wetting ability and its temperature dependence is significantly modified by the alloying elements in the Ag- based alloys. The temperature of the crossowers are not exactly the same, it is higher between the AgZn and pure Ag liquids. The existence of crossowers are probably are associated with the different shape of the appropriate phase diagrams, mainly due to the different concentration partioning between the liquidus and solidus curves. The Ag-Ga alloy exhibits the highest degree of partioning (Fig.2). Another remarkable observation is, that (Θ(T) is nearly the same for the pure Ag and the Ag(Zn), which is probably also connected with the low degree of concentration partioning between the liquidus and solidus in the Ag(Zn) alloy, as well as the wide solubility range of Zn in the Ag (see Fig.2.).

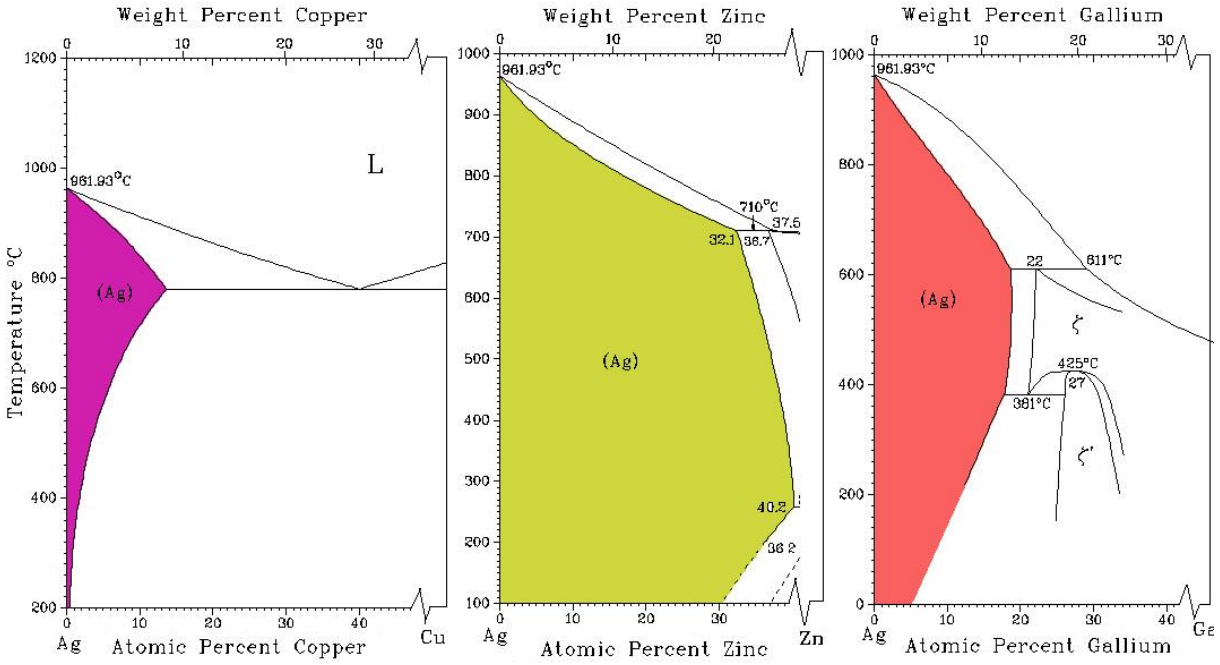


*Fig.2. The concentration range of terminal (α)-solid solutions in Ag-Cu, Ag-Zn and in Ag-Ga systems*

In Fig. 3. some conclusion can be drown regarding the Ga distribution, local concentration near the substrate layer comparing them with that in the inner side of the drop. According to this local analysis the Ga content is significantly lower at the substrate side (around 7 at %), showing the depletion of alloying element in this surface layer. In contrast the concentration is near to the nominal 10 % in the enterior of the drop. To get information about the intermixing effect at the substrate interface it would be important to detect the concentration of C, but the results of this measurement are qualitative only, due to the low sensitivity of EDAX analysis for this element, and the contaminations caused by electron beam. According to the measurements the concentration of C is higher near to the substrate/drop interface which hints to the possibility local incorporation of Carbon atoms either into the interface layer or into free surface the melt drop.

Comparing the Fig.1 and 2., the temperature range of measurements is well beyond the liquidus line in each alloy. Hence connection between the increasing slope of Θ(ΔT) and the beginning segregation in the case of Ag-Ga seems to be surprising at a first glance, because of the significant temperature difference between the appropriate liquidus and the performed measurements. Nevertheless, the segregation between the inner and the substrate side in the solidified drop is experimentally verified by the EDAX measurements, as it is illustrated in Fig.3. It is suspected therefore, that the experimentally detected concentration partioning (segregation) has probably started already in liquid state, as the equilibrium liquidus line is approached during the temperature sink. According to the spirit of this partioning, the Ga- content in the solidified drop should be lower near to the primarily solidified part of the melt, which is really in qualitative agreement with the EDAX measurements illustrated in Fig.3. As it follows from the comparison of the shape of phase diagrams, the highest segregation is expected in the case of Ag-Ga. This is really the case according to the Fig.3.

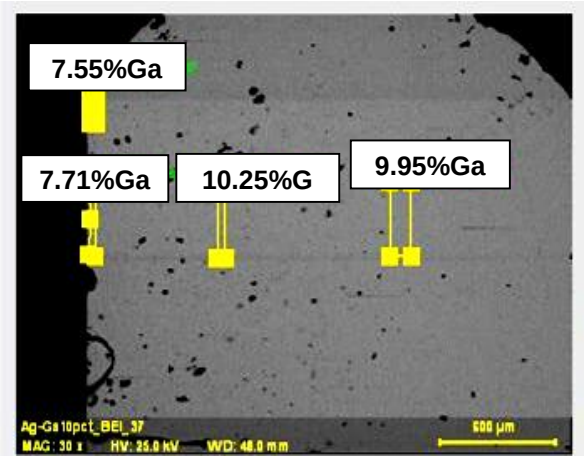


*Fig.3. The scanning electron microscopic picture from the cross section of AgGa10 sample (1200 ˚C), and the concentration values detected on the marked areas.*

Another important observation is the correlation between the character (slope) of Θ(ΔT) curves and texture development in the melt/graphite interface layer during the solidification. This effect is also more pronounced in the Ag and Ag-Ga drops. Therefore, a more detailed temperature dependence of this texture formation was investigated. The essence of texture development is that preferential crystallographic relationship is developed between the planes of growing crystallites firstly solidifying from the drop, near to the interface. In the case of Ag, Ag-Zn and Ag-Cu a strong (001) texture is formed, which means, that (100) plane are parallel orientation with the graphite surface in most of crystallites. The textured structure of the crystallites is the strongest at the interface in the Ag-Ga (1200 ˚C) sample, where the (311) peak is the most intensive. In contrast, the crystal orientation in the interior of solidified drop is nearly random. In the previous work it was found that with decreasing wetting angle texture-orientation is increasing.

Comparing the intensity values measured at 1000 ˚C and 1200 ˚C respectively, the outlined tendency is further strengthened, i.e. the textural correlation is even more pronounced in the interface layer. The existence of this correlation opens the area of speculation directing into the deepest level understanding of the outlined phenomena.

In Fig. 4. the XRD spectra are visible, taken from the graphite-side and inner part region of solidified Ag drop 2a (1200 ˚C, inner part of the sample) the typical random distribution is the most intensive reflection very similar to the typical polycrystalline “powder” sample, where the (111) peak reflection is the strongest.

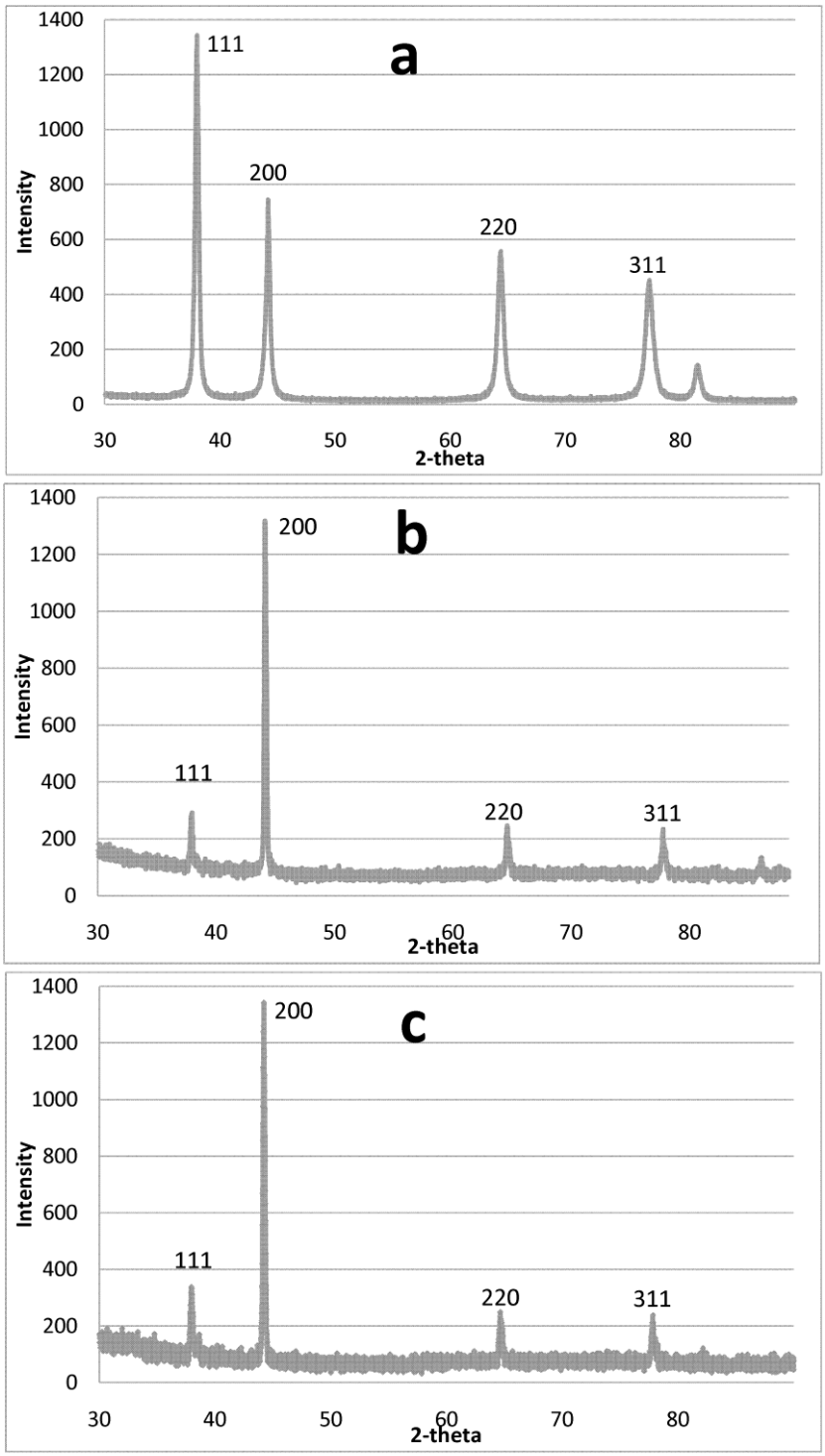


*Fig.4. XRD spectra measured on Ag sample solidified from 1200 ˚C a) middle of drop, b) at the graphite interface, c) sample cooled from 1000 ˚C*

In contrast, the (200) reflection is the dominant near the drop/ graphite interface showing, (100) planes are parallel to the graphite surface in the dominant fraction of grains. Comparing the intensity rations obtained on samples (solidified from 1000 ˚C and 1200 ˚C): I(200)/I(111) = 4.3 and 8.16, with the appropriate (Θ) values of 144˚ and 132˚ respectively, in agreement with the earlier observations.

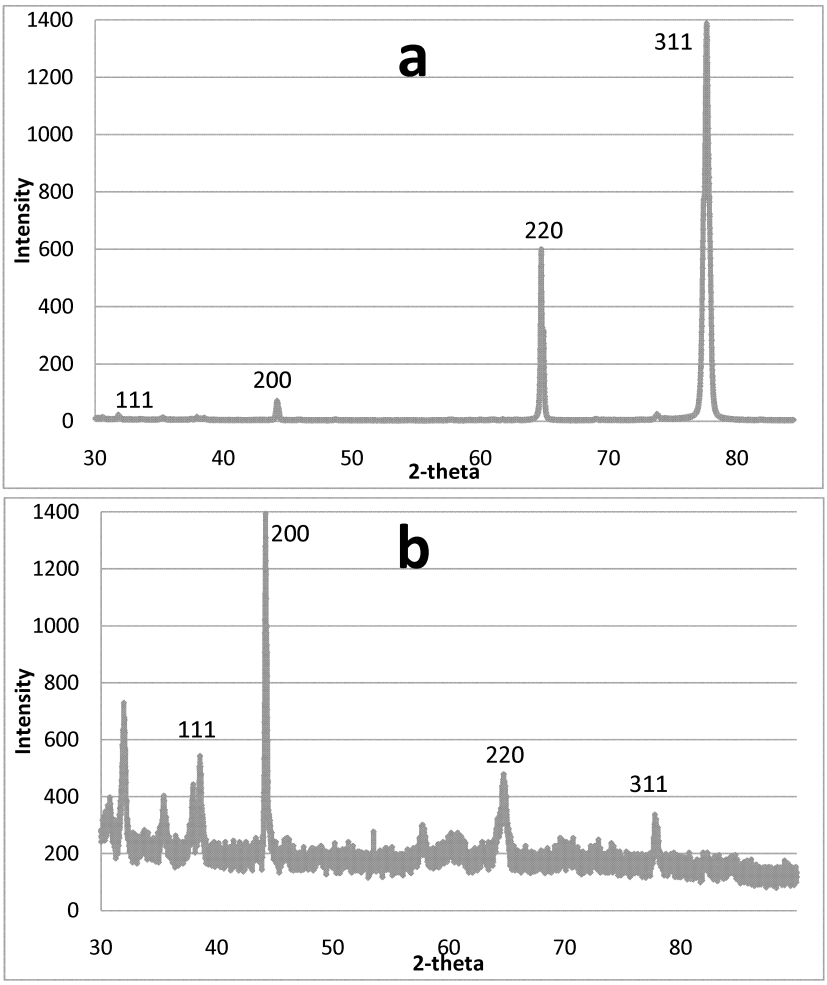


*Fig.5. The XRD spectra for Ag-Ga samples on the substrate side (a: 1000 ˚C, b: 1200 ˚C)*

In Fig.5. the XRD spectra from AgGa10 sample (cooled from 1000 ˚C) and 1200 ˚C respectively) are visible. The structure from 1000 ˚C sample is similar to the pure Ag i.e. the 200 reflection is the more pronounced reflecting the dominancy of 100 texture. The intensity ratio of reflections: I(200)/I(111) = 4.8; the appropriate value is 139˚.

In the sample with the smallest value (sample cooled from 1200 ˚C) the ratio of reflections intensities totally differs from all other samples. The (311) and (200) reflection are the most intensive contrast to the inner part of the sample, and the sample cooled from 1000 ˚C, where these intensities are extremely week. It means, that (311) and (220) planes are parallel to the graphite surface, i.e. the texture is more pronounced in the surface layer, causing the best wetting conditions, as the lowest value does also support (118˚).

## 4 Conclusions

Wetting conditions of the investigated alloy drops depend on several, often controversial factors. The resulting surface-tension vectors manifest itself in the equilibrium value of contact angle. The contact angle representing the wettability between the substrate material and the sessile drop decreases with increasing temperature for simple liquids, like in the case of pure Ag melts, when the chemical interaction is negligible (present investigations with pure Ag). On the other hand, when alloying elements are dissolved in the host metal, local (temperature dependent) local deviations may occur either around the free surface or in the substrate/melt interface layer.

The preferential depletion of certain alloying element in the drop/substrate interface layer can be definitely detected, in spite of the alloy composition, which is below solubility limit, at least in high

temperature ranges. This experimental finding hints to the fulfilment of thermodynamic tendency, which govern the decrease of the interface energy via the depletion of certain components.

The thermodynamically governed tendency can be suspected also in the development of preferential orientation between the crystal structure and substrate in the interface layers (enhanced via surface diffusion), ensuring the optimum fitting to the graphite sheet around the interface. Via this preferential orientation favourable packing density is developed in the contacting crystal planes, which can also contributes to the minimization of interface energy between the drop and graphite substrate.

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