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VISCOSITY OF THE LEAD-TIN LIQUID ALLOYS

LEPKOŚĆ CIEKŁYCH STOPÓW OŁÓW-CYNA

The capillary method was used in the measurements of the viscosity of the lead-tin liquid alloys. The experiments were performed for the lead, tin and five lead-tin alloys of the concentration 0.1, 0.261 (eutectic), 0.5, 0.7 and 0.9 mole fraction of lead and between 521 K and 871 K. The experimental data of viscosity of pure components and liquid Pb-Sn alloys were described by the exponential equation $\eta = A \exp(E/RT)$. The dependence of viscosity on temperature and concentration was modeled by the K u c h a r s k i ' s method considered in the calculations the activity coefficients, the particle molar volume of components and the molar volume of liquid alloys. Obtained isotherms of viscosity at 623 K and 823 K have shown nearly linear changes with the concentration and a reasonable agreement with the experimental data. The observed differences when compared with data from the literature do not exceed 15%.

Stosując metodę kapilarną zmierzono lepkości ciekłych stopów ołów-cyna. Pomiaru przeprowadzono dla ołowiu, cyny oraz pięciu stopów o stężeniu 0.1, 0.261 (eutektyka), 0.5, 0.7 i 0.9 ułamka molowego ołowiu, w zakresie temperatur od 521 K do 871 K. Wyniki pomiarów, zarówno dla ołowiu i cyny jak i ciekłych stopów Pb-Sn zostały opracowane zależnościami temperaturowymi postaci $\eta = A \exp(E/RT)$. Zależność lepkości ciekłych stopów Pb-Sn od stężenia i temperatury została opracowana modelem K u c h a r s k i e g o, uwzględniającym w obliczeniach współczynniki aktywności, cząstkowe objętości molowe składników oraz objętość molową ciekłych stopów a obliczone z niego izotermy lepkości w temperaturach 623 K oraz 823 K charakteryzują się niemal prostoliniowymi zmianami od stężenia i są bliskie wartości eksperymentalnych. Zaobserwowane różnice pomiędzy wartościami doświadczalnymi lepkości z niniejszej pracy i prezentowanymi w literaturze nie przekraczają 15%.

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1. Introduction

Viscosity of liquids encountered in metallurgical processes is a very important factor, which influences heat and mass transport. It is widely accepted that viscosity is closely related to the structure of the liquid. In solutions with strong interactions between the components, compounds can be formed and this results in the maximum of viscosity vs. composition curves. In pure SiO_2 and B_2O_3 which are highly polymerised melts, non-linear relations $\ln \eta = f\left(\frac{1}{T}\right)$ are often observed. Despite a large number of studies concerning the viscosity of mixtures, there are still many systems to be investigated, and multicomponent solutions are particularly neglected.

Modeling of the viscosity of complex multicomponent melts might be the solution to the problem, especially if it is possible to predict viscosity of these mixtures from the respective data for limiting binary solutions. Such modeling enables to extrapolate available experimental data on unlimited number of solutions, reducing the range of experiments and supplying data for the simulation of metallurgical processes. Due to this, the problem of modeling of viscosity has been extensively investigated during the last decades, and the proposed models can be classified into two main groups. To first group comprises models based on molecular theory of liquids, and the second group consists of models in which adjustable parameters are used.

The K u c h a r s k i 's model [1, 2] is based on the rate theory [3] and belongs to the second group of models. It has been used for metallic [1—6] and molten salt mixtures [7], reproducing successfully the experimental data.

For a binary mixture, the viscosity, molar volume and activity coefficients of the components are used and the model is expressed by the following equation:

$$\eta = X_1 \frac{V_1}{V} \left(\frac{\beta}{\beta_1}\right)^2 \gamma_1^\alpha \eta_1 + X_2 \frac{V_2}{V} \left(\frac{\beta}{\beta_2}\right)^2 \gamma_2^\alpha \eta_2, \quad (1)$$

where: the subscripts denote components 1 and 2, η is viscosity, X is mole fraction, V is molar volume, γ is activity coefficient, $\beta = X_1 V_1^{1/3} + X_2 V_2^{1/3}$, $\beta_1 = X_1 V_1^{1/3} + X_2 V_2^{4/3}/V_1$, $\beta_2 = X_2 V_2^{1/3} + X_1 V_1^{4/3}/V_2$, V_1 and V_2 are the partial molar volumes and α — is adjustable parameter.

The α parameter is practically independent of the concentration and the temperature [1] only for alloys without the presence of intermetallic compounds in the solid state. In the systems with strong interactions and the tendency for intermetallic phases formation, the α parameter varies considerably both with the temperature and composition, as reported by G a n e s a n [3] for the Al—Cu system. To solve this problem, an additional term describing the viscosity of the formed compound, which comprised its activity coefficient, was introduced in Eq. 1. Due to this, a good agreement between computed and experimental data is observed [4, 5].

The viscosity of liquid tin and lead is reported in various References [8—17], and for the Pb—Sn liquid alloys were performed by G e b h a r d and K o s t l i n [18]

T r e s h and co-workers [19], and F i s h e r and P h i l i p s [20]. The capillary and oscillating vessel methods were used in investigations of pure metals while only the oscillating techniques are applicable in viscosity measurements of liquid Pb–Sn alloys. The high-temperature viscosity measurements of pure Al were performed in our laboratory by the B r u c k f i e l d rotation viscometer (for the liquids with the viscosity higher than 4 mPa·s). After reconstruction it was possible to work at the elevated temperatures and with the liquid metals having the viscosity much lower than the calibrating liquids.

Because of various experimental difficulties a vertical capillary viscometer was constructed in our Institute allowing to perform measurements for low melting alloys. As the first step, to test this equipment it was decided to measure the viscosity of pure liquid Pb, Sn and Pb–Sn alloys, easy for preparation due to low melting temperatures. In addition, eutectic or off eutectic Pb–Sn alloys are still commonly used as a basic soldering material. Therefore the properties of each new Pb-free solder are always referred to Pb–Sn, to its melting temperature, solderability, surface tension and mechanical properties.

The scope of this paper was to perform the viscosity measurements by the capillary flow method for liquid lead, tin and lead-tin alloys at elevated temperatures and to indicate advantages of the K u c h a r s k i 's model, enabling to reduce the extent of experiments for predicting the viscosity of the liquid alloys in the entire range of concentrations and in a wide range of temperature.

2. Experimental

The viscosity of liquids can be measured using the capillary flow method based on Hagen-Poiseuille's equation

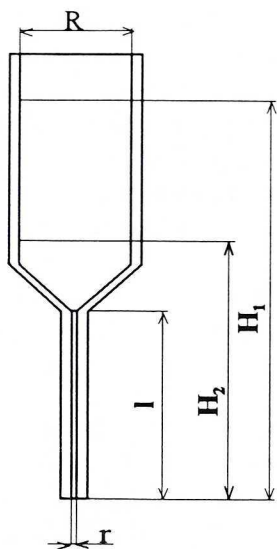
$$V/t = \frac{\pi \Delta p r^4}{8 L \eta} \quad [\text{m}^3/\text{s}] \quad (2)$$

describing the laminar flow rate of liquid (V/t) of the viscosity η , through the capillary of the radius r and the length L , caused by the constant difference of pressure between the end of the capillary and the liquid level in the reservoir equal to Δp [21–23].

In the case of the free flow of liquid from the capillary, the pressure Δp is the algebraic sum of the substitute hydrostatic pressure Δp_s and counteracting the surface tension pressure Δp_{st} , and they are expressed by the relation:

$$\Delta p = \Delta p_s + \Delta p_\gamma = \rho g (H_1 - H_2) / \ln(H_1/H_2) - 2\gamma/r, \quad [\text{Pa}] \quad (3)$$

where: r is the capillary radius, γ is the surface tension of liquid and H_1 and H_2 are the initial and final height of liquid in the reservoir of the radius R (Fig. 1), g is the acceleration of gravity and ρ is the density of the liquid.



- R - radius of the reservoir
- r - radius of the capillary
- l - length of the capillary
- H₁ - initial head of liquid
- H₂ - final head of liquid

Fig. 1. A scheme of the vertical capillary viscometer

Taking into consideration the Hagenbach's correction concerning the kinetic energy of the liquid the viscosity is calculated from the following relation:

$$\eta = \frac{\pi r^4 t}{81V} \Delta p - \frac{mV\varrho}{8\pi l t} \quad [\text{mPa} \cdot \text{s}], \quad (4)$$

where: r and l are the capillary radius and length, ϱ is the density of the liquid, t is the time necessary for the volume of liquid V to flow out from the capillary and m is the Hagenbach's coefficient dependent on the Reynolds' number. The volume of liquid is calculated from the equation:

$$V = \frac{\pi R^2}{4} (H_1 - H_2) \quad [\text{m}^3], \quad (5)$$

in which R is the radius of the reservoir connected with the capillary (see Fig. 1) and the notation of the other symbols are the same as above.

Equations 2 and 3 were tested before investigations of the viscosity of Pb-Sn liquid alloys using ethylene alcohol, distilled water, CCl_4 and calibration liquid with the viscosity $4 \text{ mPa} \cdot \text{s}$. The capillaries used in the experiments were made of high-temperature melting glass and there were tested with the mentioned liquids. The high purity argon with 20% hydrogen, additionally purified from water, oxygen and nitrogen by molecular sieve, catalytic copper and titanium sponge, was used as the protective atmosphere. The alloys before the experiments were prepared in the same atmosphere by pre-melting of suitable amounts of Pb and Sn of purity 99.995 at.%. The values of density of liquid Pb-Sn alloys were taken from Refs. [24] and [25]. The change of the capillary size with the temperature was taking into account in the calculations of viscosity.

3. Results and discussion

The measurements of viscosity were performed for liquid tin, lead and five Pb–Sn alloys of the composition 0.1, 0.261 (eutectic), 0.5, 0.7 and 0.9 mole fraction of Pb and at the temperature range from 521 K to 871 K. The results were described by Arrhenius equation, and pre-exponential coefficients A and the activation energy E were calculated by the least squares method. The resulting equations are presented in Table 1 with the coefficients of determination and the viscosity values calculated at 623 K and 823 K.

TABLE 1

The temperature dependence of the viscosity of Pb–Sn liquid alloys with the coefficient of determination and viscosity calculated at 623 K and 823 K.

X_{Pb}	$\eta = A \exp(E/RT)$ mPa·s	Coefficient of determination R-squared	$\eta_{623\text{K}}$ mPa·s	$\eta_{823\text{K}}$ mPa·s
1.000	= 0.708 exp(7073/RT)	0.9805	2.774	1.991
0.900	= 0.669 exp(7152/RT)	0.9682	2.655	1.938
0.700	= 0.601 exp(7558/RT)	0.9940	2.607	1.812
0.500	= 0.578 exp(6988/RT)	0.9855	2.228	1.605
0.261	= 0.623 exp(5677/RT)	0.9985	1.864	1.428
0.100	= 0.589 exp(5429/RT)	0.9953	1.680	1.302
0.000	= 0.658 exp(4372/RT)	0.9936	1.531	1.247

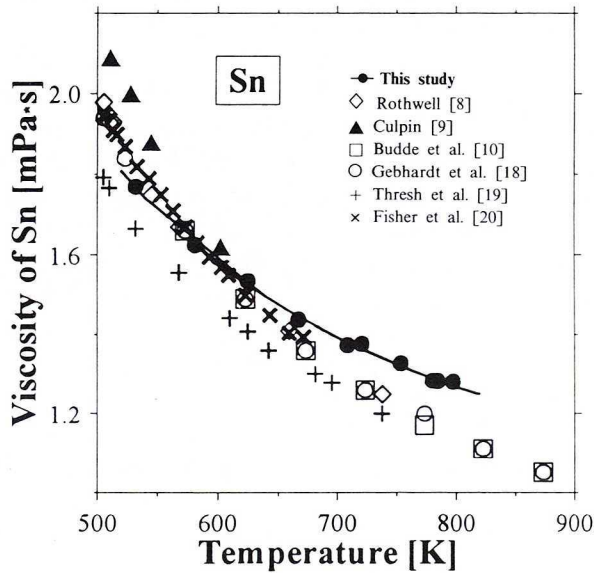


Fig. 2. Temperature dependence of the viscosity of liquid tin together with the data from earlier works. Solid curve represents the data calculated from equations reported in Table 1.

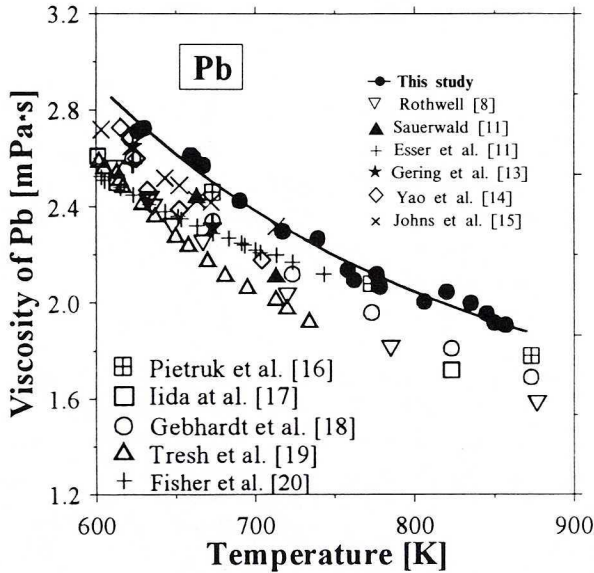


Fig. 3. Temperature dependence of viscosity of liquid lead together with the literature data and the data calculated from equation presented in Table 1 (solid curve)

The viscosity of tin and lead are presented in Figs. 2 and 3 and compared with the data from Refs. [8—20]. The viscosity of tin is shown in Fig. 2. The solid curve represents the values calculated from equations reported in Table 1. Data of this study are very close to the results of Fisher and Phillips [20] between 530 K and 675 K and to those of Gebhardt and Kostlin [18] from 530 K to 600 K. The viscosity values measured by Tresh and Crowley [19] represent the lowest values from the cited references and are also lower than our data (0.1 mPa·s to 0.15 mPa·s) at the temperatures between 530 K and 740 K. Data of Gebhardt and Kostlin [18] and Budde et al. [10] at temperatures higher than 673 K are lower by about 0.1 mPa·s to 0.15 mPa·s when compared with viscosity measured in this study. Results of Culpin [9] obtained by the oscillating vessel method between 500 K and 600 K are the highest of all References and near 600 K are nearly the same as results of this contribution. Viscosity of tin measured by Rothwell [8] are similar to data of this study at the temperature range from about 530 K to 630 K, however at higher temperatures they have the same tendency as data of Gebhardt et al. [18].

Presented in Fig. 3, the viscosity of pure liquid lead from this work and that measured in the different laboratories show the maximal differences of about 0.3 mPa·s. The solid curve shows the viscosity calculated from the equation in Table 1. A very good agreement of our data with the results of Pietruk et al. [16] is observed between 630 K and 975 K and it amounts to about 0.05 mPa·s. The differences of about 0.15 mPa·s are noted between the results of this work and those

obtained by Johnson et al. [15] and slightly higher when compared with Yao et al. [14], Gerling [13] and Gebhardt [18] et al. The viscosity of Tresh et al. [19] and Iida et al. [17] between 600 K and 825 K represents the lowest values from among all references considered in this paper and they are close to the data of Rothwell [8] (about 0.3 mPa·s lower than our data). The results of Fisher and Phillips [20], are very close to those of Tresh et al. [19] at the temperatures between 600 K and 675 K and they approach data from this work at temperatures higher than 700 K, similarly as the results of Johnson et al. [15] at temperatures higher than 650 K. Analysis Figs. 2 and 3 it should be noted that the scatter of experimental results of viscosity of pure tin and lead within the same experimental technique are of the order of 20% (data from oscillating vessel method [8, 19 and 16, 19]). Much lower deviations are observed for the capillary method (this study and Refs. [10–13]).

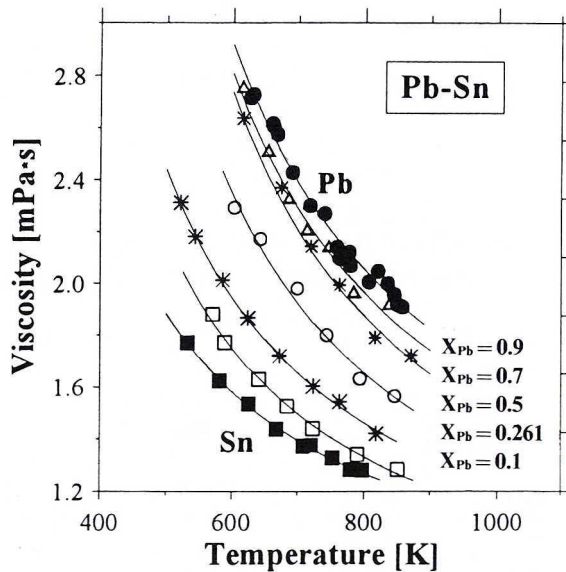


Fig. 4. Temperature dependences of viscosity of liquid Pb–Sn alloys. The points are the experimental data from this study and solid curves represent the values calculated from equations summarised in Table 1.

In Fig. 4. the experimental data of this study (points) are plotted, while the solid curves were calculated from equations reported in Table 1. Experimental results were used next in Kucharski's model and the parameter α was calculated by the least squares method, assuming that it is independent of the composition and temperature. The Pb and Sn partial molar volumes and the activity coefficients were taken from Refs. [26] and [27]. Fig. 5 shows the comparison of the viscosity, calculated from model (1) with the parameters $\alpha_{\text{Pb-Sn}} = -0.13$, and with the experimental data from this study. Except a few points a good correlation between the experimental and the modeled results is observed.

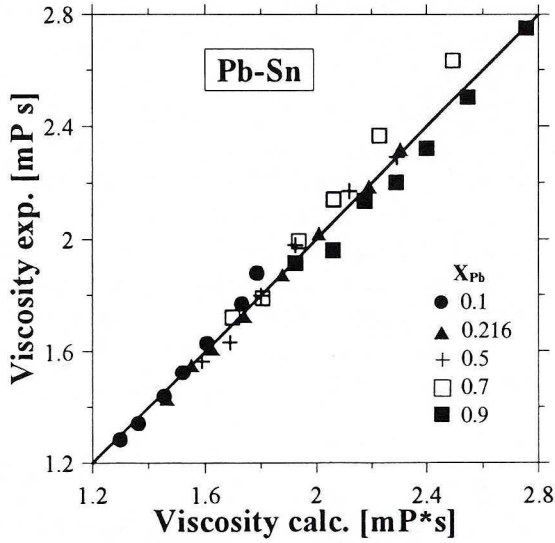


Fig. 5. Comparison of the experimental data with data calculated from Kucharski's model (Eq. 1) accepting $\alpha = -0.13$

The isotherms of the viscosity of the liquid Pb-Sn alloys calculated from Eq. 1 at 623 K and 823 K are presented in Fig. 6 simultaneously with data from Refs. [18–20].

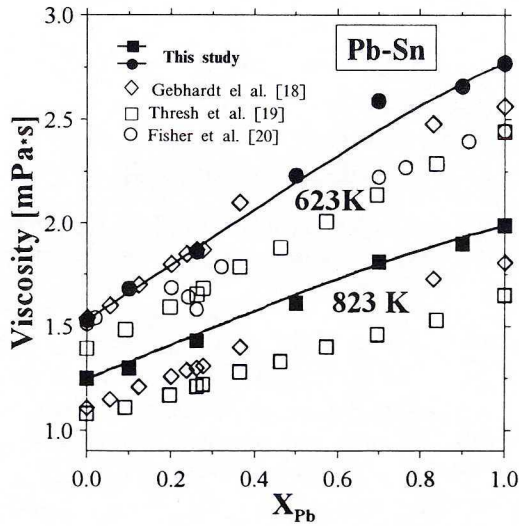


Fig. 6. The isotherms of the viscosity of the Pb-Sn liquid alloys at 623 K and 823 K calculated from Eq. 1 (continuous curves) and from equations reported in Table 1 (full points and squares) compared with the data from references [18–20]

Nearly linear dependencies of viscosity vs. composition are observed for liquid Pb–Sn alloys, similarly to the results of other authors including data of T r e s h and C r a w l e r [19]. At the temperature 623 K ($X_{\text{Pb}} = 0\text{--}0.6$) the results of G e b - h a r d t et al. [18] are almost the same as the data of this study, and the differences higher than 6% are observed in the vicinity of lead. The isotherm of F i s h e r and P h i l i p s [20] calculated at 623 K shows minimum at the eutectic composition ($X_{\text{Pb}} = 0.261$), however it was not confirmed in this study and in the works [18] and [19].

4. Conclusion

The experimental results of the viscosity of liquid lead, tin and lead-tin alloys, obtained by the capillary method (vertical viscometer), show agreement with the data obtained by the other methods within the range from 7 to 15%. The exponential dependence of the viscosity ($\eta = A \exp(E/RT)$) was observed and used for the interpretation of the temperature dependence of viscosity. By means of the minimisation method the preexponential parameter A and the activation energy E were calculated.

The K u c h a r s k i ' s model proposed in [1] was used for the interpretation of the dependence of the viscosity on the concentration and the temperature. The very good agreement between experimental and computed data, proved in Figs. 5 and 6, suggests that the model is capable for describing the viscosity of alloys over the entire range of concentrations and the extended range of temperatures, even in the case of limited experimental data. This can reduce the range of experimental studies.

It is interesting to mention that with a constant value of α , it is possible to estimate viscosity of multicomponent systems, formed from the limiting binaries without any additional adjustable parameters [2]. The model can also describe the viscosity of slags, however provision should be made for very complex ions, whose thermodynamic characteristics, and viscosities are available.

The minimum of viscosity at the eutectic composition, reported by F i s h e r and P h i l i p s [20] was not confirmed in this study, in agreement with Refs. [18] and [19].

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