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DENSITY OF THE COPPER-RICH Cu-Pb-Fe ALLOYS

GĘSTOŚĆ STOPÓW Cu-Pb-Fe O DUŻYM STĘŻENIU MIEDZI

Density of the copper-rich corner of the ternary Cu-Pb-Fe alloys was determined with the dilatometric method. Investigated alloys had constant copper content equal to 0.9, 0.8 and 0.7 mole fraction, and varied iron concentration up to 0.1 mole fraction. A model predicting the density of ternary solution from knowledge of density of pure component and the excess of molar volume for limiting binaries is proposed.

Keywords: density, Cu-Pb-Fe alloys, dilatometer method, density model

Gęstość stopów Cu-Pb-Fe o dużym stężeniu miedzi określono za pomocą metody dylatometrycznej. Zbadane stopy charakteryzowały się stałym stężeniem miedzi, które było równe 0,9; 0,8 lub 0,7 ułamka molowego oraz zmiennym stężeniem żelaza do 0,1 ułamka molowego. Zaproponowano model pozwalający przewidywać gęstość trójskładnikowych roztworów na podstawie znajomości gęstości czystych składników (tych roztworów) i nadmiarowej objętości molowej dla granicznych roztworów dwuskładnikowych.

1. Introduction

The direct-to-blister flush smelting process used in Poland yields blister copper, slag containing 12-16 wt-% Cu and offgas which contains about 13 vol-% SO$_2$. The copper in the slag constitutes 1/3 of the copper content in the smelting concentrate, and is recovered in the electric furnace with coke and limestone addition. A Cu-Pb-Fe alloy is obtained in this process as an intermediate product which is next oxidized in converter to remove the iron and lead. Composition of these Cu-Pb-Fe alloys are represented by shadowed area in Fig.1.
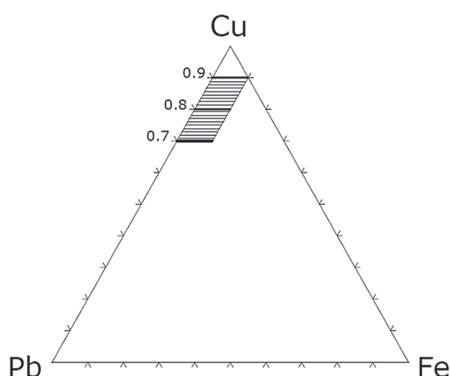

Fig. 1. Compositions of the investigated alloys Cu-Pb-Fe marked by shadowed area

Density of these alloys could be of great importance for proposed process [1] for copper recovery from slag of the direct-to-blister process. The aim of the present work was to determine density of these alloys as a function of their compositions and temperature. Densities of these alloys were measured with the sessile drop method [2], however evaporation of the lead from those samples could create a considerable error. A number of experimental techniques can be used to determine density of pure metals and its alloys [3,4]:
1. Methods employing Archimedes Principle
2. Maximum bubble pressure method
3. Sessile drop and drop levitation methods
4. Dilatometric methods
5. Pycnometric methods

Each of these methods has some limitations for its application as well as accuracy. In this study a dilatometric method was used to carry out our measurements. In general, this method has a number of modifications. The principle of this method is to measure of the volume of a known weight of liquid metal/alloy enclosed in calibrated vessel. The material of this vessel must be inert against liquid metals.

2. Preparation of the Cu-Pb and Cu-Pb-Fe alloys

To prepare Cu-Pb and Cu-Pb-Fe alloys, the pure metals were used: Cu-99.995 %; Pb-99.95% and Fe-99.99%. Iron

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dissolves in liquid copper very slowly, so is difficult to obtain homogenise liquid, and even prolonged heating these metals at high temperature did not secure dissolution iron in liquid copper. To overcome these difficulties, copper and iron were melted in alumina crucible in an induction furnace to prepare Cu-Fe master alloy containing 9.36 % of iron. The master alloy was quenched very quickly in order to prevent segregation of $\gamma - Fe$ as primary dendritic precipitates. Predetermined amounts of copper, lead and master alloy of about 3g mass, were sealed in evacuated quartz ampoules followed by prolonged heating at 1573-1623 K. After approximately 24 hours, the ampoules were very quickly quenched to secure homogenize composition of the samples. It was found that mass losses during this operation did not exceed 0.2%. Cu-Pb alloys were also prepared in evacuated quartz ampoules and heating at about 1473 K for about 24 hrs and then quenched very quickly. As these samples cannot be machined, so they were squeezed in cylindrical form to give them a cylindrical shape. Then, the sample was put into a sample container.

3. Method of determination

Densities of Cu-Pb and Cu-Pb-Fe as well as one alloy of CuFe were determined with a high temperature dilatometer DIL 402 manufactured by NETZCH, Germany. This dilatometer enables to measure a liquid metal expansion up to 1873 K. Fig. 2 illustrates the principal features of the method used in this work. A measuring container is in form of a tube with inner diameter of 6.5 ± 0.05 mm and outer diameter of 10 ± 0.05 mm and 22 mm in length. The liquid metal is closed in this container with two pistons which are fitted to the inner cylindrical hole in a such way that can move freely. One of these pistols is blocked by the sample holder made of alumina, while the second one is pressed by pushrod with a force of 30 cN and is connected with a sensor of linear displacement LVDT. Temperature of the sample is measured with thermocouple Pt-PtRh10 situated close to the sample.
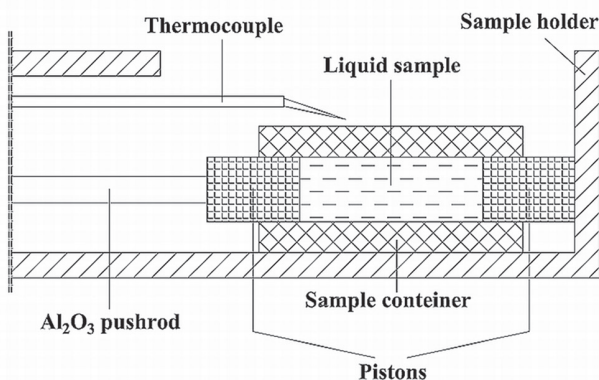

Fig. 2. Schematic of the apparatus for liquid metal expansion measurement

All measurements were carried out in helium (99.9999 % He) atmosphere maintained by this gas flowrate of 60 cm³/min. Sample holders and pistons are made of the high purity graphite. Alumina holders cannot be applied because

of CuAlO$_2$ phase formation [5] with gas product [6] at high temperatures:

$$Cu + Al_2O_3 = CuAlO_2 + AlO_{(g)} \qquad (1)$$
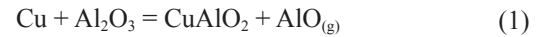
Sample containers made of boron nitride were also discharged, because on its surface at high temperature craters were formed. Because of these difficulties with materials for sample containers, high density graphite was used for its manufacturing. There was an assumption that because of small iron concentration in Cu-Pb-Fe alloys, carbon dissolution in the samples would be negligible. In addition, in order to achieve further limitation of carbon dissolution, lead vaporization, the time of the experiments was shorten by setting up high heating rate up to the first measuring temperature to 7 K/min. During experimental course, the heating rate was set up to 5 K/min.

There were some uncertainty in determination of the internal diameter of the sample holders, therefore each sample container was calibrated before experiment. Calibration consisted of measurement of liquid copper density at the temperature range 1373-1573 K. An apparent area of the cross-section of the sample container as a function of temperature was determined with the relation:

$$S(cm^2) = \frac{m_{Cu}}{\rho_{Cu}(T) \cdot l_{Cu}(T)} \qquad (2)$$

where: S - is the area of the cross-section of the sample container, m_{Cu} - mass of the copper used for calibration, $\rho_{Cu}(T)$ - density of the copper at temperature T; $l_{Cu}(T) = l_{Cu}^0 + \Delta l_{Cu}$ - length of the liquid copper sample closed in the calibrated sample container.

Density of the copper was calculated with the relation [7]:

$$\rho_{Cu}(g/cm^3) = 8.902 - 6.62 \cdot 10^{-4} \cdot T(K) \qquad (3)$$

In Table 1 an exemplary data of a such calibration is presented.

TABLE 1

Exemplary data for calibration of the sample holder in which subsequently density measurements of Cu-Fe alloy with X$_{Fe}$ = 0.1 was conducted ($l_{Cu}^0 = 0,941$).

Temperature, K	ρ_{Cu}, g/cm³	$\Delta l_{Cu} \cdot 10^4$, cm	S, cm²
1373	7.993	466.2	0.344082
1393	7.980	481.3	0.344116
1413	7.967	495.4	0.344187
1433	7.954	510.1	0.344239
1453	7.940	525.3	0.344318
1473	7.927	540.1	0.344370
1493	7.914	554.4	0.344441
1513	7.901	569.4	0.344489
1533	7.887	584.4	0.344582
1553	7.874	599.4	0.344634
1573	7.861	614.2	0.344694

Utilizing the data from Table 1, the area of this sample holder was determined as a function of temperature:

$$S(cm^2) = 0,339730 + 0,00000315 \cdot T(K) \qquad (4)$$

Fig. 3 illustrates a correlation between the data from Table 1 and relation (4).
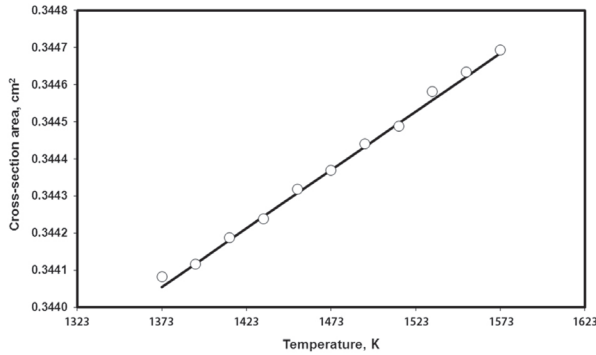

Fig. 3. A relation between area of a sample holder cross-section and temperature

Making use of the relation (4) and the experimental data for Cu-Pb-Fe alloys, their density were calculated with the relation:

$$\rho_{CuPbFe} = \frac{m^0_{CuPbFe}}{S(T) \cdot (l^0_{CuPbFe} + \Delta l_{CuPbFe}(T))} \qquad (5)$$

where: m^0_{CuPbFe} - mass of the Cu-Pb-Fe sample, l^0_{CuPbFe} - length of the sample at room temperature, $\Delta l_{CuPbFe}(T)$ - expansion (or shrinkage) of the sample at temperature "T".

It was assumed that the relation (4) holds also outside the temperature range used for the container calibration. The densities calculated with the relation (5) for Cu0.9Fe0.1 alloy is given in Table 2.

TABLE 2

Results of the density determination for Cu-Fe alloy contains 0.1 mole fraction of iron ($l^0_{CuFe} = 1.090\ cm$).

Temperature, K	Cross – section area, cm^2	$\Delta l_{CuFe} \cdot 10^4$, cm	ρ_{CuFe}, g/cm^3
1573	0.344685	212.0	7.786
1593	0.344748	232.8	7.770
1613	0.344811	252.6	7.755
1633	0.344874	272.9	7.739
1653	0.344937	295.9	7.722
1673	0.34500	323.4	7.702
1693	0.345063	343.8	7.686
1713	0.345126	362.7	7.672
1733	0.345189	381.1	7.658
1753	0.345252	398.9	7.645
1773	0.345315	416.0	7.632

4. Results

Densities of Cu-Pb-Fe alloys containing 0.9 mole fraction of copper were determined in a similar way as described above. Obtained results are given in Table 3.

TABLE 3

Density* of Cu-Pb-Fe alloys having constant copper content ($X_{Cu} = 0.9$) and varied iron concentration ($X_{Fe} + X_{Pb} = 0.1$) as a function of temperature.

T / K	X_{Fe}=0.00	X_{Fe}=0.02	X_{Fe}=0.04	X_{Fe}=0.06	X_{Fe}=0.08	X_{Fe}=0.10
1293	8.761	-	-	-	-	-
1313	8.747	-	-	-	-	-
1333	8.733	-	-	-	-	-
1353	8.718	-	-	-	-	-
1373	8.704	8.600	-	-	-	-
1393	8.689	8.586	-	-	-	-
1413	8.674	8.573	-	-	-	-
1433	8.659	8.559	-	-	-	-
1453	8.646	8.546	-	-	-	-
1473	8.632	8.534	-	-	-	-
1493	8.619	8.522	-	-	-	-
1513	8.606	8.511	-	-	-	-
1533	8.594	8.500	-	-	-	-
1553	8.583	8.490	-	-	-	-
1573	8.572	8.480	8.270	8.148	8.148	7.790
1593	-	-	8.262	8.138	8.138	7.777
1613	-	-	8.252	8.128	8.128	7.760
1633	-	-	8.243	8.118	8.118	7.747
1653	-	-	8.234	8.110	8.110	7.731
1673	-	-	8.226	8.099	8.099	7.713
1693	-	-	-	-	-	7.699
1713	-	-	-	-	-	7.684
1733	-	-	-	-	-	7.670
1753	-	-	-	-	-	7.657
1763	-	-	-	-	-	7.648

*Mean values from three independent measurements. Original experimental data are available on request.

The results of density measurements for Cu-Pb-Fe alloys with constant copper concentration ($X_{Cu} = 0.8$) and varied content of iron are given in Table 4.

TABLE 4

Density* of Cu-Pb-Fe alloys having constant copper content ($X_{Cu}= 0.8$) and varied iron concentration ($X_{Fe} + X_{Pb} = 0.2$) as a function of temperature.

T / K	X_{Fe}=0.00	X_{Fe}=0.02	X_{Fe}=0.04	X_{Fe}=0.06	X_{Fe}=0.08	X_{Fe}=0.10
1333	9.163	-	-	-	-	-
1353	9.155	-	-	-	-	-
1373	9.145	9.043	9.007	8.717	8.599	8.567
1393	9.133	9.033	8.994	8.704	8.576	8.553
1413	9.121	9.025	8.979	8.689	8.561	8.538
1433	9.108	9.013	8.964	8.675	8.545	8.523
1453	9.096	9.002	8.950	8.660	8.529	8.507

1473	9.083	8.991	8.937	8.647	8.514	8.492
1493	9.073	8.981	8.924	8.640	8.498	8.477
1513	9.062	8.970	8.912	8.621	8.482	8.461
1533	9.052	8.959	8.900	8.611	8.465	8.445
1553	9.042	8.950	8.891	8.599	8.442	8.431
1573	9.034	8.942	8.884	8.582	8.425	8.411

*Mean values from three independent measurements. Original experimental data are available on request.

The results of density measurements for Cu-Pb-Fe alloys with constant copper concentration ($X_{Cu} = 0.7$) and varied content of iron are given in Table 5.

TABLE 5

Density* of Cu-Pb-Fe alloys having constant copper content ($X_{Cu} = 0.7$) and varied iron concentration ($X_{Fe} + X_{Pb} = 0.3$) as a function of temperature.

T / K	$X_{Fe}=0.00$	$X_{Fe}=0.03$	$X_{Fe}=0.06$	$X_{Fe}=0.09$
1373	9.436	9.326	9.160	9.055
1393	9.429	9.318	9.146	9.045
1413	9.422	9.307	9.140	9.035
1433	9.412	9.299	9.130	9.025
1453	9.401	9.288	9.121	9.012
1473	9.390	9.277	9.112	9.000
1493	9.379	9.268	9.107	8.991
1513	9.368	9.259	9.096	8.982
1533	9.358	9.250	9.088	8.972
1553	9.350	9.242	9.079	8.961

1573	9.342	9.236	9.071	8.952

*Mean values from three independent measurements. Original experimental data are available on request.

A main error in the density measurement was due to evaporation of the lead from the investigated alloys during the experimental course. The masses of the samples were determined after each experiment, and the relative errors $\Delta m_{Pb(CuPbFe)} / m^0_{CuPbFe}$ expressed in per-cent are given in Table 6. As can be seen from this table, a small amount of carbon was dissolved in Cu-Fe alloy. Solubility of carbon in the other samples was limited by the fact that the surface layer of the Cu-Pb-Fe alloys is much enriched by the lead and reduced in iron and copper in comparison with the bulk phase. It is because lead's surface tension is much lower than surface tension of iron and copper [8]. In other words, the iron in the Cu-Pb-Fe samples was separated from graphite containers by this layer.

A sample weight lose generates an error in density measurement, because a lower volume of the sample is determined, while an original mass of the sample is used for density calculation. In consequence, calculated density are higher than should be. Let us consider a possible method of correction of this error. Let us assume that a sample weight loss ($\Delta m_{Pb(CuPbFe)}$) is proportional to lead partial pressure ($P_{Pb(CuPbFe)}$) above the sample, and the time (Δt) in which the sample is exposed at given temperature for a certain fit clearance between the sample container and pistons:

$$\Delta m_{Pb(CuPbFe)} = k \cdot P_{Pb} \cdot \Delta t \tag{6}$$

where: k - proportionality coefficient.

The partial pressure of lead over Cu-Pb-Fe alloy is given by the relation:

TABLE 6

The losses of samples weight in comparison to the initial masses of the Cu-Pb-Fe alloys and their composition changes during experimental course.

Composition befor experiments			$\dfrac{\Delta m_{Pb(CuPbFe)}}{m^0_{CuPbFe}} \cdot 100$, %	Composition after experiments			$\dfrac{\Delta x_{Pb}}{x_{Pb}}$, %
X_{Cu}	X_{Pb}	X_{Fe}		X_{Cu}	X_{Pb}	X_{Fe}	
0.9	0.10	0.00	-0.34	0.9011	0.0988	0.0000	1.2
0.9	0.08	0.02	-1.08	0.9035	0.0764	0.0201	4.5
0.9	0.06	0.04	-0.81	0.9025	0.0573	0.0401	4.5
0.9	0.04	0.06	-0.65	0.9019	0.0379	0.0601	5.2
0.9	0.02	0.08	-0.36	0.9010	0.0188	0.0802	6.0
0.9	0.00	0.10	+0.18	0.8916	0.0000	0.0990	0.0
0.8	0.20	0.00	-0.65	0.8024	0.1976	0.0000	1.2
0.8	0.18	0.02	-0.47	0.8016	0.1786	0.0198	0.8
0.8	0.16	0.04	-0.61	0.8020	0.1580	0.0400	1.2
0.8	0.14	0.06	-0.64	0.8020	0.1377	0.0603	1.6
0.8	0.12	0.08	-0.55	0.8017	0.1181	0.0802	1.6
0.8	0.10	0.10	-0.49	0.8014	0.0983	0.1003	1.7
0.7	0.30	0.00	-0.63	0.7022	0.2978	0.0000	0.7
0.7	0.27	0.03	-0.84	0.7029	0.2669	0.0302	1.1
0.7	0.24	0.06	-0.64	0.7021	0.2377	0.0602	0.9
0.7	0.21	0.09	-0.58	0.7018	0.2079	0.0903	1.0

$$P_{Pb(CuPbFe)} = P_{Pb}^0 \cdot a_{Pb(CuPbFe)} \qquad (7)$$

where: P_{Pb}^0 - is lead pressure over pure liquid lead at a given temperature, $a_{Pb(CuPbFe)}$ - lead activity in Cu-Pb-Fe alloy at the same temperature.

Substituting Eq. 7 into Eq. 6 the following relation is obtained:

$$\Delta m_{Pb(CuPbFe)} = k \cdot P_{Pb}^0 \cdot a_{Pb(CuPbFe)} \cdot \Delta t \qquad (8)$$

Temperature of the samples during experimental course was varied continuously with the same rate (5 K/min.), however in calculation P_{Pb}^0 and lead activity $a_{Pb(CuPbFe)}$ were taken at temperature of measurement. It was assumed that this sample started to lose its weight at a certain temperature in which the lead partial pressure is close to zero. A linear dependence between a mass lose of the sample ($\Delta m_{Pb(CuPbFe)}/m_{CuPbFe}^0 \cdot 100\ \%$) and the partial pressure of lead, was confirmed in a separate three tests, and obtained results are shown in Fig. 4. The lead pressure over pure liquid lead at a given temperature was estimated using the computer software [6]. The lead activity coefficient in Cu-Pb-Fe liquid alloys was calculated using the equation given in paper [9].
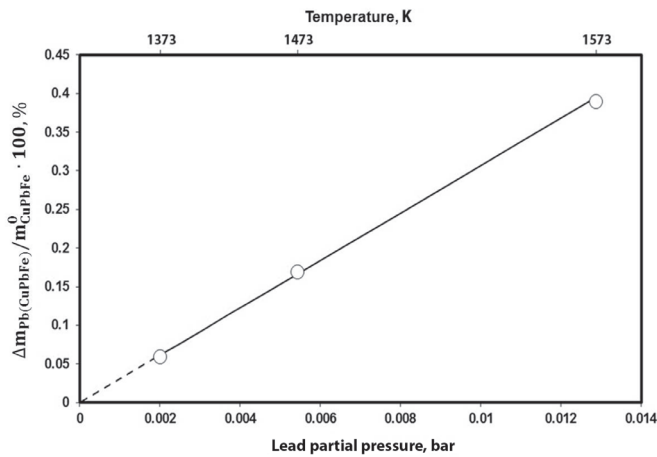

Fig. 4. Dependences of relative losses of the Cu-Pb-Fe alloy weight as a function of the partial lead pressure

Assuming that for the investigated alloys, the straight lines are passed by origin (see Fig. 4), the relative losses of the Cu-Pb-Fe alloys in selected temperature can be estimated. Therefore allowance can be made for lead evaporation from the Cu-Pb-Fe alloy during the experimental run, and obtained data were recalculated with the relation:

$$\rho_{CuPbFe}^{corrected} = \frac{m_{CuPbFe}^0}{V_{measured} + \dfrac{\Delta m_{Pb(CuPbFe)}}{\rho_{Pb}}} \qquad (9)$$

The relation (9) is rigorous under an assumption that evaporated led would take the same volume in the investigated alloy as in pure state. An example result of correction with Eq.9 can be seen in Fig. 5.
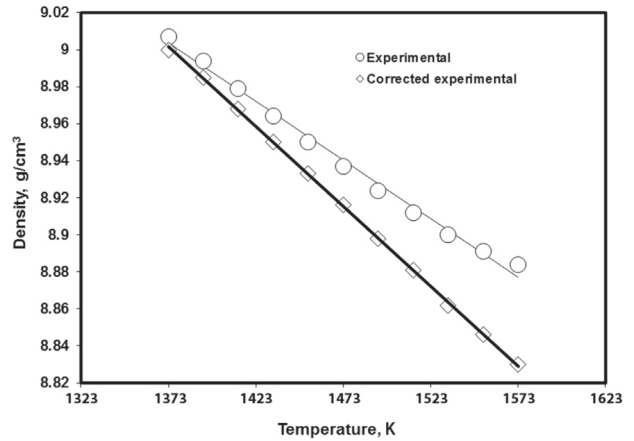

Fig. 5. Dependence of Cu-Pb-Fe density versus temperature obtained from experiments without and with corrections

Utilizing data $\Delta m_{Pb(CuPbFe)}/m_{CuPbFe}^0$ given in Table 6, the experimental density was corrected as described above, and the results were described by a linear equation. Table 7 enclosed the linear equations which described density as a function of temperature. These equations were obtained with the least squares method.

TABLE 7

Corrected density of Cu-Pb-Fe alloys as a function of composition and temperature.

X_{Cu}	X_{Pb}	X_{Fe}	$\rho(g/cm^3) = a + b \cdot T(K)$	R^2
0.90	0.10	0.00	$\rho = 9.748 - 0.00076 \cdot T$	0.9999
0.90	0.08	0.02	$\rho = 9.839 - 0.00091 \cdot T$	0.9999
0.90	0.06	0.04	$\rho = 9.393 - 0.00073 \cdot T$	0.9999
0.90	0.04	0.06	$\rho = 9.231 - 0.00070 \cdot T$	0.9999
0.90	0.02	0.08	$\rho = 9.090 - 0.00074 \cdot T$	0.9999
0.90	0.00	0.10	$\rho = 8.974 - 0.00075 \cdot T$	0.9996
0.80	0.20	0.00	$\rho = 10.205 - 0.00078 \cdot T$	0.9999
0.80	0.18	0.02	$\rho = 9.960 - 0.00067 \cdot T$	0.9999
0.80	0.16	0.04	$\rho = 10.130 - 0.00082 \cdot T$	0.9999
0.80	0.14	0.06	$\rho = 9.880 - 0.00085 \cdot T$	0.9999
0.80	0.12	0.08	$\rho = 9.962 - 0.00100 \cdot T$	0.9999
0.80	0.10	0.10	$\rho = 9..817 - 0.00091 \cdot T$	0.9993
0.70	0.30	0.00	$\rho = 10.419 - 0.00072 \cdot T$	0.9999
0.70	0.27	0.03	$\rho = 10.357 - 0.00076 \cdot T$	0.9999
0.70	0.24	0.06	$\rho = 10.077 - 0.00068 \cdot T$	1.0000
0.70	0.21	0.09	$\rho = 10.023 - 0.00071 \cdot T$	0.9999

5. Modeling of density of ternary mixtures

Let us assume that the molar volume of a ternary alloy A-B-C changes additively, so its value can be calculated from the relation:

$$V_{ABC(id)} = x_A \frac{M_A}{\rho_A} + x_B \frac{M_B}{\rho_B} + x_C \frac{M_C}{\rho_C} \qquad (10)$$

Where: $x_A; x_B; x_C$ - the mole fractions of the alloys components, $\rho_A; \rho_B; \rho_C$ - the density of the pure components, $M_A; M_B; M_C$ - the atomic weights of the alloy components.

In the other hand, the molar weight of alloy is equal:

$$M_{ABC} = x_A \cdot M_A + x_B \cdot M_B + x_C \cdot M_C \qquad (11)$$

Dividing Eq.11 by Eq.10, the density of the ideal mixture can be calculated:

$$\rho_{ABC} = \frac{1}{\dfrac{y_A}{\rho_A} + \dfrac{y_B}{\rho_B} + \dfrac{y_C}{\rho_C}} \qquad (12)$$

where: $y_A; y_B; y_C$ - are mass fraction of components, $x_i M_i / M_{ABC} = (i, wt - \%/100)$ for $i = A, B, C$.

In the case of non-ideal mixture, molar volume can be expressed by the relation:

$$V_{ABC} = V_{ABC(id)} + \Delta V_{ABC} \qquad (13)$$

where: $V_{ABC(id)}$ - the molar volume, which A-B-C mixture would have if was ideal, ΔV_{ABC} - the excess of molar volume.

The excess of molar volume mixture can be described in a way analogous to the excess molar free energy of ternary solution with use of models [10-16]. If ternary and all three binary solutions, which can be formed with ternary mixture components were regular, Toop's model [10] would describe its thermodynamic properties rigorously. In a such case, the excess of molar volume can be expressed by the analogous equation [17]:

$$\Delta V_{ABC} = (1 - y_2) \cdot \Delta V_{AB} + y_2 \cdot \Delta V_{AC} + y_1^2 \cdot \Delta V_{BC} \qquad (14)$$

where: $\Delta V_{AB}; \Delta V_{AC}; \Delta V_{BC}$ - are the excess of molar volumes of the limiting binary alloys which can be formed with components of the ternary alloys (A-B, A-C, B-C), $y_1 = 1 - x_A$, $y_2 = x_C / (x_B + x_C)$.

The excess of molar volume of binary solutions are relatively small. Hence, it was assumed that the excess molar volumes can be described with a rather good accuracy by the relations:

$$\Delta V_{ij} = x_i \cdot x_j (a_{ij} + b_{ij} \cdot T) \qquad (15)$$

where: a_{ij}, b_{ij} - adjustable parameters.

Using nondependent coordinates (y_1, y_2) and Eq. 15, the excess of the limiting binary alloys of the A-B-C mixture can be written as follows:

$$\Delta V_{AB} = y_1 \cdot (1 - y_1) \cdot (a_{Ab} + b_{AB} \cdot T) \qquad (16)$$

$$\Delta V_{AC} = y_1 \cdot (1 - y_1) \cdot (a_{AC} + b_{AC} \cdot T) \qquad (17)$$

$$\Delta V_{BC} = y_2 \cdot (1 - y_2) \cdot (a_{BC} + b_{BC} \cdot T) \qquad (18)$$

The molar volume of the ternary solution can be expressed by the relation:

$$V_{ABC} = V_{ABC(id)} + (1 - y_2) \cdot y_1 \cdot (1 - y_1)(a_{AB} + b_{AB} \cdot T) + y_2 \cdot y_1 \cdot (1 - y_1) \cdot (a_{AC} + b_{AC} \cdot T) + y_1^2 \cdot y_2 \cdot (1 - y_2) \cdot (a_{BC} + b_{BC} \cdot T) \qquad (19)$$

Dividing the molar weight (Eq. 11) of the A-B-C ternary solution by its volume (19), one can obtained:

$$\rho_{ABC} = \frac{1}{\dfrac{y_A}{\rho_A} + \dfrac{y_B}{\rho_B} + \dfrac{y_C}{\rho_C} + \alpha \cdot (a_{AB} + b_{AB} \cdot T) + \beta(a_{AC} + b_{AC} \cdot T) + \gamma \cdot (a_{BC} + b_{BC} \cdot T)}$$

$$(20)$$

where:

$$\alpha = \frac{y_1 \cdot (1 - y_1) \cdot (1 - y_2)}{M_{ABC}} = \frac{x_A x_B}{M_{ABC}},$$

$$\beta = \frac{y_1 \cdot (1 - y_1) \cdot y_2}{M_{ABC}} = \frac{x_A x_C}{M_{ABC}},$$

$$\gamma = \frac{y_1^2 \cdot y_2 \cdot (1 - y_2)}{M_{ABC}} = \frac{x_B x_C}{M_{ABC}}.$$

The presented model is similar in principles to the model presented by Brillo's and co-workers [18-21], and differs in the methods used to solve a few specific problems.

Pb-Fe solutions practically does not exist in the temperature range of interest in this work, hence it is justified to put $\Delta V_{FePb} = 0$. With this assumption, Eq. 20 takes the form for Cu-Pb-Fe alloys:

$$\rho_{CuPbFe} = \frac{1}{\dfrac{y_{Cu}}{\rho_{Cu}} + \dfrac{y_{Pb}}{\rho_{Pb}} + \dfrac{y_{Fe}}{\rho_{Fe}} + \alpha \cdot (a_{CuPb} + b_{CuPb} \cdot T) + \beta \cdot (a_{CuFe} + b_{CuFe} \cdot T)}$$

$$(21)$$

The model offers a possibility of determination density of the ternary solution exclusively with use of the excess of molar volume for limiting binary alloys and density of pure components of the ternary solution. In the case of Cu-Pb-Fe alloys density (the excess molar volume) of Cu-Pb and Cu-Fe alloys as well as densities of pure Cu, Pb and Fe are needed.

5.1 The excess of molar volume of Cu-Pb alloys

Densities of Cu-Pb liquid alloys has been determined in the earlier study [7], however, computed with these data the excess of molar volume is closed to zero ($\Delta V_{CuPb} \approx 0$).

Pelzel [22] has measured density of Cu-Pb alloys with dilatometric method. Malmberg [23] used the pycnometric technique for the specific volume determination of the Cu-Pb alloys at 1383 K. The excess of molar volume of Cu-Pb alloys

was determined with the use of copper density (Eq. 3) and lead density described by the equation [7]:

$$\rho_{Pb}(g/cm^3) = 11.426 - 12.4 \cdot 10^{-4} \cdot T(K) \qquad (22)$$

The relation (22) was established for experimental data determined at the temperature range 623-873 K. It means that for determination of lead density at 1373 K, we have to extrapolate Eq.22 for 500 K above the experimental range limit. As a consequence a considerable error could arise from a such operation. However, calculated lead density at 1383 K is in good agreement with data reported by Malmberg [23].

Density data of Łabaj et al. [24] were not taken in calculation, because their measurements are limited to a very narrow composition range. Using experiment data from the present work, an adjustable parameters of the relation for ΔV_{CuPb} were estimated:

$$\Delta V_{CuPb} = -y_1 \cdot (1 - y_1) \cdot (1.596 + 0.000127 \cdot T(K)) \qquad (23)$$

5.2 The excess of molar volume of Cu-Fe liquid alloys

Experimental data for density of Cu-Fe liquid alloys can be found in the paper of many investigators [19, 20, 25, 26]. Brillo et al. [19, 20] have measured density of Cu-Fe alloys with the electromagnetic levitation technique coupled with a digital camera which could capture image of levitating metal droplet. Their data suggests that the excess of molar volume has positive deviation from the ideal volume.

Watanabe and Saito [25] used the maximum bubble pressure to determine density of Cu-Fe liquid alloys. His data suggests that the excess of molar volume of Cu-Fe liquid alloys is close to zero.

Nizenko and Floka [26] were measure density of Cu-Fe alloys at 1873 K using "large drop" method. Their data indicates that the molar volume of Cu-Fe liquid alloys has positive deviation from ideal behavior. And finally, our experimental data for the Cu-Fe alloy having 0.1 mole fraction of iron in conjunction with iron density taken from work [27] were used for the excess molar volume determination. Utilizing these data, the excess molar volume was described by the relation:

$$\Delta V_{CuFe} = y_1 \cdot (1 - y_1) \cdot (-1.1608 + 0.00082 \cdot T(K)) \qquad (24)$$

Utilizing Eqs. 3, 21, 23 and 24, density of Cu-Pb-Fe liquid alloys was calculated, and obtained values were compared with the experimental data. A very good agreement between the model values and experimental results can be observed, as can be seen in Fig.6.
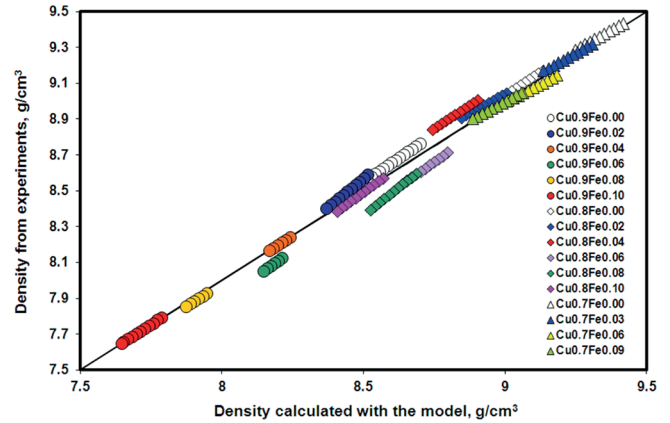

Fig. 6. Comparison of the data calculated from the model with experimental results for Cu-Pb-Fe alloys

6. Discussion

A close inspection of the experimental data revealed that there was a possibility of a systematic error to appear in measurement and arising from imperfection in manufacturing the sample containers. Let us assume that the internal hole of the sample container has not the same diameter, but is conically shaped, as can be seen in Fig 7a.
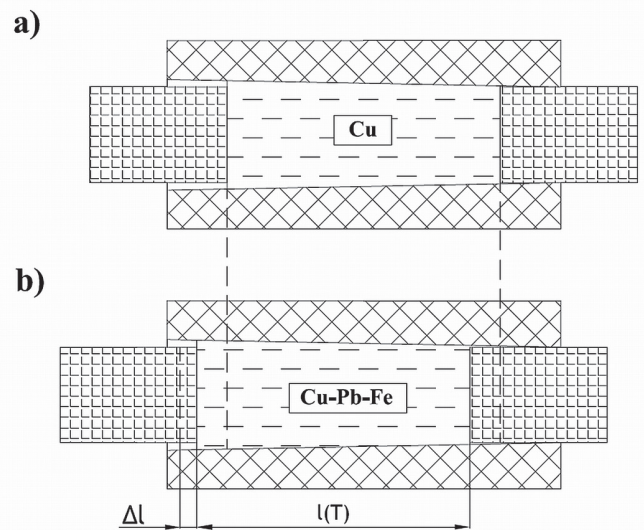

Fig. 7. Schematic illustration of an exaggerated situation in which a systematic error could be crated

Before measurements, the container is calibrated in order to determine its apparent area of cross-section. At selected temperature, the copper used in calibration occupied a certain volume. Let us assume that mass of the investigated Cu-Pb-Fe alloy was chosen in a such way, that have the same volume as the copper used in the container calibration. If this sample was placed in the same area as copper during calibration, determination of this sample would be very accurate.

Now, let us assume that the sample of the alloy was placed in a different place (Fig. 7b), and because mean value of the area of the container cross-section would be larger, then the determined length of the sample would be shorter. In other

words, the sample volume will be determined with error equal to ΔV. Density of the CuPb-Fe alloys is calculated from the relation:

$$\rho_{CuPbFe} = \frac{m^0_{CuPbFe}}{V} \qquad (25)$$

where: V - the volume of investigated alloy, which was estimated with error, because the situation described above.

In consequence, the measurement would be associated with an error ($d\rho_{CuPbFe} \approx \Delta\rho_{CuPbFe}$):

$$d\rho_{CuPbFe} = \frac{V \cdot dm^0_{CuPbFe} - m^0_{CuPbFe} \cdot dV}{V^2} \approx \frac{\Delta m^0_{CuPbFe}}{V} - m^0_{CuPbFe}\frac{\Delta V}{V^2}$$

$$(26)$$

Dividing Eq. 26 by Eq. 25 we receive:

$$\frac{|\Delta\rho_{CuPbFe}|}{\rho_{CuPbFe}} \leq \frac{|\Delta m^0_{CuPbFe}|}{m^0_{CuPbFe}} + \frac{|\Delta V|}{V} \qquad (27)$$

The first term of the Eq. 27 is very small and can be neglected, because the mass of a sample was determined with high accuracy ($\Delta m^0_{CuPbFe} \approx 10^{-4}$ g), and an error involve is less than 0.01%. The second term of the Eq.27 would be much bigger. The volume of the used samples were of order 0.35 cm^3, and every loss of accuracy in manufacturing of the sample container could cause a considerable systematic error. For example an error in diameter determination of the order of 0.03 mm cause an error of density determination equal about 1%.

A second source of errors in these measurements could be associated with the volumetric uncertainty causes by incomplete filling of the container at the sharp corners, owing to surface tension. This error was partly minimized by exerting the force (30 cN) on piston and by calibration. However, containers calibration were conducted with pure copper which has a high surface tension, while surface tension of Cu-Pb-Fe alloys are much lower due to lead surface activity in these alloys.

A model for describing of density in a ternary solution is put forward. This model can described density of ternary solutions using exclusively density of pure component and the excesses of molar volumes for limiting binary solutions. However the results of the model calculations depend very heavily on an accuracy of the density measurements of pure components and excesses of molar volume of limiting binary mixtures. This model can be easily extended to multi-component mixtures if method employed in paper [17] were adopted.

REFERENCES

[1] M. Kucharski, K. Rogóż, PL – 213767, Urząd Pat. RP (2013).
[2] M. Kucharski, P. Fima, Archives of Metallurgy and Materials **49**, (3), 565-573 (2004).
[3] S.D. Veazey, and W.C. Roe, Journal of Materials Science. **7**, 445-466 (1972).
[4] A.F. Crawley, International Metallurgical Reviwes **19**, 32-48 (1974).
[5] S. Klein, A.P. Tomsia, M. Rühlec, C. Shen, Journal of Physics **208**, 11-17 (1974).
[6] A. Roine, J. Mansikka-aho, T. Kotiranta, P. Bjorklund, P. Lamberg, HSC Chemistry 7.0 software.
[7] T. Sak, T. Sak, M. Kucharski, Rudy i Metale Nieżelazne **58**, 5-10 (2013).
[8] K.C. Mills, Y.C. Su, International Materials Reviews **51**, 329-351 (2006).
[9] J. Wypartowicz, L. Zabdyr, K. Fitzner, Archiwum Hutnictwa **24**, (4), 473-488 (1979).
[10] G.W. Toop, Trans. Met. Soc. AIME **233**, 850-855 (1965).
[11] [E. Bonnier and R. Caboz, CR. Hebd: Séancess Acad. Sci. 250, 527-529 (1960).
[12] F. Kohler, Monatsh. Chem. **91**, 738-740 (1960).
[13] C. Colinet, D.E.S. Fac. Sci. Univ. Grenoble. France (1967), (after I. Ansara: International Metals. Reviews. **1**, 20-53 (1979).
[14] Y.M. Maggianu, M. Gambino, J.P. Bros, J. Chim. Phys. **72**, (1), 83-88 (1975).
[15] K.T. Jacob, K. Fitzner, Thermochimica Acta **18**, 197-206 (1977).
[16] Zhi-Chang Wang, R. Lück, B. Predel, CALPHAD **14**, (3), 235-256 (1990).
[17] M. Kucharski, C. Acuna, Arch. Metallurgy **41**, 271-281 (1996).
[18] J. Brillo, I. Egry, Int. J. Thermophysics **24**, 1155-1170 (2003).
[19] J. Brillo, I. Egry, Z. Metallkd. **95** (8), 691-696 (2004).
[20] J. Brillo, I. Egry, T.Matsushita, Int. J. Mat. Res. (formerly Z. Metallkd.), **97** (11), 1526-1532 (2006).
[21] [21] J. Brillo, I. Egry, T.Matsushita, Int. J. Thermophys **27** (6), 1778-1791 (2006).
[22] E. Pelzel, Metall **11**. 1957, 954-958 (1957).
[23] T. Malmberg, J. Inst. Metals **89**, 137-139 (1960).
[24] J. Łabaj, B. Sikora, A. Fornalczyk, Rudy i Metale Nieżelazne **50,** 164-169 (2005).
[25] S. Watanabe, T. Saito, Trans. JIM. **13**, 186-191 (1972).
[26] W.I. Nizenko, L.I. Floka, (In Russian). Izv. Vysh. Uceb. Zaved. Cernaya Metal **9**, 13-16 (1973).
[27] S.Watanabe, Y. Tsu, K. Takano, Y.Shiraishi, J. Jap. Inst. Met. **45**, 242-249 (1981).