Wetting Ability between Silver Based Alloys and Ceramics, Supporting the Joint Formation Mechanism in Vehicle Industry
Ph.D. theses

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Introduction

The dynamically growing vehicle industry requires the technology development and, simultaneously the intensive research activity in the field of material science as well. One of the central concept in the reproducibility of the joint technology is the mutual wetting ability between the co-existing liquid and solid phases. Such technologies are the soldering, brazing, welding, etc. In the industrial praxis the wetting ability is often enhanced by the application of fluxes or coatings.

Soldering is the most popular joint technique in microelectronic and optoelectronic industries which technologies are widely used in the vehicle industry [1-4].

Ensuring good wetting conditions between the solder material and the metallic parts to be joined is of great importance in these processes [5-9, 38-39]. The Ag based alloys are particularly promising in this respect especially, when the world-wide trends in the replacement of lead-thin based alloys are considered [10-13].
**Experimental conditions**

Alloys were prepared from high purity (4N) materials, using induction melting in quartz crucible under inert (Ar) atmosphere. The substrates were prepared from high purity, porosity free base material. The substrates were mechanically polished to Ra=0.23±0.005 μm, r=1.009±0.0005, then the surface roughness was determined using a 3D laser profilometer. (Rodenstock RM600 surface topography measurement system).

The wetting experiments were performed in home-made equipment developed for sessile drop measurements. The graphite substrate and the alloy pieces were positioned into the middle of furnace at ambient conditions. The pressure was then reduced to 0.1 Pa at room temperature in the chamber. The vacuum was replaced by a 10\(^5\) Pa 99.999 % Ar gas. This procedure was repeated 3 times. Subsequently, the temperature was raised to 1273 K using a heating rate of 4 K/s. Since only a small part of the gas chamber is heated, no pressure change could be detected in the chamber (10\(^5\) Pa) during the measuring run, which was performed during the heating run at 1273, 1323, 1373, 1423 and 1473 K respectively [18].

The heating power has stopped around each measuring temperature. The equilibrium contact angle was stabilized within one minute [19]. Two minutes holding time was applied before the measurement. The contact angle was determined by measuring directly the profile of the drop. Self-made automatic software in the Matlab environment is used for fixing and processing the data. Though the uncertainty of this software is below 1 degree, the total uncertainty of the measured values is higher: ±3°. At the end of the measuring process at 1473 K, the furnace was switched off and cooled slowly to the ambient temperature (the whole cooling time is around 40 minutes). Subsequently the furnace was opened and the solidified sample was removed.

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 micro analyser system, attached to the SEM. The excitation parameters were 25 keV 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 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.
Results

The insulation of the furnace

The insulation increases the size of the internal surfaces. However, the bigger inner surface in the vacuum chamber causes bigger irremovable oxygen concentration.

The construction, which can solve the problem, is shown in Figure 1. The quartz glass is smooth enough, so the increase of the surface is as small as possible. The essence of construction is a double-wall cryostat body, which can be evacuated. This cryostat body ensure excellent heat isolation around the resistance furnace. An insulating blanket of Al₂O₃ layer is placed into the quartz glass cylinder. The quartz glass resists sudden heat shocks and its poor heat conductivity makes it suitable for the purpose. Cooling water circulates around the insulation, which cools the environment. The insulation concentrates and reduces the spread of heat produced by the resistance heating [18].

![Fig. 1 – Furnace and insulation](image)

Automation of wetting angle measurement

The automation is the solution for the elimination of deviations. The automatic evaluation program firstly converts the colourful measurement picture into a black and white image (Fig. 2). Both the substrate and the drop will be white and the environment will be black, so the outline of the drop
can be determined easier. In the next step the program starts vertical search at a specified interval from the right and left sides of the image to find the first transition points between the black and white areas. Then, the program determines the focal points of these sets of transition points on both sides. The connection line of these focal points represents the top of the substrate (see Fig. 2).

Subsequently, it starts horizontal search at a specified interval and height above the previous line to find the first transition points between the black and white areas from the right and left sides of the image. In this way two sets of points are reached (curved scatter graphs on Fig. 2) representing the contour of the drop. The program fits two circles on these point sets. Solving the geometrical equations of the line and the two circles the program obtains the intersection points of circles and the base line (see Fig. 2). Choosing the two appropriate solutions, we get the two sidewise contact points of the drop. The radiuses – connecting the intersection points and the centres of the circles – are perpendiculars to the tangents that can be drawn to the circles at the intersection points. Thus, wetting angles can be got from the angles of the base line and the radiuses via coordinate-geometrical calculations.

Fig. 2 – Molten pure Ag drop on graphite substrate

With this method the inaccuracy of human work during the manual evaluation can be eliminated. The evaluation of the experiment results is executed beside the same conditions, so the comparison of the outcomes is reliable, reflecting the real correlations.
The investigated alloys (metallurgical characterization)

It is well known, that several correlations exist between the bulk physical properties and the shape of phase diagram in metallic systems. On the other hand it was also reported already in early papers that surface molar energy of liquid metals is in close connection with the heat of vaporization [37]. The correlation is similar with the melting point of the appropriate metals. It is also known that simple relation exists for the description of phase stability and the electron structure of simple alloys. The investigated alloys were selected on the basis of outline principles [14-17].

An additional motivation in the alloy selection was the simple solidification mechanism, i.e. the simple phase relation which is developed during the solidification.

All alloys (except the 10 at% Sb alloy) do form continuous series of solid solutions after solidification, i.e. only a single phase is formed from the molten state and no second phase precipitation occurs at low temperatures.

The position of solutes in the periodic table shows the increasing group number (Fig. 3.).

![Periodic Table](image)

Fig. 3. The position of alloying elements in the periodic table

The shape of the appropriate phase diagrams (details from the Ag-rich sides) are collected in the Fig. 4. The common feature is the tendency of solid solution formation at the Ag-rich sides during the solidification. The solidified alloys are not homogeneous however, in atomic scale, as the solute segregation occur. The degree of equilibrium segregation is reflected in the shape of the individual alloys. As the actual cooling rate is low, (see the experimental description) this segregation can be regarded as “equilibrium segregation”, so the concentration difference between the solid and the liquid difference does really represent the equilibrium distribution of the solute atoms in the solidified drop. The solubility limit (stability range of \( \alpha \)-solid solutions) in these alloys is governed by saturation value of the average valence electron concentration at the Fermi level of Ag. This „electron phase”
concept is generally accepted in the metal physics, where the dominantly s and sp electrons are present in the valence band. The upper limit of this concentration is around \((e/a \sim 1.36-1.59)\) representing the stability limit of \(\alpha\)-solid solution. One can understood therefore, that alloying (partial replacement of Ag by these elements with metals) leads to the narrowing region of \(\alpha\)-phase.

![Graphs showing phase diagrams for Ag-Cd, Ag-In, Ag-Sn, and Ag-Sb systems](image)

**Fig. 4.** The range of terminal (\(\alpha\))-solid solutions in Ag-Cd, Ag-In, Ag-Sn and Ag-Sb systems [26]

On the other hand it is clear, that the stability range of these \(\alpha\) solid solutions are in close connection with the mentioned degree of segregation, which reflects the degree of difference between chemical potential of solutes between the contacting phases at a given temperature. The solubility limit can be explained on the basis of „electron phase“ concept. Accordingly, the stability range of these solid solutions is governed by average valence electron concentration at the Fermi level of Ag. The upper limit of this concentration is around \((e/a \sim 1.36-1.59)\) for the stability limit of \(\alpha\)-solid solution in Ag. One can understood therefore, that alloying (partial replacement of Ag by these elements in the sequence Cd→ In→ Sn→ Sb leads to the narrowing of the \(\alpha\)-phase region. The predictive power of this criterion is qualitatively supported by the well known Hume-Rothary solubility rules in these alloys [24-25]. The appropriate changes in the bulk physical properties in solid state have been reported already in previous papers [35-36].

The outlined tendencies can really be recognized from the comparison of the appropriate phase diagrams presented in the Fig. 4.
Sample control using electric resistance and thermopower measurements

The investigated samples are (single phase) solutions both in liquid and solid state. Though the samples were chemically analyzed (EDAX) previously in the wetting experiments, some contamination may accrue during the long time procedure at high temperatures. The possible contaminations (traces of Oxygen or C-atoms) arise from the surface of the substrate. The detection of these contaminations is difficult by EDAX measurements. Therefore, physical measurements were also introduced to control the possible change in the concentration (or the overall contamination) level before and after the wetting experiments. These methods are indirect though, they are sensitive enough for the detection of overall concentration change of solute components. Electrical resistivity and thermopower measurements are suitable for this purpose. It was reported in [27], that definite correlations exist between the shape of metallic phase diagrams and the composition dependence of electrical transport properties (conductivity) of the same alloy. The electrical resistivity rapidly increases in the range of solid solutions. This change is also specific to the chemical character of solute elements (valence and size-difference etc). When some chemical interaction occurs between the solute atoms (either chemical reaction or precipitation) the resistance changes significantly without the overall concentration level. It is supposedly, that specific resistance can supply information about the physical state of given components. This additional information is especially useful when the solute element is volatile, and the concentration [29-30]

Wetting angle measurements

The wetting angle was measured in wide temperature range. The wetting angles are illustrated as a function of the melt overheating, (defined as $\Delta T=T_{\text{obs}}-T_{\text{liq}}$, where $T_{\text{obs}}$ is the experimentally measured temperature, $T_{\text{liq}}$ is the liquids temperature for the alloy at the investigated concentration). The favour of this illustration is obvious, as the slope of liquids is very different. (see Fig.3. the phase diagrams). Comparing the Figs. 5-6 the first remarkable finding is the opposite temperature dependence of the $\Theta(T)$ slope obtained on the graphite and the Al$_2$O$_3$ substrates. It is also remarkable that the influence of the same solute atoms strongly depends on the melt superheat [20-23].

The results are collected in Figs 5-6.
Fig. 5. Temperature dependence of the wetting angle of various Ag-Cd, Ag-In, Ag-Sn, Ag-Sb and Ag liquids on graphite substrate
Fig. 6. Temperature dependence of the wetting angle of various Ag-Cd, Ag-In, Ag-Sn, Ag-Sb and Ag liquids on Al₂O₃ substrate.
As the phase-relations are very simple in these alloys (single phase nature of liquids and the solid solutions), one can suppose that the alloying induced by the electron concentration has a detectable impact not only in the stabilization of liquid state (melting point suppression) but also in the surface energy of the liquid drop. The magnitude of the wetting angle depends only indirectly on the total surface energy, which is composed from the drop/gas and the drop/substrate interface components [40].

The summary of observations is the following:

- The slope of Θ(T) for the pure Ag is positive on graphite, and negative on the Al₂O₃ substrates. This indicates the decreasing wetting ability of graphite, and the increase of Al₂O₃ versus the melt superheat, i.e. the Ag/graphite interphase formation is energetically unfavorable in the same atmospheric circumstances, as the temperature increases (the interfacial energy increases) [37].

- The influence of alloying elements on Θ(T) is also opposite in the case of two substrates. The shift (at a given superheating) increases with the solute concentration, as it is expected from the residual resistivity measurements.

- Crossovers of the Θ(T) curves are often observed.

An influence of Cd addition is exceptional: generally opposite to that found in the case of other substituent (Θ decreases compared to the pure Ag). The lowering tendency is also typical on Al₂O₃ substrates. This general observation probably arises from the intrinsic property of Cd metal (exceptional high vapour pressure) [34].
The most remarkable finding obtained by the presented experiments is the marked difference between the slope of the $\Theta(T)$ belonging to the individual solute elements. This is not expected solely on the basis of $e/a$ change, which predicts continuous bulk property change due to the also continuous electron density change around the Fermi level. This energy level should be insensitive to $\Delta T=200-300$ K change beyond the melting temperature. This variation hints to participation of additional (mainly metallurgical) factors in the investigated wetting phenomena [28].

The compositional effects, (arising from the electron density change, especially at low solute concentrations) are often smeared by the intervention of these factors. The O-traces may have primary importance in this respect. Probably the melt-substrate interaction has a significant impact. The O-contamination arises partially from the inner surface of structural elements of vacuum-chamber, which is covered by adsorbed oxygen molecules. As the temperature of the chamber does not increase the dissolved oxygen in the Ag(M) melt-drop seems to dominate. Based on this, the opposite slope of $\Theta(T)$ curves obtained on graphite and $\text{Al}_2\text{O}_3$ substrates can also be understood.

Qualitative explanation of the opposite trends observed on the investigated ceramic materials seems to be connected with the different reactivity of the two ceramics to the O traces, which can be appreciated from

Fig. 7. Ellingham of the investigated systems [33]
the Ellingham diagrams in Fig. 7. The selected data in this diagram refer to the affinity (and their temperature dependence) of the components to the oxygen which may be partly present in the environment, partly dissolved in the Ag itself (which is the dominant rough material from which the alloys were prepared). This dissolved O of Ag-O liquid will react with the graphite substrate. According to the following reaction:

\[ \text{Ag(O)}_{\text{liq}} \rightarrow \text{Ag} + \text{CO}_g \] (1)

As the T-dependence of equilibrium constant for the reaction (1) is opposite than that for the metallic oxides formation (Fig. 7.) the reaction is completed, when the temperature increases. Thus, further enrichment of CO molecules takes place at the melt/graphite interface. This reaction is dominant for the pure Ag, therefore the slope of \( \Theta(T) \) is the highest (rapid wettability decrease versus the increasing temperature).

When the liquid drop is such a solution, in which the reactivity of the dissolved M metal to the oxygen is higher than that for the Ag, (see Fig 7.), interaction between the dissolved O and the M is developed in the melt according to

\[ \text{Ag(O)}_{\text{liq}} \rightarrow \text{Ag(O-M)}_{\text{liq}} \] (2)

i.e. the metallic solute does also participate in the overall process. Hence, the activity of dissolved O is modified. At lower temperatures (near the liquidus) the reaction (1), at high temperatures the (2) reaction is the dominant (according to the spirit of the Ellingham diagram in Fig. 7).

The crossovers between the \( \Theta(T)_{\text{Ag}} \) and \( \Theta(T)_{\text{Ag-M}} \) curves can be understood based on the outlined interactions.

The opposite sign of \( \Theta(T) \) in the case of \( \text{Al}_2\text{O}_3 \) can be imagined on the basis of substrate-degassing. As the temperature increases, O-desorption from the melt/\( \text{Al}_2\text{O}_3 \) interface takes place, which will dissolve in the Ag-melt. The O-enrichment in the Ag drop results in a surface tension lowering [34].

As a whole, two types of influences can be distinguished:

One is powerful in the bulk liquid drop, near to the melting point of the drop, the second is more active at higher temperatures. Both arising from the opposite sign of the T dependence equilibrium reaction are constants C-CO, and the M- MO reactions respectively.
This means that temperature dependence wetting ability is significantly modified by alloying elements. The existence of crossovers are probably associated with the different strengths of interactions between the Ag(M)-O in the melt, as it is expected from the Ellingham diagrams.

The lowering tendency of $\Theta$ due to Cd addition observed both on the graphite and Al$_2$O$_3$ substrate is seen also in the case of Al$_2$O$_3$ substrates. This hints to the favour of melt/substrate interphase formation at the expense of melt/gas surface formation, when the Cd atoms are present in the melt drop. As it was mentioned above, the origin of this extraordinary behaviour can be attributed to the large heat of vaporization of Cd. It was reported that surface tension of metallic melts at their melting points depends on the heat of vaporization [34].

However, the reason of opposite $\Theta(T)$ dependence of the wetting ability of graphite cannot be explained in every detail. The micro-porosity of two substrates is nearly the same (see Table 1). The indirect influence of packing density of crystal planes crossing the substrate/melt interface cannot be completely excluded [41]. The chemical absorption of O-traces – arising from the heating unit – may also contribute to the observed anomalies.

Table 1. The change of the samples mass

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample mass</th>
<th>Alloying element mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before*</td>
<td>After*</td>
</tr>
<tr>
<td>Ag</td>
<td>0.2388 g</td>
<td>0.2385 g</td>
</tr>
<tr>
<td>Ag$_{95}$Cd$_5$</td>
<td>0.2395 g</td>
<td>0.2298 g</td>
</tr>
<tr>
<td>Ag$_{95}$In$_5$</td>
<td>0.2391 g</td>
<td>0.2385 g</td>
</tr>
<tr>
<td>Ag$_{95}$Sn$_5$</td>
<td>0.2350 g</td>
<td>0.2336 g</td>
</tr>
<tr>
<td>Ag$_{95}$Sb$_5$</td>
<td>0.2393 g</td>
<td>0.2337 g</td>
</tr>
</tbody>
</table>

* Wetening angle measurement

** With the pure Ag correction

As it was mentioned, the behaviour of Cd solvent is exceptional in the investigated systems:

$\Theta(T)$ usually decreases (especially at higher Cd content) which hints to increasing wettability due to the Cd addition. This tendency is particularly remarkable on the Al$_2$O$_3$ substrate. The wettability increase can be the
indirect consequence of the high vapour pressure of Cd, the overwhelming majority of Cd exhausted from the liquid during the wetting experiments (see Table 1). Consequently on the reaction suppressed, the liquid/C interface formation is energetically favourable.

Because of the exceptional high vapour pressure of Cd, this reaction opens an additional discussion to the processes proposed by the (12) equation, which is going on recently.

**Ag-Au system**

The wetting angles are illustrated as a function of the experimentally measured temperature. The Fig.8. shows that the wetting angles are rising while the temperature was increased. The shapes of the curves are still similar in every case. It is also remarkable, that the slope of each curve (except for the Ag<sub>97</sub>Au<sub>3</sub>) lower compared to the pure Ag.

![Fig. 8. The temperature dependence of the wetting angle of pure Ag, Au and Ag alloyed with 3, 5, 10, 20 at.% of Au on graphite substrate](image)

The ratio of the electrical conduction and wetting angle changes are shown in fig. 9. The ratio were calculated from the difference between the pure Ag and the alloy compositions and correlated to the biggest difference. The rate of change of the electrical conduction and wetting angle changes seems to be similar in the Ag<sub>95</sub>Au<sub>5</sub>, Ag<sub>90</sub>Au<sub>10</sub>, Ag<sub>80</sub>Au<sub>20</sub> samples. The results of Ag<sub>97</sub>Au<sub>3</sub> show bigger difference. The change of the wetting angle is smaller than the change of the electrical conduction. The alloying effect is less relevant for the
wetting angle in the case of Ag\textsubscript{97}Au\textsubscript{3} alloy composition.

![Graph showing rate of changes vs Au content](image)

**Fig. 9.** Property changes of the investigated alloys

**Ag-Cu system**

This research is focused on analysis of the copper solid phase. Two alloys are in this phase (Cu\textsubscript{97}Sn\textsubscript{3}, Cu\textsubscript{95}Sn\textsubscript{5}), so Cu is one reference and Cu\textsubscript{90}Sn\textsubscript{10} is the other reference outside of the α-phase. It is important to focus on the changing where a phase changing border is (9.1% Sn content). In this case we observe the effect of changing systematically the electronic structure with changing the combining content (Sn).

The Fig.10. includes the result of the measuring.

![Graph showing contact angle vs temperature](image)

**Fig.10.** The temperature dependence of the wetting angle of pure Cu, and Cu alloyed with 3, 5, 10, at.% of Sn on graphite substrate
By increasing the combining content systematically changes of the electronic structure causes huge differences in many properties even if they are in the same phase. It seems that clear copper has the best wetting properties at every temperature and with increasing the combining content it worsens the wetting properties \([31-32]\).

**Ag-Sn system**

Experimentally measured contact angle values at an average temperature of \(T = 1373\) K are shown in Fig. 11.

![Fig. 11. The concentration dependence of the calculated results at 1273 K (lower line), at 1473 K (upper line) and the measured at \(T = 1373\) K (points) contact angle values.](image)

The following conclusions can be drawn:

- The contact angle of pure tin on graphite also slightly increases with temperature from \(129^\circ\) to \(132^\circ\). The absolute value of this contact angle appears to be somewhat lower compared to literature data of \(144^\circ\) \([37]\) and \(155^\circ\) \([38-39]\).
- The contact angle slightly increases with temperature for all alloys (with a few exceptions). However, this change is within the experimental uncertainty.
- The concentration dependence of the contact angle goes through a wide maximum with two minima at single components and two peaks at around 5 at% Sn and at around 30 at% Sn. However, all these changes are within the experimental uncertainty.
- The Butler equation was extended to calculate the concentration dependence of the solid/liquid interfacial energy and the contact
angle theoretically. The method presented here is applicable only to such A-B (liquid) / C (solid) systems, in which there is no mutual solubility between the A-B liquid solution and the pure, one-component C solid substrate and in which the solid/gas interfacial energy is independent of the liquid composition. The theoretical values reasonably re-produce the measured values without any fitting parameters (Fig.2) [J12].

The results of the XRD measurements follow the same trend of the phase formations as follows from the well established phase diagram [40]. In some phases a small amount of supersaturation is observed, being due to high solidification rate of the alloys. However, it has no influence on the contact angle of the liquid alloys on solid graphite.

Possible correlations between the interphase segregation tendencies and the contact angle

In some cases however, when the slope of liquidus and solidus significantly differ, segregation tendencies can be developed, especially in the vicinity of surfaces, i.e. the drop is not perfectly homogeneous. Hence some uncontrolled chemical differences can be developed between the regions near to the melt/gas or melt/substrate interfaces. Such effects can be expected at high concentration. It is important to note, that no detectable partitioning exists when the run of liquidus and solidus is very close (Ag-Cd). In contrast, the $\Theta(T)$ slope for AgSn10 and AgGa10 are very different (Phase Diagram Ag-Ga [26]). As an example, significant surface segregation can really be detected in AgGa10 alloy by the EDAX analysis of the cross section of solidified AgGa drop (see Fig.12).
Based on the shape of phase diagrams, the highest segregation can really be expected in this case. This is also supported by the results of cross-sectional analyses (Fig. 12).

The Ga concentration is identified here by EDAX measurements near the substrate, comparing them with the inner side of the drop. The Ga-content is significantly lower near the substrate interface. (around 7 at %), showing the depletion of alloying element in this region.

**Solidification texture formation in the vicinity of the liquid-graphite interface.**

Texture formation in the solidified drop was observed near the graphite/drop interface, which seems to be in correlation between the degrees of melt superheated.

In Fig. 13, the XRD spectra are visible, taken from the graphite-side and inner part region of solidified Ag drop 2a (1473 K, inner part of the sample). The random distribution is the most intensive reflection very similar to the typical polycrystalline “powder” sample, where the (111) peak reflection is the strongest.
Fig. 13 XRD spectra measured on Ag sample solidified from 1473 K: a) middle of drop, b) at the graphite interface, c) sample cooled from 1273 K.

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 ratios obtained on samples (solidified from 1273 K and 1473 K): 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.

In Fig. 14 the XRD spectra from AgGa10 sample (cooled from 1273 K and 1473 K respectively) are visible. The structure from 1273 K sample is similar to the pure Ag, i.e. the 200 reflection is the more pronounced reflection the
dominancy of 100 textures. The intensity ratio of reflections: \( I(200)/I(111) = 4.8 \); the appropriate value is 139°.

![XRD spectra for Ag-Ga samples on the substrate side (a: 1273 K, b: 1473 K)](image)

Fig.14. The XRD spectra for Ag-Ga samples on the substrate side (a: 1273 K, b: 1473 K)

In the sample with the smallest value (sample cooled from 1473 K) the ratio of reflections’ intensities differs completely from all other samples. The (311) and (200) reflections are the most intensive in contrast to the inner part of the sample, and the sample cooled from 1273 K, 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 also supports (118°).

Though direct correlation between the slope of \( \Theta(\Delta T) \) curves and texture formation is obviously not expected, one can speculate that some unspecified, high temperature chemical etching occur at the interface beneath the melt drop, which may act as a catalytic surface-effect on the subsequent texture formation, when the solidification has started. Preferential, orientation dependent surface etching during high temperature vacuum-treatments is not unknown in the metallurgical praxis. Such effects can also occur beneath the
melt drop. This effect is also more pronounced in the Ag and Ag-Ga drops. The
details of this effect (temperature dependence of texture formation), directed to the
more detailed understanding of this texture formation should be further investigated
in the future. In the Fig. 12 the textured structure of the crystallites is the strongest
at the interface in the Ag-Ga (1473 K) sample. It can be seen that the (311) peak is
the most intensive. In contrast, the crystal orientation in the interior of solidified
drop is nearly random. Comparing the intensity values measured at 1273 K and
1473 K respectively, the outlined tendencies are further strengthened by the
temperature increase as it can be drown from the Fig 10-11.

Wetting angle (θ) measurements were performed on graphite substrate at 1200°C
for the pure Ag, AgCd5, Ag In5, Ag Sn5 and Ag Sb5 respectively, Weltsch et al.
[4]. In contrast with the predicted tendency the contact angle does not change
monotonously with increasing electron density (e/a) caused by the alloying
elements. The wetting angles detected in the case of samples alloyed with Cd and
In are lower then, the pure Ag has, though their surface tension is higher in
consequence of the increased e/a ratio. It means the surface tension is one of the
important parameter only among other effects, like adhesion processes taking place
at the substrate interface.

XRD patterns measured on the substrate side of the pure Ag and its alloys are
plotted versus the experimentally determined wetting angle in Fig.15a. According
to the ratio of the intensity maxima it can be established, that all of the investigated
drops are characterised with a strong (100) texture near to the graphite substrate.
This can be understood taking account the fact, that the size of the (200) lattice
distances in Ag crystal is nearly the same as the (101) in the graphite. Comparing
the values of contact angles measured at 1200°C with the degree of the texture
determined by XRD, it turned out the contact angle is smaller the degree of texture
higher (Fig.15b) The same tendency was found also in the case of Ag-Zn, Ag-Cu
and Ag-Ga alloys, Weltsch et al. [7]. It means, that the better wetting properties
(characterised by decreasing contact angle) are in strong correlation with the
arrangements of the crystallites at the substrate. Via this preferential orientation
favourable packing density is developed in contacting crystal planes, which can
contribute to the interface energy minimization between the drop and graphite
substrate. Enhanced surface diffusion, which plays an essential role in the
development of preferential orientation, is promoted by the alloying elements.
Fig 15. XRD patterns measured on pure Ag and Ag alloyed with 5at.% of Cd, In, Sn or Sb samples at the substrate of the solidified drops (a), and the ratio of the measured intensity I(200)/I(111) versus wetting angle(b).

Comparing the Ag and Cu metals, their crystallographic and chemical similarities are remarkable: the fcc-crystal structure, valence state, with the nearly same electron negativity. Only their molar volumes differ (The ratio of their atomic diameter (d) ~1.5). Consequently the similarity of Ag-Cu alloy to the elementary Ag is expected (See its XRD pattern on Fig. 16.). The crystal structure of Ag-Zn and Ag-Cu alloys is also identical. In contrast Ag-Ga alloy most of the crystallites are arranged in the (311) direction at the substrate surface (See Fig. 16). It is remarkable, that Ag-Ga sample exhibits about 22% amorphous phase according to the XRD pattern. The possible reason is the interaction between the graphite substrate and the molten drop at the vicinity of interface as a consequence of intermixing at the graphite substrate.
Fig. 16. XRD patterns measured on Ag-Zn, Ag-Cu and Ag-Ga samples at the substrate of the solidified drops.

Comparing the values of contact angles measured at 1200°C and the degree of the texture evolution in the primarily solidified layer (determined by XRD), it can be established, that the better wetting properties (characterised by decreasing contact angle) are in a strong correlation with the arrangements of the crystallites at the substrate. The contact angle is smaller when the degree of texture is higher (Table 2.).

Table 2. Wetting angles measured at 1200°C and the preferred orientations detected by XRD at the substrate of the solidified drops.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wetting angle</th>
<th>Preferred orientation</th>
<th>Ratio of the measured intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgZn10</td>
<td>136°</td>
<td>(100)</td>
<td>( \frac{l_{(200)}}{l_{(111)}} = 5.9 )</td>
</tr>
<tr>
<td>Ag</td>
<td>133°</td>
<td>(100)</td>
<td>( \frac{l_{(200)}}{l_{(111)}} = 8.16 )</td>
</tr>
<tr>
<td>AgCu10</td>
<td>130°</td>
<td>(100)</td>
<td>( \frac{l_{(200)}}{l_{(111)}} = 10.8 )</td>
</tr>
<tr>
<td>AgGa10</td>
<td>118°</td>
<td>(311)</td>
<td>( \frac{l_{(311)}}{l_{(111)}} = 105.2 )</td>
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The new scientific results – theses

1. Method and equipment have been developed for the observation of the wetting phenomena between non-reactive alloy melts and solid ceramics, making possible the observation of contact angle at high temperature range up to 1200°C [J2, J8, J15, B1].
   a. A double wall thermal isolation system have been constructed and built developed from quartz tubes for eliminating the oxygen traces in the surrounding atmosphere. With this construction, the high specific surface Al₂O₃ isolation media was successfully replaced.
   b. An automatic contact angle measuring method is developed in MATLAB environment, which is able to evaluate the contact angles, minimizing simultaneously the experimental errors. The process based on a picture conversation searching borderlines and contour changings from pixel to pixel and work also at 1200°C temperature red-hot droplets.

2. The wetting ability among Ag based alloys, Ag (Cd, In, Sb, Sn) among graphite and Al₂O₃ substrates is determined, using the sessile drop method [J1, J2, J4, J5, J6, J7, J9, J12, J13, J15, B3].
   a. The temperature dependence of contact angles and Ag, AgCd, AgIn, AgSb AgSn is determined in the temperature range of 1000-1200°C. Systematic relation between the contact angle and the electronic structure was found.
   b. A tendency-like relation is found between the specific resistance of AgIn5, AgSb5, and AgSn5 solid solutions and their contact angle on graphite substrate: both of the specific resistance in solid state and the wetting angle in liquid state increases with the valence number difference between the Ag host metal and the solutes.
   c. The correlation of wetting ability and electronic structure of Ag₉₀Cu₁₀, Ag₉₀Ga₁₀ and Ag₉₀Zn₁₀ melts on graphite substrate is partially suppressed by the presence of second solid phase.

3. The wetting ability of AgAu (3, 5, 10, and 20 at% Au) and CuSn (3, 5, and 10 at% Sn) melts on graphite substrate is investigated with the sessile drop method [C6, C7].
a. It was found, that wetting angle increases with Au content in the continuous series of solid solutions of AgAu alloys.

b. A tendency-like relation was found between the electrical resistance in solid state (obtained from the literature) and the contact angles of liquid AgAu alloys: both of the resistance and the wetting angle increases with the Au content.

c. The wetting angle of melts CuSn melts increases with the Sn concentration within the solid state solubility limit of Sn in α-CuSn phase

d. At Cu$_{90}$Sn$_{10}$ alloy, where the combining out of the dissolve border, I have measured decreased contact angle (at 1100°C the decrease is 17°).

4. Using XRD measurements the development of texture was observed in the vicinity of interface between the liquid drop and substrate after solidification. Definite relation exists between the degree of texture development and the contact angle in liquid state [J4, J7, J12, J15, C4].

a. The degree texture developed during solidification increases when the temperature melt is raised within the range of 1000-1200°C.

b. The relation between the contact angle of Ag$_{95}$In$_5$, Ag$_{95}$Cd$_5$, Ag$_{95}$Sb$_5$ and Ag$_{95}$Sn$_5$ and Ag$_{90}$Cu$_{10}$, Ag$_{90}$Zn$_{10}$, and Ag$_{90}$Ga$_{10}$ melts and the appropriate degree of structure was determined. Stronger solidified textural relation is coupled with decreasing contact angle.

5. It is experimentally documented, that correlation exists between the shape of phase diagram and the change of contact angle in the liquid state [J5, J12, J13, J15].

a. I have determined with 13 different composition AgSn alloy that above the monophasic area in the equilibrium phase diagram in liquid phase measured contact angle is increased, so the transformation has a unambiguous effect to the contact angle.

b. The previous statement support the XRD, TEM and SEM measurements results.

c. The experimental results exhibit pronounced similarity with the results of theoretical calculation proposed by Kaptay.
List of related publications

Journal


[J9] Z. Weltsch, A. Lovas, G. Tichy, Z. Vandrus: Bulk Electron Concentration and the Surface Tension of Liquid Ag-Based Solutions, Perner’s Contact, Special Issue 2, Volume VI, Pardubice (2011), ISSN 1801-674X, pp. 221-227


[J14] Z. Weltsch, J. Hlinka: The Effect of Reflow on Wettability of Sn 96.5 Ag 3 Cu 0.5 Solder, Materials Engineering 20, pp 32-39, (2013), ISSN 1338-6174


Conference papers


International Conference on Innovative Technologies, Bratislava, Slovakia, 2011


Books
References


[17] Z. Weltsch, A. Lovas, G. Tichy, Z. Vandrus: Bulk Electron Concentration and the Surface Tension of Liquid Ag-Based Solutions, Perner’s Contact, Special Issue 2, Volume VI, Pardubice (2011), ISSN 1801-674X, pp. 221-227


[40] G. Kaptay: Classification and general derivation of interfacial forces, acting on phases, situated in the bulk, or at the interface of other phases – J.Mater.Sci, 2005, vol.40, pp.2125-2131