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Surface tension and density of copper–Zirconium alloys in contact with fluoride refractories

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The surface tension and density of copper–zirconium alloys were measured over a wide range of zirconium concentration (from 7.182 to 74.0 at.%) at temperatures between 1000 and 1250°C by the "large drop" method in cups made on calcium fluoride. The surface tension and density polytherms are straight lines with negative temperature coefficients. The excess volume of mixing is negative, the maximum decrease in volume, observed for a 47.0 at.% Zr alloy, being 3.4%

1. Introduction

The zirconium alloys present a strong interest for several applications, for instance as metallic glasses. The knowledge of their capillary (surface tension, contact angle) and bulk (specific volume) properties and of the change of these properties with temperature and composition are useful when processing materials based on these alloys. However, in the literature there are only few or no data on surface tension and density of zirconium alloys because these alloys wet and react with nearly all known refractory materials which could be used as substrates or crucibles when the above properties are measured. In our previous investigations [1, 2] the surface tension and density of highly aggressive copper—titanium melts were measured by the "large drop" technique using cups made on new fluoride refractory materials. These fluoride materials are inert and are not wetted by highly reactive alloys containing active titanium, zirconium or hafnium [3, 4]. In the present study the surface tension and density of binary copper—zirconium alloys are measured by the "large drop" method using cusps prepared with this type of materials.

2. Experimental

The experiments were performed in vacuum (pressure of 1×10^{-3} Pa) in the presence of titanium getter at temperatures between 1000 and 1250°C. High purity copper (99.999%) and iodide purity zirconium (99.995%) were used in this study. Copper was previously etched by nitric acid and was melted in vacuum in a graphite crucible at 1200°C. The alloys were previously prepared by melting in calcium fluoride crucibles at 1200°C. The pollution of alloys by calcium due to the contact with the fluoride refractory is, after melting at 1250°C for one hour, less than 0.01%. Refractory cups with an interior diameter was 12–15 mm (Fig. 1) made on calcium fluoride ($T_{\text{melting}} = 1420$°C) were produced by a powder metallurgy method consisting in sintering a compact under vacuum. Note that CuZr alloys do not wet calcium fluoride, the contact angles being close to 110° whatever the composition of the alloy. The adhesion of the alloys to CaF_2 after cooling is weak.

In the "large drop" method, developed by one of the authors of this paper [5], axisymmetrical drops are formed on the circular sharp edge of the cup. The internal volume of cup at room temperature was determined by measuring the mercury volume which could put into the cup. The expansion of material cup with temperature, needed for the evaluation of the internal volume of cup at the experimental temperature, was also taken into consideration by measuring the expansion coefficient of the fluoride. The shape of the drop was photographed through the window in the high temperature chamber to calculate the surface tension using the Laplace equation. The measurements of linear dimensions of drop profile were performed by a special microscope. The surface tension and drop volume were calculated using the Bashforth and Adams tables [6]. The measurement accuracy for the density was approximately 0.5%, and for the surface tension between 0.5 and 1%. The details of the method were described earlier [5, 7].

3. Results and discussion

The surface tension and density polytherms are approximated by Equations 1 and 2 and are given by straight lines with negative temperature coefficients which have been calculated by the method of least squares (Table I)

$$\rho = \rho_o + \partial\rho/\partial T * T \quad (1)$$

$$\sigma = \sigma_o + \partial\sigma/\partial T * T \quad (2)$$

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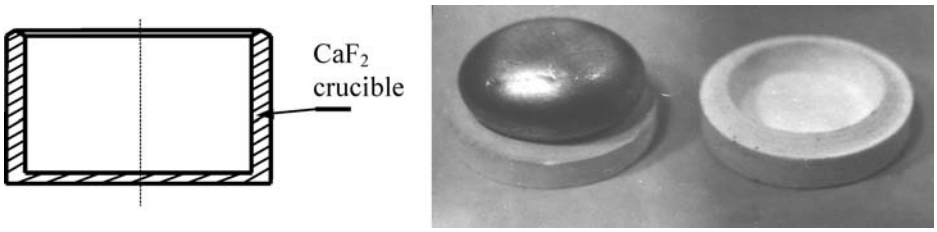
TABLE I Temperature coefficients of surface tension and density of copper - zirconium alloys

Molar fractions (X_{Zr})	Surface tension (σ_o, mJ/m^2)	Temperature coefficient ($-\partial\sigma/\partial T$, mJ/m^2 $*$ deg)	Density (ρ_o, kg/m^3)	Temperature coefficient ($-\partial\rho/\partial T\cdot$, kg/m^3 $*$ deg)
0.07182	1632 ± 23	0.218 ± 0.0091	10214 ± 3	1.68 ± 0.01
0.0892	1632 ± 39	0.215 ± 0.0211	9645 ± 4	1.3 ± 0.01
0.14	1716 ± 12	0272 ± 0.002	9521 ± 3	4.27 ± 0.01
0.1933	1613 ± 34	0194 ± 0.018	9158 ± 2	1.11 ± 0.01
0.25	1666 ± 26	0.22 ± 0.01	9525 ± 4	0.71 ± 0.02
0.295	1618 ± 53	0.182 ± 0.03	9304 ± 4	1.3 ± 0.02
0.3589	1687 ± 8	0.218 ± 0.0006	9494 ± 2	1.5 ± 0.01
0.3974	1734 ± 43	0.243 ± 0.024	9366 ± 2	1.48 ± 0.05
0.4016	1727 ± 20	0.234 ± 0.0073	9382 ± 4	1.51 ± 0.2
0.4514	1711 ± 3	0.215 ± 0.0034	8098 ± 4	0.67 ± 0.02
0.4908	1718 ± 5	0.218 ± 0.0023	7757 ± 3	0.47 ± 0.01
0.5437	1749 ± 13	0.231 ± 0.0023	7467 ± 1	0.36 ± 0
0.6055	1764 ± 17	0.229 ± 0.0063	7699 ± 3	0.59 ± 0.01
0.6294	1787 ± 19	0.237 ± 0.0069	7474 ± 2	0.48 ± 0.01
0.7227	1799 ± 21	0.233 ± 0.0074	7516 ± 4.5	0.6 ± 0.02
0.74	1841 ± 14	0.256 ± 0.002	7492 ± 7	0.6 ± 0.06



(a) (b)

Figure 1 Schematic representation of a crucible (a), the photograph of the sample (left) and of the crucible used in the "large drop" method (right) (b). The interior diameter of the crucible is 12–15 mm.

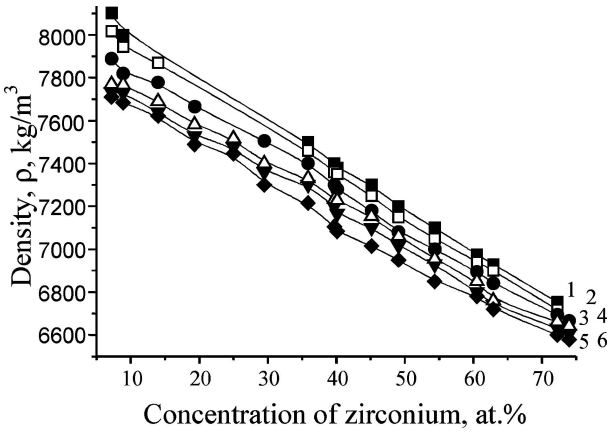


Figure 2 Surface tension of Cu-Zr alloys at 1000°C (1), 1050°C (2), 1100°C (3), 1150°C (4), 1200°C (5) and 1250°C (6).

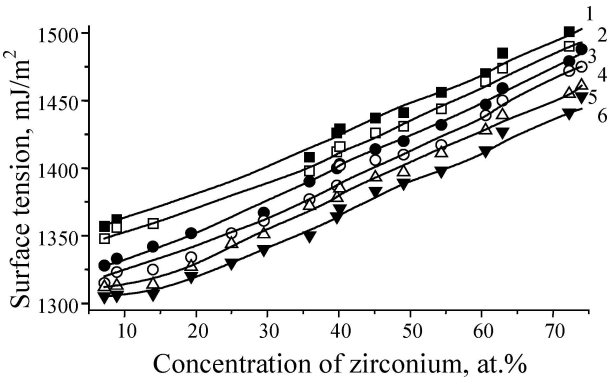


Figure 3 Density of Cu-Zr alloys at 1000°C (1), 1050°C (2), 1100°C (3), 1150°C (4), 1200°C (5) and 1250°C (6).

Figs 2 and 3 show the concentration dependencies of surface tension and density for six copper–zirconium alloys. The surface tension σ increases and the density ρ decreases with increase of zirconium concentration, for example at $T = 1250$°C from 1305 ± 11 mJ/m^2 and 7710± kg/m^3 for 7.182 at.% Zr to 1453 ± 10 mJ/m^2 and 6578 ± 2 kg/m^3 for 74.0 at.% Zr.

Figs 4 and 5 present the isotherms of specific volume and surface tension. The density and surface tension of copper at its melting point and the temperature coefficients of these quantities were taken from [8]. The surface tension and density of pure zirconium at its melting point are 1456 mJ/m^2 and 6050 kg/m^3 [8]. The surface tension for zirconium supercooled at 1200°C

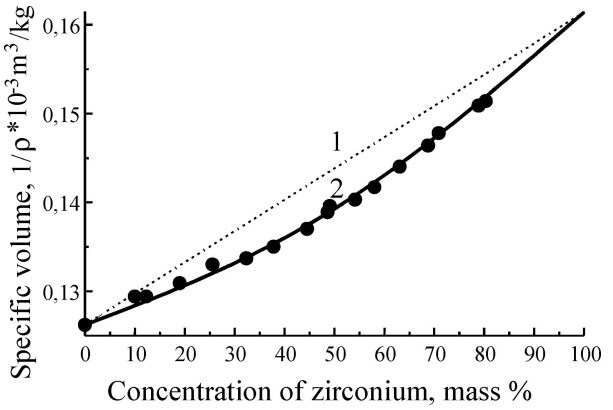


Figure 4 Change of specific volume of Cu-Zr alloys with Zr concentration (in mass%)at 1200°C: additivity law (1) and experimental (2) curves.

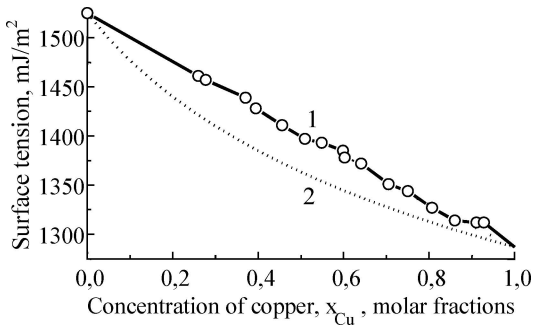


Figure 5 Dependencies of surface tension of Cu-Zr alloys on Zr molar fraction at 1200°C: experimental curve (1), calculated according to Equation 3 (curve 2).

was calculated taking for the temperature coefficient of surface tension the value -0.105 mJ·m$^2 *$ deg [9]. The density of supercooled zirconium at 1200°C was calculated using the value $\partial\rho/\partial T = -0.228$ kg/m$^3 *$ deg estimated according to [10].

The isotherms of specific volume (Fig. 4) and surface tension (Fig. 5) are smooth curves. The experimental values of specific volume are lower than the values calculated supposing additivity. Negative values of the excess volume of mixing are typical of alloys which, as CuZr alloys, present negative deviations from Raoult law. Indeed the integral molar enthalpy of mixing of CuZr alloys at $\mathbf{X}_{Zr} = 0.48$ is -18.0 ± 2.7 kJ/mol [13]. The maximum deviation of specific volume from ideality, observed for a 47.0 at.% Zr alloy, is -3.4%.

In Fig. 5 the experimental isotherm of surface tension at 1200°C (curve 1) is compared to a theoretical one calculated using Equation 3 proposed by Zhychovitsky for binary ideal solutions [11] (curve 2).

$$\sigma = \sigma_{\mathrm{i}} + \frac{RT}{\varpi_{\mathrm{i}}} \ln \frac{x_{\mathrm{i},\varpi}}{x_{\mathrm{i}}} \qquad (3)$$

In this equation σ_{i} is the surface tension of pure i, x_{i} is the molar fraction of iin the alloy $x_{\mathrm{i},\sigma}$ the molar fraction in the surface approximated by one monolayer and ϖi the molar area of i calculated from the molar volume of i. The experimental values of surface tension exceed the calculated ones, a behavior which is expected for solutions with negative deviation from Raoult's law. This corresponds to general principles of behavior of surface tension isotherms for binary metallic systems with chemical compound [12].

4. Conclusions

Using non-wetted and inert calcium fluoride materials as cups it is possible to apply the "large drop" method for surface tension measurements of highly reactive alloys, in particular of zirconium containing alloys. Straight lines with negative temperature coefficients describe the surface tension and density polytherms of Cu-Zr alloys measured by this way. The excess volume of mixing of these alloys is negative as expected for alloys that exhibit negative deviation from Raoult law.

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