Structure of liquid Fe–Al alloys

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Abstract

The atomic structure of liquid Fe–Al alloys within the whole concentration range (including pure components) has been studied at 1820 K by X-ray diffraction technique. Experimental data were compared with micro-heterogeneous model calculations. Reported physical properties of liquid Fe–Al alloys have been also considered. It is shown that all investigated melts of the Fe–Al system are micro-inhomogeneous and contain atomic micro-formations (clusters), which are distinguished by composition and atomic packing. There are four types of cluster, two of them contain atoms of one sort (Fe or Al); composition of two other types of cluster respects to the stoichiometry of solid Fe_2Al_5 and Fe_3Al phases. The variation of the component concentrations in Fe–Al alloys results in changing of volume fraction of each cluster type whereas the atomic composition and arrangement inside the clusters remains constant. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Fe–Al alloys possess attractive properties making them very interesting for industrial applications [1–3]. This is mainly due to their relatively low density, excellent oxidation and corrosion resistance and significantly better wear and frictional behaviour, as compared with carbon- or stainless steel. Besides, iron aluminides are considered as a starting material for many multi-component industrial alloys. Some of them are only potential candidates up to now, but several are already used, e.g. for heat-treating posts in carburising furnaces, for rails of walking-beam furnaces, for cast tubes of radiant-burner tubes with operating temperatures approaching 800–900 °C, for porous gas–metal filters in coal gasification systems.

One of the most important recent aims of materials science is the improvement of the physical properties of a cheap bulk material by surface modification [3]. The idea is to cover it by a 'noble' surface layer and to transfer in this way the excellent properties of the layer to the whole product.

The Fe–Al system is characterised by a complex phase equilibrium diagram [4,5]: several stoichiometric compounds and a large variety of metastable non-equilibrium phases exist in the solid state. Since FeAl and Fe_3Al phases are ordered solutions of Al and Fe, their structure and properties, in comparison with structure and properties of complex $FeAl_3$, Fe_2Al_5 and $FeAl_2$ intermetallic compounds, are more similar to those of pure iron. Therefore, the physical properties of aluminium coatings could be improved by the existence of Fe-rich phases (Fe_3Al and FeAl) in the diffusion layer below the surface. In order to understand the mechanism and to control the process of the surface modification it is important to know the structure and to comprehend structural changes in the Fe-rich iron aluminides at a microscopic level in the liquid as well as in the solid state.

So far, the structure of Fe–Al alloys in the liquid state was studied in some works. Most of them are limited to a certain part of the Fe–Al phase diagram. For example [6] dealt with the Fe-rich alloys in the region of 0–40 at.% Al. The alloys in the concentration range up to 50 at.% Fe have been investigated in [7].

In present work, liquid alloys of the Fe–Al system were investigated within the whole concentration range

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(including pure Al and Fe) under constant experimental conditions. The experimental results are then interpreted using a model for the micro-inhomogeneous structure of multi-component melts [8].

2. Experimental

To choose the composition of Fe–Al alloys for investigation it is necessary to consider the intermetallic compounds existing in the solid state — some of them could exist as a stable structural unit in liquid state. The alloys selected should also be well distributed over the phase diagram. Therefore, pure Al and Fe, five Fe–Al alloys of intermetallic compound composition, and four alloys with 12.5 and 40 at.% of each component have been investigated.

X-ray patterns of the samples were obtained in a high-temperature θ–θ diffractometer with Mo–K$_\alpha$-radiation at 1820 K. A graphite single crystal was used for monochromatisation of X-rays scattered by the sample. The magnitude of diffraction vector $Q = 4\pi \sin \theta/\lambda$, where θ is half the scattering angle and λ is the radiation wavelength, ranged from about 0.7 to 12.5 Å^{-1}. The scanning step 2θ was 0.2° in the region of the first peak (16–20 °), 0.5° in the interval from 5 to 16° and from 20 to 45°, 1° in the region from 45° to the end. Statistical error of counting at the 'tail' of the scattering curve did not exceed 1.5%. Three sets of data were obtained for each alloy.
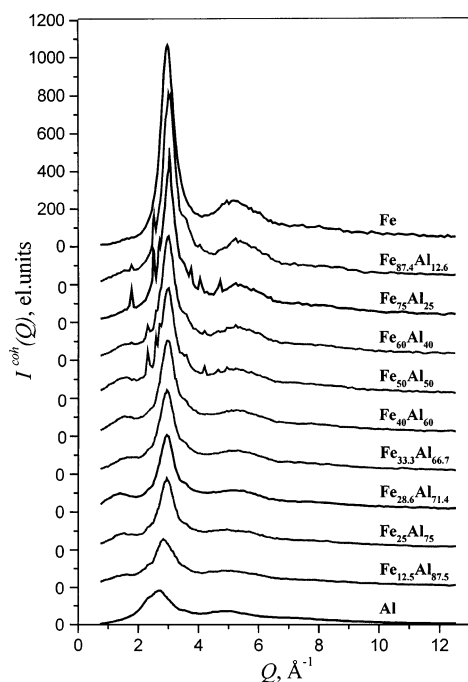
The samples were prepared from pure aluminium and iron (99.99%) by melting at 1920 K for 10 min (chamber was evacuated to $\sim 5 \times 10^{-5}$ mbar and filled with helium in the 1.0–1.1 bar range before heating), then cooled down to 1820 K and held for 30 min before starting the experiment.

The scattering intensity measured in arbitrary units was converted into the coherent scattering intensity per atom in electron units, $I_{e.u.}^{coh}$, using the generalised Krogh–Moe–Norman method [9,10]. Compton scattering has been corrected using the values given by Cromer and Mann [11].

3. Results and discussion

The experimental scattering intensity functions in electron units, $I(Q)$, for all investigated alloys in the Fe–Al system in the liquid state are given in Fig. 1. The small peaks observed in the intensity functions of the Fe-rich alloys are attributed to oxides on the surface of the melt. They do not influence significantly the general features of the diffraction curves. However, when such reflexes belong to the region of the main peak of the intensity functions, they may shift the position of the first peak and change its height. Therefore, this effect was taken into account in the analysis of the concentration dependencies of the structural characteristics of the investigated melts.

From the model of micro-inhomogeneous structure [8] and previous works [12–18], multi-component systems are characterised by some special alloys (so-called reference alloys) consisting of the atomic micro-formations or clusters of one type. The alloys situated between the nearest reference alloys (within one concentration range) contain clusters of two or more types that distinguish by the atomic composition and packing, and scatter X-rays independently. The number of clusters depends on the number of components in the alloy and on the type of interaction between different kinds of atoms in the liquid state. The composition of the clusters remains constant if the alloy composition changes within one concentration region, and only the relative number of each cluster-type varies.

Such a representation of the constitution of liquid alloys enables one to calculate the respective functions for an alloy of arbitrary composition inside the concentration range from experimentally measured correlation functions of reference alloys. In [8] a complete derivation of the needed model equations is presented. The most simple equation is obtained for coherent scattering intensity. For an arbitrary multi-component alloy it can be written as

Fig. 1. Experimental X-ray scattering intensity functions of Fe–Al liquid alloys at 1820 K.

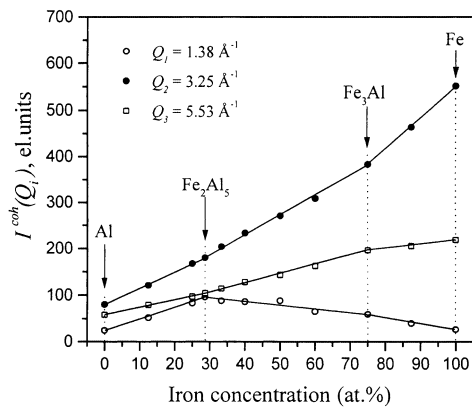$$I(Q) = \sum_j k^j I^j(Q). \tag{1}$$

Fig. 2. Concentration dependencies of the scattering intensity at constant value of Q (the lines are guides for the eye).

Here j is the number of types of clusters in the alloy under investigation, $I^j(Q)$ the coherent scattering intensity of the reference alloys and k^j is the volume fraction of the each type of cluster ($\Sigma_j k^j = 1$).

In the case of binary alloys which contain, for example, clusters of α- and β-type, the scattering intensity $I(Q)$ can be expressed by:

$$I(Q) = k^\alpha I^\alpha(Q) + k^\beta I^\beta(Q). \qquad (2)$$

Here $I^\alpha(Q)$ and $I^\beta(Q)$ are experimental coherent scattering intensities of the reference alloys consisting of the clusters of α- and β-type, respectively; k^α and k^β defined as

$$k^\alpha = \frac{c_1^x - c_1^\beta}{c_1^\alpha - c_1^\beta} \quad \text{and} \quad k^\beta = \frac{c_1^\alpha - c_1^x}{c_1^\alpha - c_1^\beta}, \qquad (3)$$

denote, respectively, the volume fractions of the α- and β-type clusters in the alloy considered ($k^\alpha + k^\beta = 1$). c_1^α, c_1^β, c_1^x are the atomic concentrations of the first component in the reference alloys and in the alloy under investigation. The respective quantities for the second component are c_2^α, c_2^β, c_2^x.

Thus, a reliable definition of the reference alloys is the most important and significant step. Indeed, following the model, determination of all reference alloys of the system examined means detection of all structural units of the system in the liquid state. Moreover, it signifies knowledge of the concentration ranges of their existence.

We have discussed methods of defining reference alloys in previous works [12–18]. The most simple method for binary alloys is plotting the heights of the scattering intensity functions at fixed Q-value against the concentration. As it follows from Eq. (2), the intensity for any value of the diffraction vector between two reference alloys should change linearly. If the model is suitable for the system considered, then the plots consist of joined line segments, and the deflection points are the compositions of the reference alloys. Our

experience indicates that the reference alloys can be determined by deflection points or anomalies at different 'property versus concentration' dependencies, e.g. from plots of electrical resistivity, thermoelectric power, magnetic susceptibility, mean number density, thermodynamic properties of mixing versus concentration.

Concentration dependencies of $I(Q)$ at the three fixed values of the diffraction vector for Fe–Al liquid alloys are plotted in Fig. 2. Despite of principally different features of the three sets of points one can see three straight-line intervals and deflection points at 28.6 and 75 at.% of Fe. In terms of the micro-inhomogeneous model, the whole concentration range of Fe–Al system consists of three concentration intervals, (1) from 0 to 28.6 at.% Fe; (2) from 28.6 to 75 at.% Fe; (3) from 75 to 100 at.% Fe.

The first deflection point (28.6 at.% Fe) corresponds to the stoichiometric composition of the compound Fe_2Al_5. It is in a good agreement with [7] where the same result was obtained by analysing the mean nearest neighbour distance and isothermal electrical resistivity as a functions of concentration. The fact that microformations of the Fe_2Al_5-type exist in the liquid state is confirmed also by the prepeak on the left-hand side of the main maximum of the Fe–Al X-ray scattering intensity functions. It has been shown in [19], for example, that the presence of a prepeak indicates a strong interaction between unlike atoms and formation of clusters in a melt. It is seen in Fig. 1 that the prepeak is most distinct for the Fe_2Al_5 alloy.

The second deflection point falls at 75 at.% Fe and is nearly in the middle of a wide region of solid solution of aluminium in iron (maximum solubility of Al in Fe is 53 at.% at the room temperature and decreases up to 49 at.% at 1505 K). An anomalous behaviour of electrical resistivity, ρ, and electrical conductivity, σ, around $Fe_{75}Al_{25}$ composition has been also observed in Fe–Al melts [20]. Extreme values at 75 at.% Fe in the isothermal concentration dependencies of ρ and σ (ρ of Fe_3Al is less and σ of Fe_3Al is greater than the respective parameters for pure Fe) are assumed [20] to be connected with the special character of arrangement of Fe and Al atoms in the melt. In accordance with our structural study, these anomalies seem to be caused by chemical short-range order in the liquid Fe_3Al alloy.

Thus, we can conclude that in terms of the used model the concentration intervals in the Fe–Al system are, Al–Fe_2Al_5, Fe_2Al_5–Fe_3Al and Fe_3Al–Fe. The intensity functions for the investigated alloys have been calculated (Eqs. (2) and (3)) using the respective functions of the reference alloys indicated by bold lines in Fig. 1. Agreement between the experimental and calculated curves plotted in Fig. 3 shows that the micro-inhomogeneous model describes very well the atomic distribution in liquid alloys of the Fe–Al system.

The present study also confirms a strong interplay between liquid and solid structures in the Al-rich Fe–Al alloys. Indeed, the Fe_2Al_5 phase is the only compound that melts congruently in the Fe–Al system [4]. Besides, our results correlate with recent data on the structure and properties of amorphous Fe–Al alloys. For example, the investigation of bulk amorphisation in the Fe–Al system [21] has shown that the alloys containing up to 75 at.% Al were crystalline. A further increase in the Al concentration leads to the formation of the amorphous state. It was found that the amorphisation takes place by the formation of Al–Al pairs outside the Fe_2Al_5-like crystalline phase. The fact that the Fe atoms try to keep the Fe_2Al_5-like short-range order shows, that this structure must be favourable from the thermodynamic point of view. In an other study [22], it has been shown that the electrical resistivity of the amorphous Fe–Al films at the Al-rich side is very high, especially in the region between 25 and 30 at.% Fe. In addition, a large negative temperature coefficient of the resisitivity and high thermal stability (properties expected for systems containing elements with covalent bonds) were observed. It was concluded that such phase stability is enhanced by the resonance between the electronic and the atomic systems. Taking into account that the amorphous and liquid states are very similar structurally, these results are believed to confirm very well our conclusion concerning the existence of stable atomic micro-formations of the Fe_2Al_5 composition in Fe–Al liquid alloys.
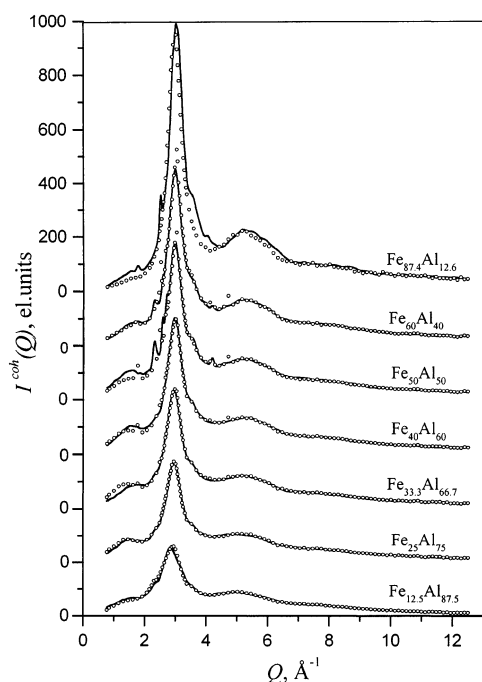
As regards the clusters of the $Fe_{75}Al_{25}$ composition, a direct correspondence between the liquid and the solid state is not observed. In fact, the ordered compound Fe_3Al in the solid state exists only up to 790 K. With the Fe–Al phase diagram in mind, it is not possible to explain the existence of atomic micro-groupings in pure Fe, too. It is believed that these properties of the liquid Fe–Al alloys are also caused by their electron structure. However, from this, additional investigations are required.

4. Conclusion

The present study has shown that the atomic distribution in liquid Fe–Al alloys can be described well by the model of micro-inhomogeneous structure. The whole concentration range of the Fe–Al system can be subdivided into three concentration intervals separated by alloys of $Fe_{75}Al_{25}$ and $Fe_{28.6}Al_{71.4}$, compositions that correspond to the stoichiometry of the solid Fe_3Al and Fe_2Al_5 phases. The alloys within the concentration intervals consist of clusters whose composition is the same as that of the alloys bounding the respective interval. The variation of the component concentrations in Fe–Al alloys results in changing of volume fraction of each cluster type whereas the atomic composition and arrangement within the clusters remain constant.

Fig. 3. Fe–Al X-ray diffraction intensity functions at 1820 K, full line, experimental results; circles, model predictions.

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