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Temperature and time dependent structure of the molten $Ni_{81}P_{19}$ alloy by neutron diffraction

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ABSTRACT

The temperature and time dependent structure of molten NiP alloy of eutectic composition has been studied by neutron diffraction. Ni particles were found to exist in the melt at temperatures at least up to about 150 degrees above liquidus. The amount varies reversibly as temperature increases but decays slowly with time. Remarkably, particles still exist even after that the melt has been kept more than 30 h at different temperatures in the molten state. The static structure factor and the pair distribution function obtained at 1050 °C are presented.

1. Introduction

It has been debated for a long time whether metals and alloys are homogeneous after melting or not at the atomic scale and this has been the subject of many theoretical and experimental studies. A variety of different experimental techniques have been used in order to find an answer to this question and results have been interpreted along different lines, one being that the structure of a molten alloy is inheriting much of the structure of the original ingot [1–5] while others are stressing the existence of strong short range order and atomic cluster formations (see for example [6]). An example of the theoretical approaches used to look at this problem are models for the structure of liquid alloys such as those developed in [7,8]. The possible existence of a liquid-liquid phase transition has been an issue for several investigations [9–15]. However, systematic experimental investigations in terms of composition, temperature and time dependencies of the physical properties of molten alloys have not been performed. Thus, in spite of all performed studies, a full understanding of the structure of a melt on a length scale going from some tens of a nanometer to several microns and its physical properties in terms of composition, temperature and time is still lacking.

In many investigations anomalies in measured property/temperature quantities (density, viscosity, surface tension, electrical resistivity, internal friction, etc.) of molten binary alloys are found during stepwise heating/cooling temperature cycles well above the liquidus temperature, while in other studies the quantities were found to vary in a regular way ([16] and references therein). Samples used for these studies are very often synthesized by mixing the elements by arc melting and an ingot for further studies is produced by casting. The ingot is afterwards re-melted several times in order to ensure that the sample to be studied is homogeneous with regard to its elemental composition and the measurements are performed in a heating/cooling sequence. However, the time and the temperature which are two very important parameters for the effect of the performed heat treatment of the ingot are very rarely mentioned. In other studies the melts to be studied have been produced in an induction furnace and the physical properties have been measured during cooling. These two fundamentally different ways to measure a specific physical property of a melt do not necessarily give the same result [16].

As mentioned above several explanations for the existence and non-existence of anomalies in measured physical properties have been given. In some cases the anomalies have been interpreted as indications of the existence of liquid-liquid phase transitions, while in others they have been found to be related not only to the thermal history of the melt but also of the ingot [1–5]. A possible presence and disruption of oxides during heating of the melt has also been suggested to influence the experimental results [17]. In other studies it has been suggested that the existence of atomic clusters in molten alloys is of thermodynamic origin and that the status of the melt corresponds to specific metastable temperature-dependent states [7,18,19]. Furthermore, it was shown that microheterogeneous states may exist as separate non-ergodic phases in molten binary alloys [20,21]. In all these cases a melt may be considered as a microstructural multi-phase system, a view that has been supported by results from investigations utilizing neutron and X-

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ray scattering techniques [20–25]. However, the influence of two very important parameters, temperature and time, on the existence of anomalies in the measured quantities has not been considered.

The influence of the melt status on the structure, the microstructure and the physical properties of vitrified $Ni_{81}P_{19}$ metallic glass ribbons but also several other glasses has been studied extensively [3,4,18,22,23,26,27,29–32]. It was generally concluded from these studies that the nucleation and growth processes proceed along different routes depending on the thermal history of the melt and, as a result, influences the microstructure of the solidified alloy. Studies of physical properties of the NiP system in solid phase as obtained from both experimental [33,34] and theoretical [35,36] investigations have also been performed. The relation between the structure of the melt and the structure of solidified alloy has also been discussed [23,27].

In this paper the time dependence of temperature changes on the structure of the eutectic NiP melt in a temperature region close to the liquidus is reported. The static structure factor and the pair distribution function are also presented.

2. Theoretical background

The measured intensity in a diffraction experiment on a disordered material is proportional to the total static structure factor $S(Q)$ that for a binary system in the Faber-Ziman formalism is given by [37].

$$S(Q) = \{I_a^{coh}(Q) - [<b^2> - <b>^2]^2\}/ <b>^2 = \sum_{\alpha}\sum_{\beta} c_\alpha c_\beta b_\alpha b_\beta S_{\alpha\beta}(Q)/ <b>^2 \quad (1)$$

$I_a{}^{coh}(Q)$ is the intensity per atom of coherently scattered neutrons and c_i and b_i are the concentration and scattering amplitude of atoms α and β, respectively. $< b >$ is equal to $c_\alpha b_\alpha + c_\beta b_\beta$ and $< b^2 >$ to $c_\alpha b_\alpha{}^2 + c_\beta b_\beta{}^2$. $S_{\alpha\beta}(Q)$ is the partial structure factor, which describes the spatial correlations between α and β ions in the system. Q is the wavevector transfer the neutron experiences in the scattering process and it is given by $Q = 2k\sin(\Theta)$ where k is the neutron wavevector and 2Θ is the scattering angle. From the definition it follows that $S(Q)$ is equal to one at large Q. The scattering amplitudes for Ni and P are 10.3 and 5.13 fm and thus the relative weight factors in Eq. (1) for the homogeneous eutectic NiP alloy are 0.80, 0.19 and 0.01, for $S_{NiNi}(Q)$, $S_{NiP}(Q)$ and $S_{PP}(Q)$, respectively.

3. Experimental details

The neutron diffraction experiments were performed on the D4 diffractometer at the Institute Laue-Langevin, Grenoble, France [38]. The wavelength of the incident neutrons was chosen to 0.703 Å. The corresponding Q range was accordingly $0.4 < Q < 16.5\,Å^{-1}$ and considered to be large enough to derive a reliable $g(r)$ from the measured $S(Q)$. The D4 instrument is equipped with 9 separate position sensitive detectors fixed relative to each other in a bank. Each detector is spanning a scattering angle range of 8 degrees. Thus, in order to scan the full angular range (i.e. from 1.5 to 140 degrees) the whole detector bank is rotated in a stepwise fashion. This means that the scattered intensity at a particular scattering angle (Q value) is measured by several detectors but at different times according to the position of the detector bank. However, even if the intensity is not recorded simultaneously at every Q it is possible to study the time dependence of particular features of the measured scattering curves.

The $N_{81}P_{19}$ sample ingot was made by melting pieces of metallic glass ribbons produced by melt spinning from very high chemical purity materials and reported in previous publications [23,26,27,39]. The resulting ingot was introduced in a silica tube with an inner diameter of 15 mm and height about 70 mm. The silica tube was sealed under argon atmosphere and was introduced in a standard ILL vanadium furnace, which allows temperatures up to about 1100 °C to be reached. The lower edge of the neutron beam being set to a height of 18 mm was impinging on the silica tube 6 mm from its bottom. It is known that the NiP alloy is disintegrating because of the significant P vapor pressure developing at high temperatures for a P content larger than 40 at.% [33]. Even with the tendency to disintegrate for smaller P contents, this experimental setup ensures that the measurements really are performed at the required melt composition. The temperature was measured by a pyrometer with a ± 2 °C accuracy. The time necessary in order to record diffraction patterns of relevant statistical accuracy for one position of the detector bank was about 20 min. In order to cover the entire Q range patterns were recorded at 6 different detector bank positions.

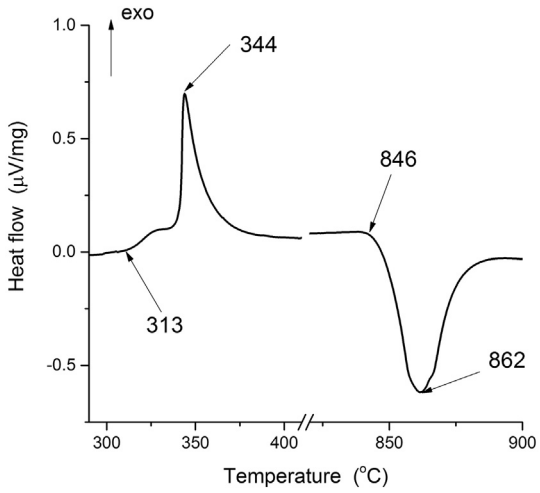

Fig. 1. Measured DSC curves in the temperature regions corresponding to the amorphous-to- crystalline transition (left) and the melting process (right). Relevant temperatures for the two processes are indicated.

The melting temperature for $N_{81}P_{19}$ published in the literature varies between 870 and 891 °C. In order to get more precise information and at the same time control the status of the amorphous ribbons measurements with differential scanning calorimetry (DSC) were performed. The heating rate was chosen to 30 K/min. Measured curves are shown in Fig. 1 over two temperature regions, the first corresponding to the amorphous-to-crystalline transition and the second to the melting process. The curve in the first region has an identical shape to the one published in [27] on the same samples. The melting process, however, takes place at a somewhat lower temperature than the ones earlier published on alloys produced in different ways ([33] and references therein).

The aim of the measurements was to determine the temperature dependence of the static structure factor $S(Q)$ but also to study the effect of a sudden temperature variation on its shape. For this purpose the time/temperature scheme shown in Fig. 2 was adopted. The time for a temperature change was a few minutes.

4. Experimental results

The NiP sample was kept at a temperature well above the melting point for more than three hours before the data recording started (see the arrow in Fig. 2). The time-averaged static structure factor $S(Q)$ obtained during the 8.6 h of measurement at a temperature of 904 °C is shown in Fig. 3. The $S(Q)$ curve has a shape characteristic of a molten system but some small superimposed peaks can also be seen. It can be concluded that in spite of the long holding time before the start of the measurement, well-defined crystalline inclusions are present in the melt. According to the phase diagram [33] the solidification of NiP of eutectic composition will result in the formation of Ni and Ni_3P crystalline phases. As mentioned above the sample was made by melting metallic glass ribbons. The ribbons were very likely to have an outer layer of oxides but no sign of a presence of oxides within the neutron