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Research Article

Viscosity of liquid Ga_xNi_{100-x} alloys

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Abstract. We studied the viscous properties of molten Ga_xNi_{100-x} alloys in the concentration region between two peritectic points ($77 < x < 94$). The measurements of the viscosity coefficient were carried out using an oscillating crucible method. Temperature dependence of viscosity revealed anomalous behavior in the vicinity of the melting point, particularly for the $Ga_{80}Ni_20$ melt. This feature was analyzed, taking into account the formation of clusters. We show that the formation of chemically ordered clusters is the main reason for the atypical behavior of the dependence of viscosity on temperature and concentration. The obtained results are in agreement with structural parameters obtained from X-ray diffraction.

Keywords liquid alloys – viscosity – cluster formation – chemical bonding in liquid alloys

1 Introduction

Binary Ga-Ni is a component of higher-order systems widely used in industry. For example Co-Ni-Ga and Ni-Mn-Ga can be used as shape memory materials (Chumlyakov et al., 2004). Moreover, the phase diagram of Ga-Ni consists of only a few chemical compounds. Such compounds retain their chemical ordering in a liquid state and influence the atomic distribution of molten alloys of similar concentrations (Massalsky, 1990). Understanding the behavior of physical properties is important for many technological processes, thus driving the investigation of structure-sensitive properties.

In particular, the viscous properties of liquid Ga_xNi_{100-x} alloys rich in Ga are of special interest. These alloys are thought to be sensitive to an applied magnetic field, because it is thought that they contain Ni-based magnetic clusters. Simultaneously, it is still unclear whether melts of peritectic concentration are related to the structure of molten alloys of similar concentration.

1.1 Experimental Details

The samples were prepared from nickel and gallium with a purity of 99.99 % and 99.999 %, respectively. Their dynamic viscosity was investigated using an oscillating cup viscometer (Mudry et al., 2008). The temperature was measured and controlled using a WRe-5/20 thermocouple placed below the sample. Our aim was to measure the parameters of rotational oscillations. Viscosity was calculated according to the relationship between the logarithmic decrement, the time period and viscosity by means of the modified Roscoe equation (Vollmann and Riedel, 1996). The accuracy of the obtained viscosity values was higher than 5 %.

We carried out diffraction studies using a high-temperature X-ray diffractometer (Plevachuk et al., 2009). Cu-K_α radiation monochromatized by a LiF single crystal as a monochromator with Bragg-Brentano focusing geometry was used. The scattered intensities were recorded with an angular step of 0.05° within the region of the principal peak and 0.5° for the remaining values of the scattering angle. Intensity curves were corrected for polarization and incoherent scattering (Cromer and Waber, 1965) and were subsequently normalized to electron units by the Krogh-Moe method (Krogh-Moe, 1956). The structure factors $S(k)$ were calculated on the basis of the obtained intensity curves.

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2 Results and discussion

The temperature dependence of the dynamic viscosity of the melts under investigation showed differing (Arrhenius or non-Arrhenius) behavior, dependent on the alloy composition (Figure 1). Particularly, for the molten $Ga_{94}Ni_6$ alloy, the viscosity increased with a decrease in temperature according to the Arrhenius law:

$$\eta = A \exp^{(\frac{E}{RT})} \tag{1}$$

where η is the viscosity coefficient of the liquid; A is a constant; E is the activation energy of viscous flow; R is the universal gas constant; T is the temperature. The values of parameters A and E are given in 1.

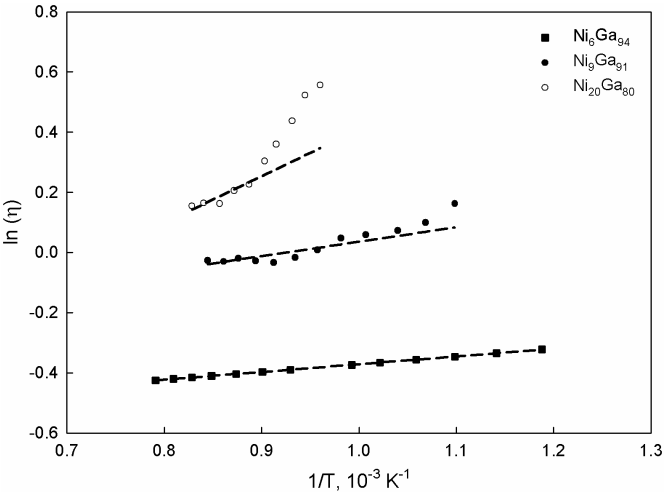

Figure 1: The temperature dependence of viscosity for liquid $Ni_{100-x}Ga_x$ alloys.

Experimental data of the viscosity versus temperature can be used to calculate the activation energy of viscous flow E by fitting into the Arrhenius-type equation, given by equation 1.

As seen in Table 1, a small addition of Ni to Ga (6 at. %) decreases the activation energy, while higher contents of Ni causes a drastic increase of the activation energy. The viscosity isotherm, together with the dependence of the activation energy of viscous flow on the content of Ni is presented in Figure 2. For alloys with 6 at. % nickel, the viscosity coincides with that of liquid Ga. Following the addition of nickel, the viscosity coefficient increased. In contrast to viscosity, the activation energy increased when nickel content was 20 at. %.

The data indicates that the energy of activation assumed higher values at temperatures close to the melting point. Taking into account these data, as well as the dependence of viscosity on temperature and concentration, we conclude that the addition of Ni atoms significantly affects the viscous properties of melts enriched with Ga.

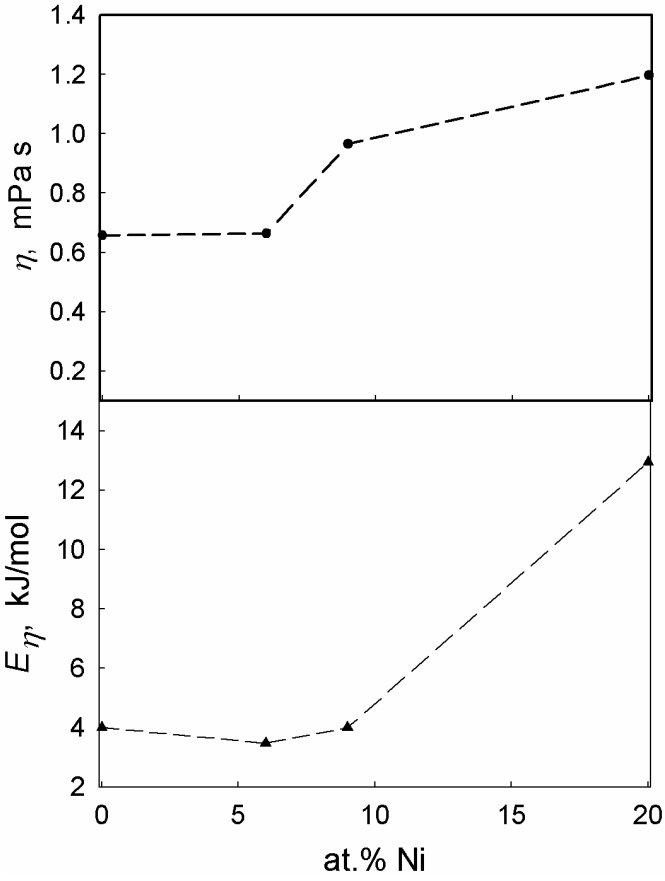

Figure 2: Isothermal viscosity (upper figure) and activation energy (bottom figure) for liquid Ga_xNi_{100-x} alloys at 1173 K.

The obtained results suggest that Ni atoms diluted in Ga are randomly distributed and preferentially surround themselves with neighbours unlike them. With an increase in Ni content, the interaction of unlike atoms becomes stronger, which results in an increase in viscosity and in the energy of activation. When the concentration of Ni reaches 20 at. %, such interaction is even stronger and promotes the formation of chemically ordered structural units (clusters). Thus, we were able to identify two major factors responsible for an increase in both the viscosity and the energy of activation, i.e. the preferred interaction of unlike atoms that result in the formation of chemically ordered clusters and an increase in the size of such clusters.

Naturally, such changes in the interatomic interaction must be related to structural features in the liquid state. Therefore, we also carried out diffraction studies of these liquid alloys. The structure factors $S(k)$ revealed a profile atypical for metallic melts Figure 3. All curves were different from the $S(k)$ for liquid Ga. Although the content of Ga prevailed in this alloy, the structure factors were significantly different from those

Table 1: Activation energies for Ga-enriched melts.

Alloy composition (at.%)	A (mPa s)	E (kJ mol^{-1})	Source
Ga	0.44	4.00	(Battezzati and Greer, 1989)
$Ga_{94}Ni_6$	0.53	2.14	this work
$Ga_{91}Ni_9$	0.64	4.00	this work
$Ga_{80}Ni_{20}$	0.32	12.94	this work

of Ga. A wide principal peak can be interpreted as a sum of submaxima corresponding to structural units with atomic distribution, the structure of which was similar to that of Ga and Ni, respectively. The profile of the principal peak changes significantly upon the addition of Ni atoms. This profile corresponded to the diffraction peaks of Ga_4Ni, Ga_3Ni_2 and GaNi formed due to peritectic reactions. It is possible that molten alloys enriched with Ga rearrange their atomic distribution upon cooling in order to form clusters whose structure would be similar to that of the above-mentioned chemical compounds.

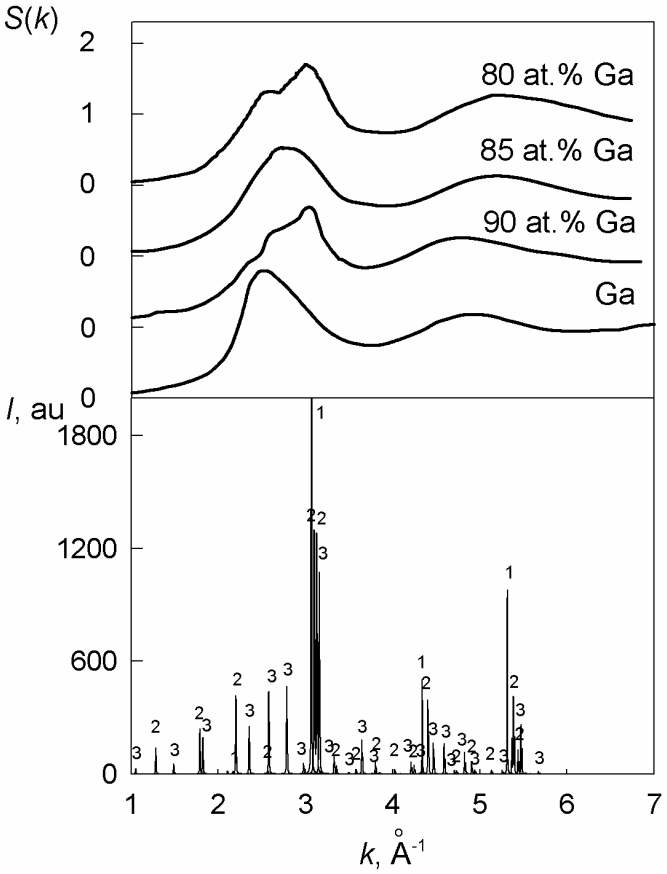

Figure 3: Structural factors for Ga-Ni liquid alloys (upper figure) compared with diffraction patterns for intermetallic phases of GaNi (1), Ga_3Ni_2 (2) and Ga_4Ni (3) (bottom figure).

Taking into account these features, we assume that a certain fraction of Ni atoms form chemically ordered clusters with a structure similar to that of Ni. These clusters are randomly distributed in the matrix of Ga. The fraction of clusters increases with an increase in the content of Ni. This assumption is in accordance with the results of viscosity measurements.

3 Conclusions

The changes of the viscosity coefficient with temperature and concentration for Ga-enriched molten Ga_xNi_{100-x} alloys revealed the existence of inhomogeneous structure, characterized by the presence of a Ga-based matrix and Ga_nNi_m clusters with a wide range of compositions. The viscosity data are in agreement with the results of X-ray diffraction, which also confirm the trend to chemical ordering in the liquid state for Ga-enriched alloys of the Ni-Ga binary system.

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