The structure of Ni–enriched Al–Ni molten alloy before solidification

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Abstract

The structure of Ni–based molten alloy, containing 88,02w.%Ni and dopped both with Zr (0,46w.%) and B (0,02w.%) has been studied by means of X–ray diffraction method at temperature 1500 K. Structure factor and pair correlation function were obtained from diffraction data and analyzed. Principal peak position in structure factor for doped molten alloy is compared with one for liquid Ni$_3$Al intermetallics. Another structural parameters–most probable interatomic distance and number of neighbours have been also determined from pair correlation function and compared with parameters of crystalline structure for Ni$_3$Al chemical compound. The structure data are interpreted with using of cluster models of metallic melts.

Key words: crystallization, aluminum–nickel alloys, melts, short range order, intermetallic compounds, chemical ordering.

1. Introduction

Influence of thermodynamic and structural state of melt before solidification on properties of solid materials most cases is significant. On that reason growing interest to studying of liquid alloys by means of various experimental and theoretic methods increases. Among materials, interested from the viewpoint of application are light alloys, first of all – Al–based ones. Having high plasticity, corrosive resistance, electroconductivity these alloys exhibit a low hardness and other mechanical properties. In order to improve them the addition of other elements and thermal treatment are commonly used. One of the systems, most attracted the attention of researchers is Al–Ni binary. Unfortunately, major interest has been focused mainly on Al–enriched side of this system because the first aim was to improve the properties of aluminium [1-5]. Al and Ni alloys have been studied by various

experimental methods both in liquid and solid state. It was shown that addition of Ni-atoms to aluminium significantly changes the atomic distribution and as result the main properties. These changes are observed yet before transition from liquid state to solid. It is established also that at addition of Ni to Al in liquid state the formation of chemically ordered Al$_3$Ni clusters occurs and in such way the structure becomes more inhomogeneous. Besides, a small part of Ni atoms, whose atomic radius is less than one for Al, can be diluted in liquid aluminium. Upon crystallization these diluted atoms causes the stresses, which are responsible for mechanical properties improving.

Results on physical–chemical properties measurements in binary Al–Ni liquid alloys show the existence of anomalous regions in their concentration dependences. Particularly, there are significant compression in mole volume values [6], negative deviation from ideal behaviour of activity coefficient [3], maxima in viscos-

ity and electroresistivity isotherms at equiatomic composition [7,8].The main results of these works is the conclusion that inhomogeneous atomic distribution exists on the reason of preferred interaction between Al and Ni atoms.It was suggested that specific electron structure on Ni, who belongs to group of 3d-transition metals, causes such strong interaction because Ni most attempts to complete the 3d-band in comparison with Fe and Co.

Electron structure studies for intermetallics indicate [9] the increase of covalent bonds fraction in total chemical bonding with Al–content increasing. It occurs due to transfer of some part of electrons from aluminium to. 3d-band of Ni which is fully completed at content of Al 55 at.% .

Results on X-Ray diffraction studies [1,10] show the strong interaction of unlike kind atoms with increasing of topologic and chemical ordering. Moreover it was shown [10] that clusters with icosahedral structure are maim structural units in liquid state.

As it was mentioned above the studying of Ni–enriched alloys in liquid state is scarce. Interest to such alloys increases rapidly because they can be used for producing of superplastic materials with good mechanical properties [11-15]. On that reason we have focused our attention on structure investigation of liquid Ni_3Al doped with Zr and B. This alloy due to dopants and special cooling conditions shows the formation of nanocrystals which existing in crystalline matrix promote the improving of many properties.

2. Experimental

Alloy under investigation was prepared from iron, nickel, zirconium and boron of high purity (99,99%). Sample was alloyed in arc melting furnace, filled with pure argon in order to avoid the oxidation. The quality of sample was checked by means of weighting before and after alloying and with using of X–Ray microanalysis.

The diffraction studies were carried out using a high temperature diffractometer with a special attachment that makes it possible to investigate solid and liquid samples at different temperatures up to 2000K. The Bragg –Brentano focusing geometry was used to obtain the diffraction patterns with high accuracy and resolution. The MoK_α radiation was monochromatized by a graphite crystal installed in diffracted beam. The scattered intensities as function of scattering angle were recorded within the range $10 \text{ nm}^{-1} < s < 120 \text{ nm}^{-1}$ using a special electronic system. In order to obtain more accurate scattered intensities, the scan time was equil to 10s, whereas the angular step was 15' in the scattering angle region $3°÷47.5°$ and 30' in the region $25°÷47.5°$. Compton scattering was taken into account before normalization of the intensity curve.

The diffracted intensity was recorded using a NaJ(Tl) scintillator detector in conjunction with an amplification system. The sample was placed in cup, produced from Al_2O_3.

After the correction for incoherent scattering and polaryzation, the patterns were normalized to electron units by a modified form of Krogh-Moe's equation. After this procedure, intensity functions were used to calculate the structure factor $a(s)$. Pair correlation function has been calculated by Fourier transformation of $a(s)$:

$$g(r) = 1 + \frac{1}{2\pi\rho_0 r} \int_0^\infty [a(s)-1]s \cdot \sin(sr)ds ,$$

where ρ_0 is the mean atomic density, $s = \frac{4\pi \sin \vartheta}{\lambda}$ the wave vector, ϑ – half of scattering angle and λ is the wavelength.

We have also calculated the radial distribution function of atoms $G(r)$:

$$G(r) = 4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty [a(s)-1]s \cdot \sin(sr)ds,$$

where $\rho(r)$ is radial dependence of atomic density.

This function was used for determination of number of neighbours in structure, whereas the most probable interatomic distances were estimated from $g(r)$ function.

3. Results and Discussion

The intensity curve for Ni_3Al dopped with Zr and B liquid alloy, obtained at T=1775 K is shown in *Fig.1a*. In this figure the intensity curve for molten alloy is compared to diffraction pattern, which was calculated for crystalline Ni_3Al The structure factor, calculated from this curve is represented in *Fig.1b*. As it can be seen there are four intensive diffraction peaks within $10÷120 \text{ nm}^{-1}$ interval of wave vectors. All the maxima have a symmetric profile not revealing the submaxima or shoulders. The principal peak, which is the most informative among others, shows the height 1,80. This value is significantly less than one for typical liquid metals and their alloys ($\approx2,5$). As it is known the height of principal maximum for simple liquids according to hard sphere model is proportional to atomic density value. If compare this parameter of structure factor with ones for pure liquid components of this system (2,48 for Al and 2,44 for Ni) one can see the significant difference in their values. Consequently, one can suggest that packing density of liquid Ni_3Al intermetallic is less than in both liquid components. Such packing density decrease is supposed to be caused by transformation of interatomic bonding from metallic to covalent one. It should be noted that only some part of chemical bonds is covalent and rest of them are metallic. Such mixture of bonds creates the favourable conditions for inhomogeneous structure formation.

Other structure parameters for liquid alloy were also compared with the same parameters of liquid Al and Ni. Principal peak position is located at $s = 30,5 \text{ nm}^{-1}$, whereas these parameters for Al and Ni equal to 26,5 and $30,6 \text{ nm}^{-1}$ respectively. Therefore one can suppose that alloy under investigation has a structure, which is far from random atomic distribution. But it should be noted that atomic distribution in undoped Ni_3Al is somewhat different from those for dopped intermetallic [10]. Comparing their parameters of structure factors it can be seen that principal peak positions are in fact the same, whereas their heights show the large difference. For undopped melt principal peak height equals to 2,34, whereas for dopped one, as was determined above, it is 1,80. Consequently the Zr and B dopants do not promote the drastic structure changes, but they stimulate the formation of less density atomic distribution.

Analysis of pair correlation function (see *Fig.2*) confirms this assumption. Most probable interatomic distance r_1 equals to 0,245 nm and is more close to one of pure Ni (0,253 nm), than for Al (0,282 nm). But it is important to note that r_1 for Ni$_3$Al is less than this parameter for liquid Ni. Therefore, the structure of dopped molten intermetallic can not be considered as a simple atomic solution. If suppose that melt under investigation is a mixture of Al and Ni atoms with random atomic distribution, r_1, calculated according to additive law, was founded to be 0,252 nm, showing the significant disagreement with experimental value. Reducing of most probable interatomic distance in liquid intermetallic in respect to constituents, is the evidence of the formation of chemically ordered clusters. We have analyzed also the squire under first peak of radial distribution function G(r) and compare it with same values for In and Ni which are commonly interpreted as mean coordination numbers. This parameter for liquid Ni$_3$Al dopped with Zr and B was founded to be 7,5 what is significantly less than for Al(11,5) and Ni(11,6) indicating the decrease of atomic distribution density.

Most probable interatomic distance (0,245 nm) has been com-

pared with ones for crystalline Ni$_3$Al for which $r_{Al-Ni} = r_{Ni-Ni} = 0,253$ nm and $r_{Al-Al} = 0,357$ nm. It can be seen that this distance for liquid alloy is less than r_{Ni-Ni} showing the increase of interaction between unlike kind atoms.

It is important to know how Zr and B-atoms are distributed in liquid Ni$_3$Al. Since the atomic radius of boron is 0,091 nm it can occupy the octahedral voids in cell of intermetallic, because the distance to nearest atom in these voids is significantly large and equals to 0,178 nm. On other hand Zr–atoms have a higher radius (0,16 nm) and on that reason they can not be introduced into voids. These atoms most probably substitute the atoms of nickel. It is also known that Zr and B attempt to form the intermetallic compounds with both components of Ni$_3$Al intermetallic. Therefore one can suppose that Zr and B dopants change the chemical interaction in crystalline alloy.

As follows from our studies of this alloy and literature data for other systems, there is both topologic and chemical short range before transition from liquid state to solid one. Consequently, one can suggest that atomic distribution for dopped Ni$_3$Al alloy in solid and liquid state at distances within few coordination spheres is similar.
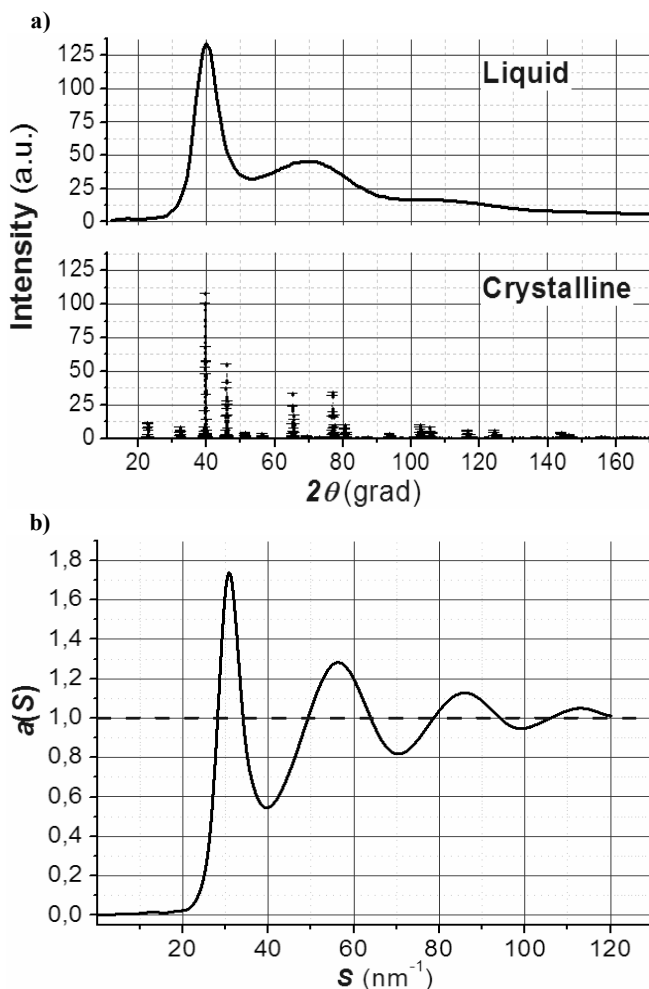
a)

b)

Fig. 1. Intensity curve (a) and structure factor (b) of liquid Ni$_3$Al doped with Zr and B at $T = 1775$ K.
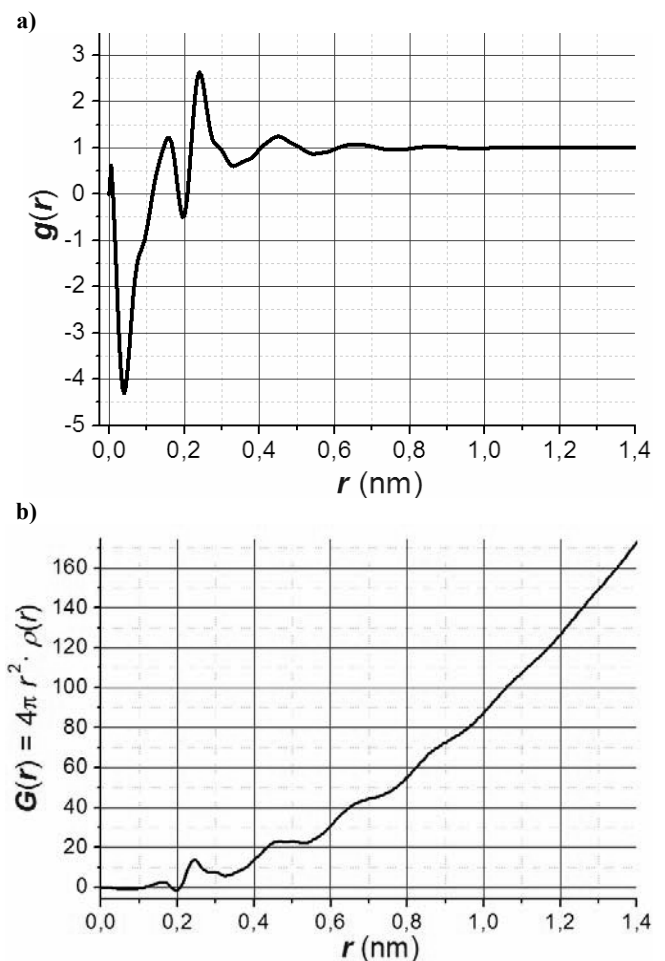
a)

b)

Fig. 2. Pair correlation function – a) and atomic radial distribution function –b) of liquid Ni$_3$Al, doped with Zr and B.

4. Conclusions

Liquid Ni_3Al intermetallic dopped with Zr and B at temperatures near the crystallization point reveals the structure with chemical short range order. The significant decrease of packing density in dopped melt in comparison with undopped one indicates the changes in chemical interaction. Tendency to cluster formation in melt is supposed to be influenced by Zr and B dopants and it is transferred into solid state.

References

[1] S. Mudry, T. Lutsyshyn. Influence of Ni on the structure of aluminium. Journal of alloys and compounds, 367 (2004) 289-292.

[2] L.F. Mondolfo. Aluminum alloys: Structure and properties, London, 1976, p.118

[3] H. Batalin, E. Beloborodova, V. Kazimirov. Thermodynamic and structure of aluminium–based liquid alloys. Moscow, Metallurgija., 1983, 160p. (in Russian).

[4] X.Z. Li, K.H. Kuo. Decagonal quasicrystals with different periodicities along the tenfold axis in rapid solidified Al–Ni alloys. Phil.Mag. Letters,1988, v.58, 3 p.167–171.

[5] S. Mudry, V. Sklyarchuk, A. Yakymovych. Influence of doping with Ni on viscosity of liquid Al, J. Phys. Stud., 2008, v.12, No. 1, p. 1601-1 – 1601-5.

[6] G. V. Ajushina, E. Levin, P. Held. Influence of temperature and composition on density and surface energy of liquid aluminum and nickel, Journal of Physical Chemistry, 1969, v.43, 11, p.2756-2760.

[7] E. Levin, G. Ajushina. Studying of some physical–chemical properties of Ni–Al melts.,Proceedings Academy of Science of USSR, Metals, 1971, 1, p.227-229.

[8] E. Levin, G. Ajushina. Electroconductivity of Ni-Al alloys, Proceedings Academy of Science of USSR, Metals, 1972, 5, p.143-146.

[9] A. Landa, A. Juriev, M. Romankevych. Calculation of thermodynamic and kinetic properties of transition metal melts with simple metal by means of nonlocal model psevdopotential, Melts, 1991, 2 , p.20-39 (in russian)

[10] A. Rojik, A. Samsonnikov, V. Kazimirov, V. Sokolskij. X-Ray diffraction studies of structure in Al–Ni melts, Proceedings Academy of Science of USSR, Metals, 2006, 3, p.24-31.

[11] P. Jóźwik, Z. Bojar, J. Bystrzycki, W. Przetakiewicz, Nanostructured Ni3Al Intermetallic Alloy Processed by Severe Rolling at Liquid Nitrogen Temperature and Annealing, Solid State Phenomena Vols. 101-102 (2005) 61-64.

[12] Z. Bojar, P. Jóźwik, J. Bystrzycki, Tensile properties and fracture behavior of nanocrystalline Ni3Al intermetallic foil, Scripta Materialia 55 (2006) 399-402.

[13] P. Jóźwik, D. Zasada, Z. Bojar, Wpływ obróbki cieplnej na strukturę i właściwości mechaniczne stopu na osnowie fazy międzymetalicznej Ni3Al (Zr, B). Archiwum Odlewnictwa 16 (2006) 249-254.

[14] P. Jóźwik, Z. Bojar, Analysis of grain size effect on tensile properties of Ni3Al. – based intermetallic strips, Archivies of Metallurgy and Materials Vol. 52 (2007) 321-327.

[15] P. Jóźwik, Z. Bojar, D. Zasada, Influence of heat treatment on structure and mechanical properties of Ni3Al (Zr, B) intermetallic alloy, Inżynieria Materiałowa 3-4 (2007) 169-174.