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Influence of Ni Additions on the Viscosity of Liquid Al_2Cu

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Abstract: The viscosity of the liquid Al–Cu–Ni alloys has been studied by means of an oscillating crucible method. The activation energy of viscous flow was estimated from temperature dependences of the viscosity. The analysis of concentration dependence of the viscosity across a section $Al_{67}Cu_{33}$–Ni reveals its negative deviation from the linear dependence. Such behaviour of the viscosity coefficient upon additions of Ni into the liquid $Al_{67}Cu_{33}$ alloy could be caused by change of the interaction parameters between different structural units in the investigated melts.

Keywords: viscosity, activation energy, molten Al–Cu–Ni alloys

Introduction

Aluminium-based alloys are of great interest due to their practical use, especially in aircraft industry. It is well known that the addition of 3d-elements to Al effectively improves main physical characteristics of this metal [1]. Furthermore, the addition of rare-earth elements results the better mechanical properties [2]. Therefore, the influence of minor additions of rare-earth elements on other physical–chemical properties of pure Al in liquid and solid states has extensively investigated during the last decade.

The X-ray study of liquid Al-enriched $Al_{100-x}Ni_x$ alloys suggests that strong chemical interactions between Al and Ni atoms change the structure of liquid alloys from a random distribution of atoms to one with short-range order [3]. This phenomenon was later confirmed in Ref. [4], on the basis of the viscosity measurements of liquid $Al_{100-x}Ni_x$ alloys. Viscosity is one of the most structure-sensitive transport properties in the liquid state. An anomalous behaviour of this quantity versus concentration and/or temperature could be evidence of the structure changes in the liquid alloys, which affect other properties in the liquid state, as well as the structure in the solid state [5–7].

Al–Cu–Ni system belongs to systems with ternary chemical compounds in the solid state [8]. An increasing interest to Al–Cu–Ni alloys over recent years is caused by their use in different applications (medicine, robotics, micro- and nano-electromechanical systems) due to their shape memory properties. These alloys are also interesting due to good superplasticity properties and stress-induced martensitic transformation [9]. According to the phase diagram, Al-enriched alloys consist of two phases: $Al_2Cu + Al_3Ni$, and each of them is the main constituent of eutectic alloys $Al_2Cu + Al$ and $Al_2Ni + Al$ [8].

The Al_2Cu phase is predominant in the formation of Al–Cu and Al–Cu-based alloys and has the greatest impact on the physical–chemical properties of these alloys. The Al_2Cu intermetallic compound is also related to ageing processes, important for industrial processes such as properties improvement by means of thermal treatment [10].

The main goal of this paper is to investigate the impact of minor additions of Ni on the viscosity of the liquid Al_2Cu. According to the liquidus surface of Al-based Al–Cu–Ni alloys [8], even at such small Ni additions, the melting temperature of Al_2Cu significantly increases up to about 1,273 K for 10 at. % Ni (Figure 1, grey circles correspond to concentrations of the investigated alloys). Therefore, the competition between Al_2Cu and Al_3Ni compounds is expected to influence the viscosity in liquid Al-based Al–Cu–Ni alloys. This relationship between intermetallic compounds competition and the viscosity behaviour has been shown for liquid In–Bi alloys [11]. To the best of our knowledge, the temperature dependence of the viscosity was investigated only for the liquid $Al_{85}Ni_{10}Cu_5$ alloy [12]. It was found that the temperature dependence of the liquid $Al_{85}Ni_{10}Cu_5$ alloy consists of two parts: a low-temperature area (LTA) in the range between the liquidus point (LP) and 100 K above LP – a high-temperature area (HTA). In this case, the authors of Ref. [12] estimated a variation of the activation energy of viscous flow with the temperature for Al–Ni-based alloys.

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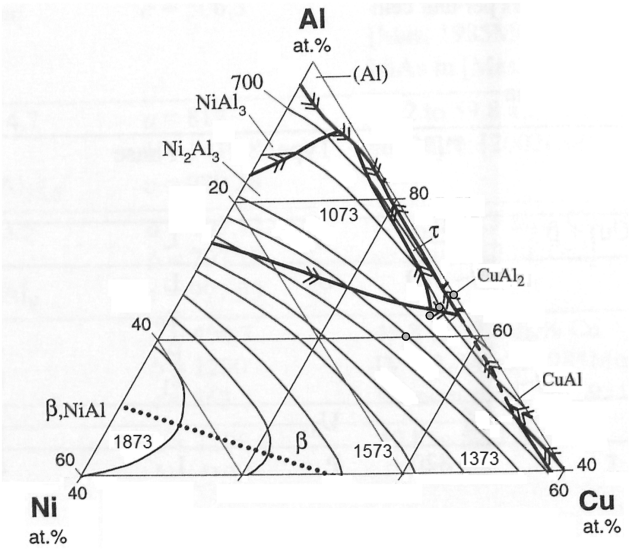

Figure 1: Liquidus projection of Al–Cu–Ni system (• – investigated alloys; τ – ternary $Al_{31}Cu_{16}Ni_4$).

Therefore, temperature and concentration dependences of the viscosity of the liquid $Al_{67}Cu_{33}$ alloy were investigated by additions of 0, 3, 5 and 10 at. % Ni (Figure 1).

Experimental

The viscosity measurements were carried out using an oscillating-cup viscometer [13]. Samples were prepared by arc melting high purity Al, Cu and Ni (99.99 %) under Ar atmosphere. The sample was placed into a graphite container, which was placed into a steel crucible attached to the torsion wire. The experiments were performed in a helium atmosphere. The temperature was estimated by WRe-5/20 thermocouples. The viscosity was determined with an average error of about 5 %.

The dynamic viscosity was calculated from the logarithmic decrement and the period of oscillations using the modified Roscoe equation [14]:

$$\begin{aligned}
\eta &= \left(\frac{I(\delta-\delta_0)}{\pi R^3 Hz}\right)^2 \frac{1}{\pi\rho\tau},\\
z &= \left(1+\frac{R}{4H}\right)a_0 - \left(\frac{3}{2}+\frac{4R}{\pi H}\right)\frac{1}{p} + \left(\frac{3}{8}+\frac{9R}{4H}\right)\frac{a_2}{2p^2},\\
a_0 &= 1-\frac{3\Delta}{2}-\frac{3\Delta^2}{8}-\frac{\Delta^3}{16},\\
a_2 &= 1+\frac{\Delta}{2}+\frac{\Delta^2}{8}-\frac{\Delta^3}{16},\\
p &= R\sqrt{\frac{\pi\rho}{\tau\eta}},\\
\Delta &= \frac{\delta}{2\pi},
\end{aligned} \tag{1}$$

where η is the viscosity of the liquid; I is the moment of inertia; δ_0 and δ are the logarithmic decrement of the empty system and of the system with the sample, respectively. Likewise, τ_0 and τ are the period of the oscillations of the empty system and of the system with the sample; R is the radius of the crucible; H is the height of the liquid; ρ is the density of the liquid.

Results and discussion

The viscosity measurements were performed for pure Al and $Al_{67}Cu_{33}$ alloy to compare experimental values with literature data. Figure 2 shows a good agreement between experimental and literature viscosity for liquid Al [15] and a satisfactory agreement for liquid $Al_{67}Cu_{33}$ alloy [16] over a wide temperature range. The viscosities increase when the temperature is lowered according to the Arrhenius-type equation:

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right), \tag{2}$$

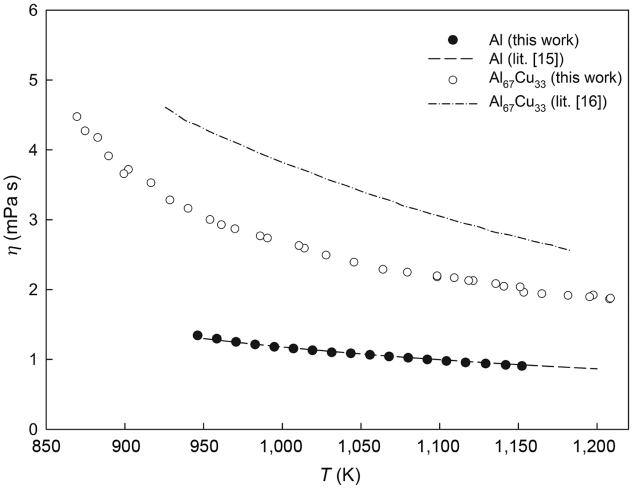

Figure 2: Temperature dependence of the viscosity for liquid Al and liquid Al_2Cu compound.

where η_0 is a constant; E_η is the activation energy of viscous flow; T is the absolute temperature, and R is the ideal gas constant. These fitted parameters were determined using the experimental η values and are listed in Table 1.

The temperature dependences for liquid $(Al_{67}Cu_{33})_{100-x}Ni_x$ alloys, where $x = 0$, 3, 5 and 10 at. % are shown in Figure 3. According to the obtained results, the

Table 1: Fitting numerical parameters of the Arrhenius-type eq. (2).

Sample (at. %)	η_0 (mPa s)	E_η (10^3 J mol^{-1})
Al	0.170	16.0
$Al_{67}Cu_{33}$	0.298	18.3
$Al_{65}Cu_{32}Ni_3$	0.038	34.2
$Al_{64}Cu_{31}Ni_5$	0.088	24.2
$Al_{60}Cu_{30}Ni_{10}$	0.015	40.6

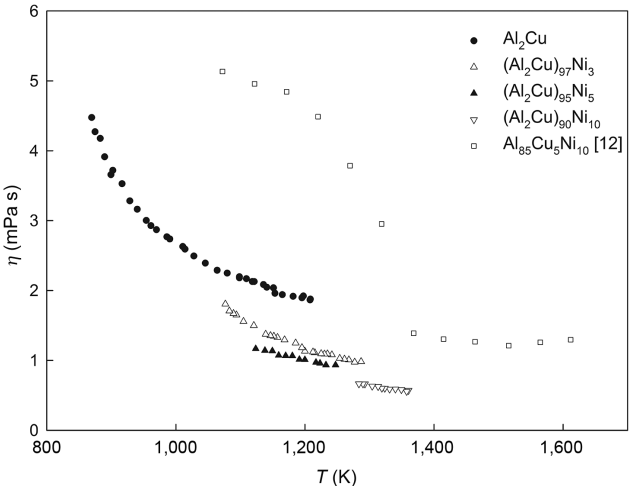

Figure 3: Temperature dependence of the viscosity for liquid Al–Cu–Ni alloys.

viscosity of the liquid $Al_{67}Cu_{33}$ alloy decreases by Ni additions. The temperature dependences of the viscosity for liquid $(Al_{67}Cu_{33})_{100-x}Ni_x$ alloys were fitted according to the Arrhenius-type equation. Fitting parameters are listed in Table 1. On the basis of the obtained results of viscosity measurements, we cannot confirm or deny, indicated in Ref. [12], transition in the viscosity behaviour from the HTA to the LTA.

Figure 4 shows the concentration dependence of the viscosity by Ni additions to the liquid Al_2Cu compound at the temperatures 20, 50 and 100 K above the melting point. A small addition of Ni atoms, up to 3 at. %, drastically decreases the viscosity coefficient. Such viscosity behaviour could be attributed to the breaking of Al–Cu bounds by the added Ni atoms. The most probable reason of such atomic reordering is that the strong interaction between Al and Ni atoms results in attempts of Ni to have Al atoms as neighbours, taking electrons to complete the Ni 3d-electron level. It is suggested that these transformations lead to the transition from a more chemically ordered structure to a more homogeneous, and the

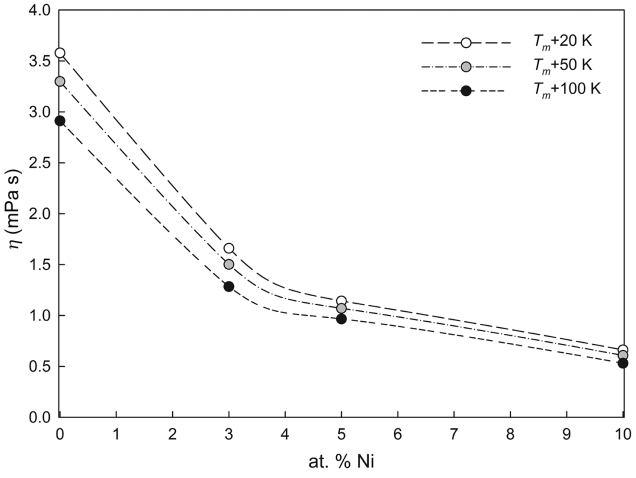

Figure 4: Influence of Ni on the viscosity of liquid Al_2Cu compound at the temperatures on 20, 50 and 100 K above the melting point (T_m).

mean size of chemically ordered clusters is reduced. On the other hand, Ni atoms form Al–Ni micro-regions with chemical short-range order and should also increase the viscosity. However, such tendency is not dominant because of the small number of Ni atoms in the alloy. At the addition of 5 at. % Ni, we observed further decrease of the viscosity.

At the addition of 10 at. % Ni, the viscosity decreases less dramatically in comparison with smaller Ni additions. Such behaviour should be attributed with attempts of Ni atoms to substitute the atoms of Al in short-range chemically ordered clusters. Our suggestion is in agreement with Ref. [4], where Ni addition to the liquid Al more than 7.5 at. % leads to an increase of the viscosity caused by a contribution of Al_3Ni or AlNi associates in the liquid Al–Ni alloys. The possible formation of ternary Al–Cu–Ni clusters following increase of Ni in the liquid alloy should be also taken into account.

Several thermodynamic models and semi-empirical equations were developed to evaluate the viscosity of liquid metal alloys. We decided to use two of them in order to investigate the effect of mixing processes by Ni additions to liquid Al_2Cu compound. Romanov et al. [17] described the viscosity of a liquid multi-component metal alloys using the following equation:

$$\ln(\eta) = \sum_{i=1}^{n} x_i \ln(\eta_i) - \frac{\Delta H}{3RT}, \qquad (3)$$

where η is the viscosity coefficient of liquid; η_i and x_i are the viscosity and the atomic fractions of the i component, respectively; ΔH is the enthalpy of mixing.

The viscosity of liquid Al–Cu–Ni was also estimated using Chhabra's model [18]:

$$\log(\eta + 1) = 10^{b_1} T^{b_2}; \quad (4)$$

$$b_1 = \sum x_i b_{1,i}, \quad (5)$$

$$b_2 = \sum x_i b_{2,i}, \quad (6)$$

where $b_{1,i}$ and $b_{2,i}$ are the fitting parameters of the i component. This empirical equation did not demonstrate any strong correlation between fitting parameters b_1 and b_2, but it is claimed that this equation gives improved description of viscosity values over the Arrhenius equation [19].

The enthalpy of mixing data were taken from Ref. [20]; the viscosity values for pure Ni and Cu were taken from Refs. [21, 22].

Table 2: Experimental and calculated viscosity values at 1,200 K.

Sample (at. %)	η (mPa s) Exp. values	η (mPa s) From eq. (3)	η (mPa s) From eq. (4)
$Al_{67}Cu_{33}$	1.86	2.03	1.34
$Al_{65}Cu_{32}Ni_3$	1.19	2.39	1.43
$Al_{64}Cu_{31}Ni_5$	1.00	2.65	1.49
$Al_{60}Cu_{30}Ni_{10}$	0.89	3.38	1.65

The viscosity predictions were performed at 1,200 K and compared with experimental values (Table 2). Predicted viscosity values by Chhabra's model are in better agreement with the experimental data than predicted values obtained by the Kozlov–Romanov–Petrov approach. However, in contrast to experimental results, the calculated viscosity increases with the addition of Ni. This discrepancy should be connected with the fact that the interaction parameters and the size unit factor are the two main parameters which impact on the viscosity changes. The viscosity values calculated using the Kozlov–Romanov–Petrov approach are higher than experimental values, which is connected with positive contribution of the excess viscosity related to the enthalpy of mixing. It also means that changes in the structure due to the decomposition of one and formation of other structure units have an impact on the viscosity values decreasing (negative contribution of the excess viscosity). At the same time, the enthalpy of mixing values for liquid Al–Ni alloys is more exothermic in the comparison with liquid Al–Cu and Cu–Ni alloys in the investigated concentration range. This could also be evidence of preferred interactions between Al and Ni atoms, which should lead to above mentioned structure transformations.

Conclusions

The measured viscosity of liquid $(Al_{67}Cu_{33})_{100-x}Ni_x$ alloys, containing 0, 3, 5 and 10 at. % Ni, shows the decrease in values with addition of Ni atoms. Such behaviour of the viscosity coefficient is likely caused by the decrease of micro-regions with Al_2Cu short-range order through the Ni effect and accompanied by structural unit size decrease. On the basis of the obtained viscosity data, it could be suggested that Al atoms have stronger interactions with Ni in the comparison to Cu. By increasing the Ni content in the liquid $(Al_{67}Cu_{33})_{100-x}Ni_x$ alloy, these interactions should be dominant and lead to the formation of Al–Ni- or Al–Cu–Ni-based micro-regions with the short-range chemical order.

References

[1] L.F. Mondolfo, Aluminum Alloys: Structure and Properties, Butterworths, London; Boston (1976).
[2] Z.R. Nie, T.A. Jin, J.B. Fu, G.F. Xu, J.J. Yang, J.X. Zhou, et al., Mater. Sci. Forum, 396–4 (2002) 1731–1735.
[3] S. Mudry and T. Lutsyshyn, J. Alloy. Compd., 367 (2004) 289–292.
[4] S. Mudry, V. Sklyarchuk and A. Yakymovych, J. Phys. Stud., 12 (2008) 1601–1605.
[5] Z.M. Wang, H.R. Geng, G.R. Zhou, Z.Q. Guo and X.Y. Teng, China Foundry, 7 (2010) 138–142.
[6] S. Mudry, A. Yakymovych, I. Shtablavyi, V. Sidorov and K. Shunyaev, Bull. Mater. Sci., 35 (2012) 83–87.
[7] F.X. Guo, W. Wang, H.L. Yang, J.Y. Qin and X.L. Tian, T. Nonferr. Metal. Soc., 22 (2012) 3113–3119.
[8] Al-Cu-Ni (Aluminium-Copper-Nickel), in: G. Effenberg, S. Ilyenko (Eds.) Light Metal Systems. Part 2, Selected Systems from Al-Cu-Fe to Al-Fe-Ti, Springer Berlin Heidelberg, Berlin, Germany (2005), pp. 104–126.
[9] R. Dasgupta, A.K. Jain, P. Kumar, S. Hussein and A. Pandey, J. Mater. Res. Technol, 3 (2014) 263–274.
[10] A.P. Mouritz, Introduction to aerospace materials, American Institute of Aeronautics and Astronautics; Woodhead Pub., Reston, VA, Cambridge, UK (2012).
[11] S. Mudry, V. Sklyarchuk, A. Yakymovych and I. Shtablavyi, Phys. Chem. Liq., 45 (2007) 675–681.
[12] X.F. Bian, M.H. Sun, W. Lei and S.J. Cheng, Mater. Res. Bull., 37 (2002) 1451–1458.
[13] Y. Plevachuk, V. Sklyarchuk, A. Yakymovych and I. Shtablavyi, EPM 2009, Forschungszentrum Dresden-Rossendorf, Rossendorf, Germany (2009), pp. 415–418.
[14] J. Vollmann and D. Riedel, J. Phys.: Condens. Mater., 8 (1996) 6175–6184.

[15] M.J. Assael, K. Kakosimos, R.M. Banish, J. Brillo, I. Egry, R. Brooks, et al., J. Phys. Chem. Ref. Data, 35 (2006) 285–300.
[16] T. Sato and S. Munataka, Bull. Res. Inst. Min. Dress. Met. Tohoku Univ., 11 (1956) 183–187.
[17] L.Y. Kozlov, L.M. Romanov and N.N. Petrov, Izv. vysch. uch. zav., Chern. Metall., 3 (1983) 7–11.
[18] R.P. Chhabra, J. Alloy. Compd., 221 (1995) L1–L3.
[19] R.F. Brooks, A.T. Dinsdale and P.N. Quested, Meas. Sci. Technol., 16 (2005) 354–362.
[20] J. Miettinen, Calphad, 29 (2005) 40–48.
[21] M.J. Assael, A.E. Kalyva, K.D. Antoniadis, R.M. Banish, I. Egry, J.T. Wu, et al., J. Phys. Chem. Ref. Data, 39 (2010) 033105.
[22] M.J. Assael, A.E. Kalyva, K.D. Antoniadis, R.M. Banish, I. Egry, J.T. Wu, et al., High. Temp. High. Press., 41 (2012) 161–184.