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# Investigation of interaction of metal melts and zirconia

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The wetting of zirconia by a number of pure metals was studied.

The wetting of zirconia by Cu-Ga-Ti, Cu-Ga-Zr, Cu-Ge-Ti and Cu-Ge-Zr alloys was studied. For Cu-Ga-Ti the minimal contact angle was near 60°, for Cu-Ga-Zr it was near 30°. Cu-Ge based alloys wet the zirconia worse because of the low solubility of titanium and zirconium in germanium.

The wetting of different zirconia ceramic by a few molten alloys was compared. Contact angles for equal alloys are close. The substrate structure influences the wetting: polycrystal zirconia is wetted by active alloys worse than monocrystal form.

The kinetic of $ZrO_2$ variation of stoichiometry in contact with active alloys was investigated. The dark zone dimension was found to very according a to parabolic law; and the diffusion coefficients of *F*-centers in $ZrO_2$-ceramic were calculated.

For Cu-Ga-Ti on zirconia adsorption of titanium on the substrate surface and the formation of a TiO layer close to zirconia was revealed. Similarly, for Cu-Ga-Zr adsorption of zirconium on substrate was also found. Interface reactions were described, showing negative Gibbs energy. The average *F*-centers concentration was calculated.

Metals wet better nonstoichiometric than stoichiometric zirconia. At contact to noble metals melts in a vacuum nonstoichiometric (black) zirconia becomes white. Obviously Zr—O bond are weak in black zirconia and a larger quantity of zirconium/metal bonds forms, so the black zirconia is wetted better. When in contact to noble metals some part of zirconium diffuse into metal and so the oxygen deficit disappears.

Finally, The brazing of zirconia to metal was briefly discussed.

## 1. Main part

Wetting of zirconia by metals was not studied so wide like one for such materials as alumina or silicon nitride. So, a research programme was undertaken to study this question systematically.

As the main object of research monocrystals of 3% yttria-stabilized zirconia were selected, together with some polycrystalline $ZrO_2$-ceramic. Samples surface was polished by 0.3–0.7 $\mu$m diamond powder. The sessile drop method was used. Wetting experiments were performed in a vacuum $10^{-3}$ Pa. In Table I the results of wetting experiments for pure metals are presented.

Active metals (aluminum and vanadium) wet the zirconia, inert metals (tin, copper, silver) do not wet it. But the dependence of wetting on the affinity to oxygen is not so simple, silicon does not wet the zirconia whereas germanium wets it. In this last case the interaction of germanium with zirconium cations could play a major role, because strong intermetallides exist in Ge-Zr system; a similar picture was observed for germanium and rare-earth elements oxides interaction [7]. As for silicon, the non-wetting is explained by the formation, at the interface, of volatile compound (probably, SiO).

The wetting of zirconia by active alloys was also studied. The Cu-Ga and the Cu-Ge systems were selected as the base alloys, titanium, zirconium and vanadium were used as the active additions.

In Fig. 1 the results of wetting experiments of zirconia monocrystals by Cu-Ga-Ti, Cu-Ga-Zr, Cu-Ge-Ti Cu-Ge-Zr and alloys as a function of the active addition concentration are represented. The addition of titanium and zirconium improve the wetting, zirconium influences the contact angle more than titanium (probably because it has higher affinity to oxygen) and at a concentration near 15 at.% the minimal contact angle was reached (60° for titanium and 30° for zirconium), further additions of active metal do not influence the wetting. Vanadium at concentrations lower than 1.8 at.% improve the wetting better than Ti and Zr, but at higher concentrations it does not dissolve in base alloy. For Cu-Ge-Ti and Cu-Ge-Zr systems a similar behaviour was observed, but the minimum contact angles were higher and reached at lower concentrations of active additions then for Cu-Ga because of low dissolution of Ti and Zr in this base alloy.

In Table II the wetting of different types of zirconia ceramic by metal melts is presented. As one can see, for the same melts the contact angles are similar on different types of ceramic, so, the composition of ceramic does not influence the wetting significantly. However, plycrystallyne and monocrystalline zirconia

TABLE I Wetting of zirconia monocrystals by pure metals

| Metal | $\Delta H_0$ of metal oxide in recalculation on 1/2 mole of $O_2$ (kJ/mole) | Temperature (°C) | Contact angle, degrees |  |
|---|---|---|---|---|
|  |  |  | Our data | Literature data and reference |
| Ga | −359 | 750 | 160 | — |
|  |  | 800 | 151 | — |
|  |  | 900 | 140 | — |
|  |  | 1000 | 139 | — |
|  |  | 1050 | 139 | — |
|  |  | 1200 | 139 | — |
| In | −309 | 160 | 125 | — |
|  |  | 900 | 125 | — |
| Sn | −290 | 900 | 145 | — |
|  |  | 1000 | 145 | 140 [1] |
| Al | −558 | 700 | 110 | — |
|  |  | 800 | 90 | — |
|  |  | 900 | 84 | — |
|  |  | 1000 | 71 | 40 [2] |
|  |  | 1100 | 55 | 59 [3] |
| V | −410 | 1900 | 65 | — |
| Cu | −166 | 1100 | 131 | 116 [3] |
|  |  | 1150 | 130 | 140 [2] |
| Ag | −30,6 | 1000 | 126 | 120 [3] |
| Au | −3,35 | 1150 | 125 | — |
| Si | −428,5 | 1430 | 105 | 92 [4] |
| Ge | −269,9 | 1000 | 95 | — |
|  |  | 1100 | 60 | — |
| Ni | −244,6 | 1500 | 90 | 96 [4], 95 [5], 130 [1] |
| Co | −239,5 | 1500 | 105 | — |
| Fe | −266 | 1550 | 93 | — |
| Pd | −115,6 | 1560 | 98 | 95 [6] |
| Pt | −41 | 1800 | 93 | — |
| Rh | −94 | 2000 | 105 | — |

TABLE II Wetting of different types of zirconia ceramic by some metal melts

| Melt | Contact angle on different types of $ZrO_2$-ceramic |  |  |  |
|---|---|---|---|---|
|  | $ZrO_2 + 3Y_2O_3$ | $ZrO_2 + 3.5Y_2O_3$ | $ZrO_2 + 15CaO$ | $ZrO_2 + 2.5Y_2O_3 + 2.5Ce_2O_3$ |
| Cu-17.5Ga | 140 | 140 | 137 | 142 |
| (Cu-17.5Ga)-10Ti | 91 | 92 | 90 | 96 |
| (Cu-17.5Ga)-15Ti | 62 | 60 | 63 | 67 |
| (Cu-17.5Ga)-10Zr | 95 | 92 | 91 | 96 |
| (Cu-17.5Ga)-15Zr | 38 | 41 | 40 | 44 |
| Brazing filler Cu-Sn-Pb-Ti | 20 | 20 | 20 | 25 |

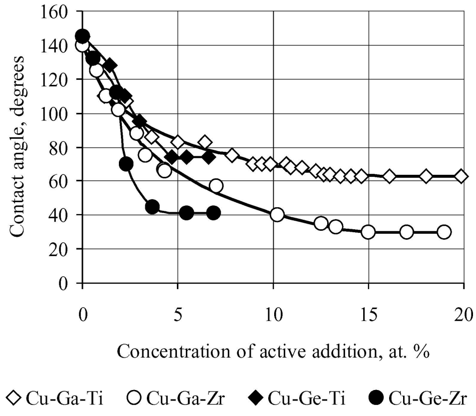


*Figure 1* Wetting of zirconia by Cu-17.5Ga and Cu-16.9Ge melts with active addition of titanium and zirconium.

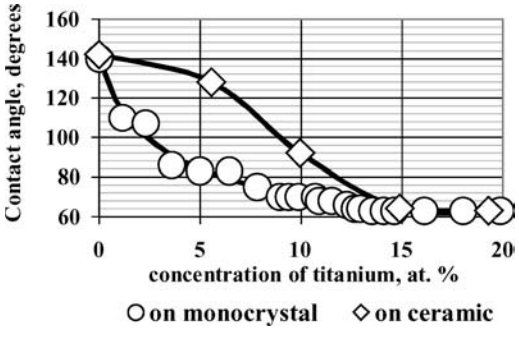


*Figure 2* Wetting of zirconia ceramic and monocrystal by Cu-Ga-Ti melts.

are wetted to a different extent: in Fig. 2 the wetting of zirconia by Cu-Ga-Ti alloys is shown, the higher curve corresponding to zirconia ceramic, the lower one—to zirconia monocrystals. So, the structure of zirconia material influence the wetting behaviour much more, than its composition.

Zirconia may lose oxygen (for example at annealing in vacuum) with formation of nonstoichiometric phases. Such material contains *F*-centers (anion

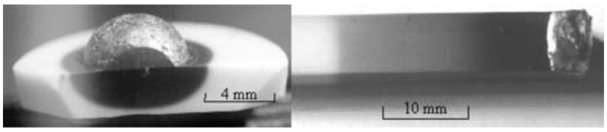


*Figure 3* Darkening of $ZrO_2$-ceramic after contact to active metal (dark zone has a sharp board).

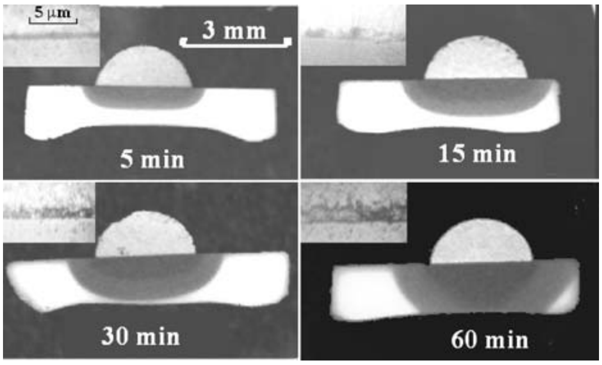


*Figure 4* Kinetic of dark zone spreading at contact of $ZrO_2$-ceramic and (Cu-17.5Ga)-10Ti melt, temperature 1150°C.

vacancies, held electrons), which are responsible for the darkening of the oxide. At simple vacuum annealing intensive loss of oxygen occurs after 1600°C, but the darkening of zirconia due to contact to active metal melt was observed at much lower temperatures—near 1000°C. The monocrystals turn black fully, and on the polycrystals (ceramic) surface the formation of a dark zone with sharp edge was observed (probably, due to breaking of $F$-centers move at grain boundaries), for example as on Fig. 3. The kinetics of dark zone spreading was studied (Fig. 4) by measuring the width of dark zone around the drop for different holding time. The dark zone growth slows down with time.

Dark zone spreading is due to diffusion of $F$-centers from the ceramic-metal interface to the bulk ceramic and has to follow to main diffusion laws, namely:

$$x^2 = 2Dt \tag{1}$$

where $x$—the dark zone width; $t$—holding time; $D$—coefficient of diffusion.

On Fig. 5 dependences of square of dark zone width on holding time were constructed for some systems. It is visible, that the initial parts of the curves are straight, so the Equation 1 is true for dark zone spreading. The diffusion coefficient of $F$-centers was calculated in the order of $10^{-5}$ $sm^2/sec$.

The microstructure of Cu-Ga-Ti/$ZrO_2$ interface was studied. The transition layer was revealed (layer 2 on Fig. 6a). In this layer only titanium is present in large amount (Fig. 6b), concentrations of zirconium (Fig. 6c), oxygen (Fig. 6d), copper (Fig. 6e) and gallium (Fig. 6f) are very low. So, titanium adsorbs on zirconia surface.

X-ray phase analysis has shown the presence of TiO in this system. The layer of TiO forms on zirconia surface and becomes visible at long holding time (layer 2 on Fig. 7).

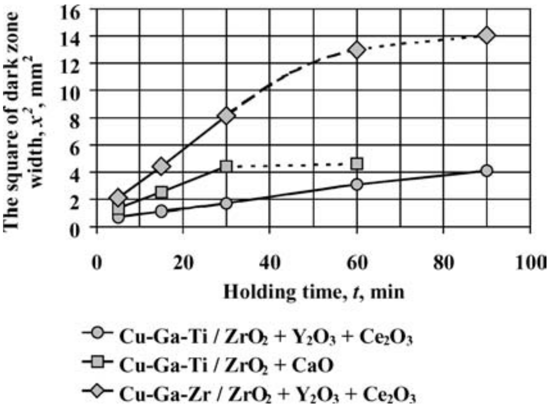


*Figure 5* The dependence of square of dark zone width on the holding time for different systems: initial parts of lines are straight

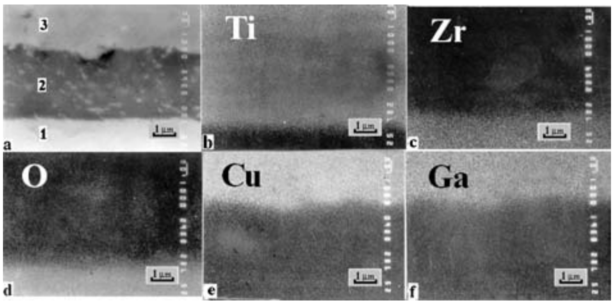


*Figure 6* Raster electronic microscopy of interface zone between (Cu-17.5Ga)−10Ti and $ZrO_2$ (a) and distribution of elements in it on data of a characteristic X-rays: (b) Ti, (c) Zr, (d) O, (e) Cu, (f) Ga. (×7800) Phase composition of contacting materials: 1 – $ZrO_2$, 2 – $\alpha$-Ti(O), 3 – $\gamma$-$Ti_2Cu$.

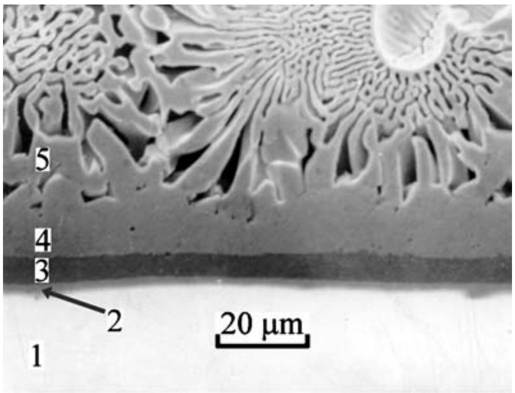


*Figure 7* The microstructure of the cross-section of the contact couple (Cu-17.5Ga)-10Ti/$ZrO_2$-ceramic. 1 — $ZrO_2$; 2 — TiO; 3 — $\alpha$-Ti(O); 4 — $\gamma$-$Ti_2$(Cu, Ga); 5 — $Ti_2$(Cu, Ga) + $\delta$-Ti(Cu, Ga). Temperature 1150°C, holding time 90 min.

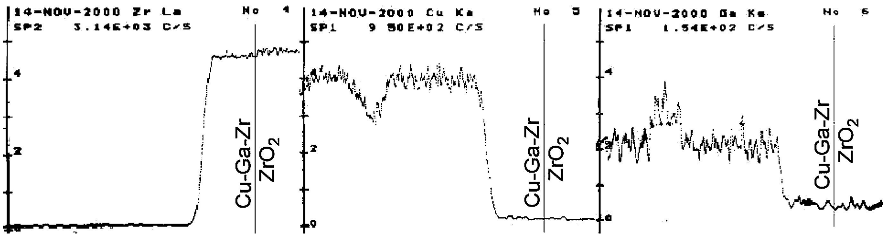
For Cu-Ga-Zr a picture, similar to Cu-Ga-Ti was observed: adsorption of the zirconium at the interface (Fig. 8). X-ray investigations also revealed the presence of ZrO in the system.

So, the processes at the interface may be discribed by the following reactions:

$$ZrO_2 + xTi = ZrO_{2-x} + xTiO \tag{2}$$

$$ZrO_2 + xZr = ZrO_{2-x} + xZrO \tag{3}$$

The Gibbs free energy for these reactions are $\Delta G_0^{(2)} = -20.115$ kJ/mol for reaction (2) and $\Delta G_0^{(3)} = -45.45$ kJ/mol for reaction (3).



(a) (b) (c)

*Figure 8* Distribution of elements near the Cu-Ga-Zr / $ZrO_2$ interface . (a) *distribution of zirconium;* (b) *distribution of copper;* (c) *distribution of gallium.*

From the micrograph presented in Fig. 7 the average concentration of $F$-centers in the substrate may be calculated if we assume that all oxygen, which has left the substrate, has reacted with titanium forming of TiO. The average concentration of $F$-centers is in the order of $10^{19}$ per cubic centimeter. It is worth reminding that only $10^{17}$ $F$-centers per cubic centimeter are necessary to zirconia becomes black [8].

The stoichiometry influence on wetting of zirconia by metals was investigated. For this aim part of monocrystal zirconia substrates were annealed in vacuum at 1900°C and became nonstoichiometric (black). The wetting of these substrates by different metal melts was studied and the results were compared to that on white monocrystal substrates. The results are presented in Table III. As one can see, black zirconia is wetted by inert (Cu, Sn, Ag, Au, Pd, Pt, Cu-Ga, Pd-Rh) and by low active (Al, Cu-5Zr, (Cu-17.5Ga)-10Ti) melts in some degree better than the white one, for active melts contact angles on black and on white substrates are close to each other.

It was also observed, that in wetting experiments with palladium and platinum the substrates have retained their white color, although when annealing in a vacuum at such high temperatures zirconia has to become nonstoichiometric. Control samples (without metals on the surface) really turned black (Fig. 9). Moreover, after contact with gold, platinum and palladium black samples acquired a white color.

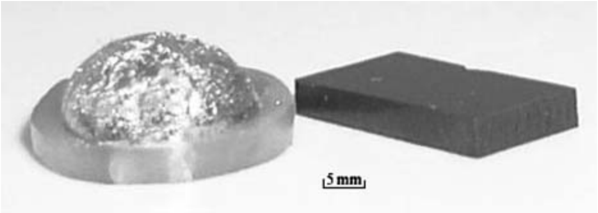


*Figure 9* Zirconia monocrystal substrates, annealed in vacuum together, on left substrates the piece of platinum was situated and it has remain the white color, right substrate was clear and became black.

TABLE III Influence of zirconia stoichiometry on wetting by molten metals

| Melt | Temperature (°C) | Contact angle, degrees | |
|---|---|---|---|
| | | On white | On black |
| Cu | 1150 | 147 | 120 |
| Sn | 1000 | 145 | 100 |
| Ag | 1000 | 148 | 130 |
| Au | 1150 | 125 | 115 |
| Ni | 1480 | 90 | 85 |
| Al | 1000 | 71 | 67 |
| V | 1900 | 65 | 60 |
| Pd | 1560 | 98 | 84 |
| Pt | 1800 | 94 | 80 |
| Rh | 2000 | 105 | 105 |
| Pd-35Rh | 1850 | 99 | 84 |
| Cu-17.5Ga | 1150 | 140 | 131 |
| Cu-5Zr | 1150 | 66 | 57 |
| (Cu-17.5Ga)-10Ti | 1150 | 70 | 65 |
| (Cu-17.5Ga)-10Zr | 1150 | 40 | 40 |
| (Cu-17.5Ga)-15Ti | 1150 | 60 | 60 |

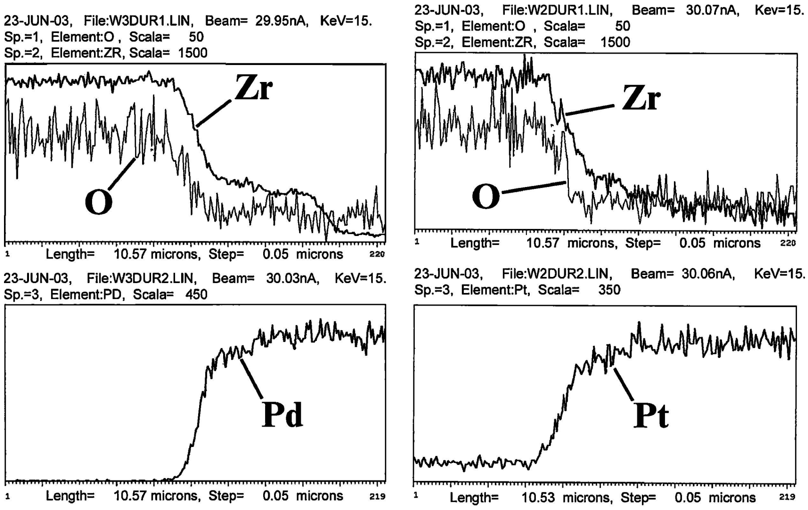
So, on one hand stoichiometry influences the wetting of zirconia by metals, and on other hand, the contact with noble metals hinders the reduction processes of zirconia in a vacuum.

To clarify this phenomenon the distribution of elements on $ZrO_2$/Pd and $ZrO_2$/Pt interfaces was investigated. The results are presented in Fig. 10: there are some quantities of the zirconium present in layers of noble metals close to oxide surface (the “stair” on zirconium concentration curves), so noble metals interact with zirconium in oxide structure an some of zirconium pass to noble metal from the substrate. Probably in nonstoichiometric zirconia for some of zirconium cations the bond to oxygen is weak and chemical bond to atoms of metals in melt forms with a higher probability, so inert metals wet the black zirconia better, than the white one. Also, the oxygen deficit may by considered as the zirconium surplus, this surplus zirconium passes to the melt, the oxygen deficit disappears and black zirconia becomes white. The process may be described by reaction:

$$ZrO_{2-x} \rightarrow ZrO_2 + x\mathrm{Zr} \qquad (4)$$

The same wetting of black and white zirconia by active melts may be explained as follows: when white zirconia is in contact with an active metal it immediately starts to lose oxygen and becomes nonstiochiometric directly under the drop, so the active melts wet the black zirconia.

So, when contact of zirconia and active metals the main role play the metal to oxygen interaction, as result zirconia loses the oxygen and becomes nonstoichiometric (black), but in case of noble metals the zirconium to metal interaction take place and



(a) (b)

*Figure 10* Distributions of elements on the interfaces Pd – $ZrO_2$ (a) and Pt – $ZrO_2$ (b)

opposite process is observed: the turning white of black zirconia.

The question of $ZrO_2$-ceramic to metal brazing was also touched.

For Cu-Ga-Ti alloy the minimal contact angle on zirconia is near 60°, for direct brazing contact angles not higher 40° are needed. The method of capillary infiltration was used to braze $ZrO_2$-ceramic with metal, with titanium powder in gap between joined details and pieces of Cu-Ga alloy placed near the brazing gap near the top detail. The Cu-Ga melt impregnate the metal powder and in such a way fill the brazing gap. After the brazing the average strength was 250 ± 60 MPa. The Weibull modulus $m = 6.5$.

Cu-Ga-Zr alloys give low enough contact angles for brazing. Three methods were tested for brazing of $ZrO_2$-ceramic to metal: (1) a mixture of copper, gallium and zirconium powder was used, (2) copper-gallium plates covered with zirconium powder were applied, (3) capillary infiltration was selected. In the case of the first and second methods the filler spreads on the metal much faster than on the ceramic and the joint strength was very low. The best results were obtained for capillary infiltration: joint strength from 220 to 292 MPa, with an average—260 MPa, Weibull modulus $m = 11.3$.

When Cu-Sn-Pb-Ti standard filler was used to braze zirconia and metal a preferred spreading of the filler on metal was also observed and the joint strength was from 100 to 220 MPa—lower than for Cu-Ga-Ti and Cu-Ga-Zr. So the two stage brazing was used: the ceramic surface was firstly metallized by the filler alloy and after that ceramic was brazed to metal. The joint strength was higher: 166–274 MPa.

## 2. Conclusion

The complex investigation of zirconia to metal melts interaction was performed.

The wetting of zirconia by lot of pure metals (Ga, In, Sn, Al, Cu, Ag, Au, Ge, Si, Fe, Co, Ni, V, Pd, Pt, Rh) was studied. The main part of metals does not wet the zirconia. Just aluminum, germanium and vanadium show lower than 90° contact angles, probably because its high affinity to substrate components (oxygen for Al and V and zirconium for Ge).

The wetting of zirconia by Cu-Ga-Ti, Cu-Ga-Zr, Cu-Ge-Ti and Cu-Ge-Zr alloys was studied. For Cu-Ga-Ti the minimal reached contact angle was near 60°, for Cu-Ga-Zr it was near 30°. Cu-Ge based alloys wet the zirconia worse because of low solubility of titanium and zirconium in melt.

The wetting of different zirconia ceramic by a few melt alloys was compared, contact angles for the same alloys are close. Substrate structure influences the wetting: polycrystal zirconia is wetted by the active alloys worse than monocrystal one.

It was revealed, that when zirconia contact with metal melt containing the element with the chemical affinity to oxygen the nonstoichiometric zirconia with deficient of oxygen forms. The kinetic of this process for $ZrO_2$-ceramic was investigated. The dark zone spreading subordinates to parabola law.

The microstructure of the ceramic—metal interface was investigated. For Cu-Ga-Ti alloy on zirconia the adsorption of the titanium on substrate surface and formation of TiO layer close to zirconia was revealed. For Cu-Ga-Zr alloy on zirconia the adsorption of zirconium on substrate was revealed also. Interface reactions when active metal melts contact to zirconia were described, the thermodynamics consideration of this processes was given. The average $F$-centers concentration was calculated.

The influence of stoichiometry on wetting of zirconia by liquid metals was researched. It is established, that nonstoichiometric zirconia is wetted by metals in some degree better than stoichiometric. For contact of zirconia to inert metals (Au, Pd, Pt) destoichiometrization does not occurs, moreover, black (nonstoichiometric) zirconia substrates becomes white after wetting by noble metals at high temperature (up to 1600°C). These phenomena were explained by interaction of metal melts and zirconium in $ZrO_2$ structure. It was confirmed by microstructure investigation.

The brazing of $ZrO_2$-ceramic to metal was studied. The mathod of capillari infiltration of the Cu-Ga melt through the layer of active metal (Ti, Zr) powder situated in brazing gap was elaborated, joint strength was near 250 MPa. Standard Cu-Sn-Pb-Ti filler was tested for brazing of $ZrO_2$-ceramic to metal, when direct brazing was used the joint strength was just 100–220 MPa, when preferably metallization of the ceramic surface by brazing filler was applied, the results was improved to 166–274 MPa.

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