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High-Temperature X–ray Diffraction Studies of Al–Ni–Hf Ternary Alloys

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Phase content and temperature dependences of cell parameters for intermetallics $HfNi_2Al_5$, $Hf_6Ni_8Al_{15}$ and Ni_2Al_3, existed in Al-Ni-Hf ternary system have been studied by means of X-ray diffraction method. Experimental values of cell parameters at different temperature were used to calculate the thermal expansion coefficients and their temperature dependences. It is shown that for intermetallic phase with cubic structure temperature dependence of thermal expansion coefficient is significantly different than for l one with tetragonal structure.

Keywords: cell parameters, aluminum alloys, thermal expansion coefficient.

Introduction

Ternary Al–Ni–Hf alloys attract the attention as a perspective light materials, which can be strengthened by means formation of nanoparticles of intermetallics in al-based matrix. These alloys reveal the concentration region of easy amorphyzation and can exist in amorphous state upon rapid cooling from liquid state. Therefore there are potential ability to form a different phases in order to improve the properties and first of all the mechanical ones.

It is shown [1, 2] that solid-solution hardening of Ni_3Al depends on the substitutional behavior of alloying elements, atomic radii difference and deviation from stoicheometry. It is also established that Hf additions a effectively improve a high-temperature properties and other important characteristics. In order to control the formation of intermetallic phases, strengthening Al-based alloys ternary phase diagram is needed. Unfortunately, such diagram is not completely investigated, especially for Al-rich region that motivates further investigation of alloys of this system. From published data follows that solubility of Hf in most stable intermetallics AlNi, $AlNi_3$ is about 5 and 10 % respectively.

It is also shown that there are $HfNi_2Al$ and HfNiAl intermetallics in this system. Pseudobinary systems of binary and ternary compounds have been investigated be X-ray diffraction and physical properties measurements. As it is concluded in [3] pseudebinary eutectic reaction L ↔ NiAl + $HfNi_2Al$ takes place at 1350 °C, but no more publications, confining this reaction occurrence. Also the existence of two transition invariant reactions L + Ni_3Al + Hf_2Ni_7 and Al (Ni) + HfNi + Hf_2Ni_5 have been reported to take place. Another invariant reactions are predicted but their existence should be confirmed in further investigations. Some calculations showed presence (Ni) + $HfNi_5$ + Hf_2Ni_7 three phases field. Analyzing results on structure studies, physical properties measurements and calculated data one can see any contradiction between them that motivate further investigation of this ternary system.

I. Experimental

The alloy was prepared from ingots of constituent elements (not less than 99.6 wt.%) by arc melting in a high-purity argon atmosphere. X-ray diffraction studies have been carried out by means of high temperature diffractometer, which allowed to investigate solid and liquid materials within temperature range from room temperature up to 1600 K. Sample was placed in vacuum chamber filled with pure helium in order to prevent oxidation of sample. Breg-Brentano focusing geometry was used [4]. Temperature was controlled with accuracy -+2 K. Atomic parameters in the crystal structures of the compounds were refined for the first time from X-ay powder diffraction data using the program FullProf [5].
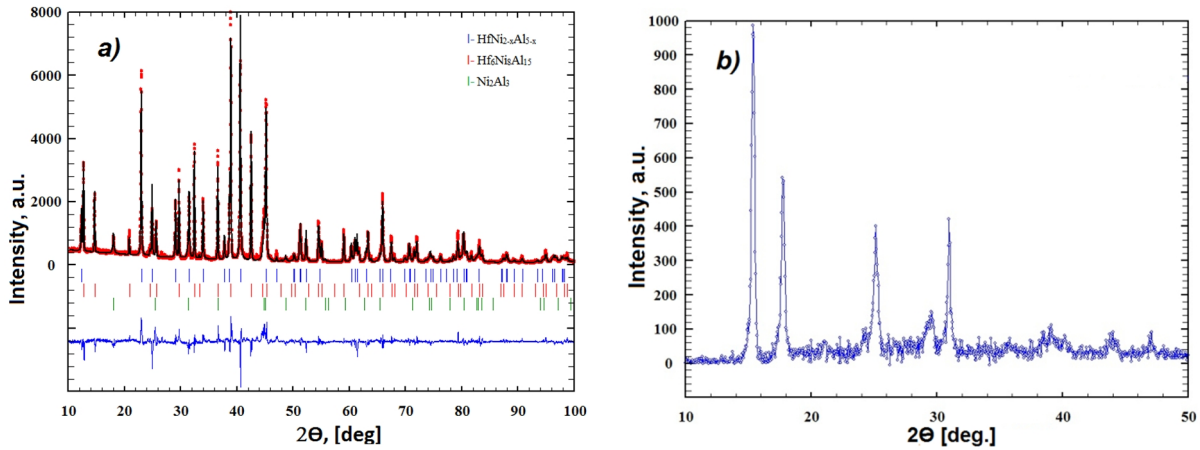
Fig. 1. Diffraction pattern for alloy, containing 62.5 at.% Al, 25 at.% Ni and 12.5 at.% Hf at T = 295 K (*a*) and T = 1725 K (*b*). The vertical bars indicate the calculated Brag positions of peaks of components of alloy; the dots shown experimental data; solid lines – calculated, and $Y_{exp.}$-Y_{calc} line is the intensity difference between diffractograms.

Table 1

Phase analysis and structural parameters of compounds in $Hf_{12.5}Ni_{25}Al_{62.5}$ alloy

Content Hf-Ni-Al, at.%	Phase content	Content of intermetallic, %	Space group	Structure type	Cell parameters, nm		
					a	*b*	*c*
12.5-25-62.5	$HfNi_{2-x}Al_{5-x}$	40.29	*I4/mmm*	$HfNi_2Al_5$	0.4011599(9)	-	1.419948(47)
	$Hf_6Ni_8Al_{15}$	25.97	*Fm-3m*	Th_6Mn_{23}	1.199608(24)	-	-
	Ni_2Al_3	33.74	$P\bar{3}m1$	Ni_2Al_3	0.404132(29)	-	0.490173(68)

II. Results and discussion

Ternary alloy, containing 62,5 at.% Al, 25 at.% Ni and 12,5 at.% of Hf has been studied in solid state at temperatures 295 and 1725 K. Due to poor information on phase equilibrium in this system the temperatures is of phase transitions are not available but we suppose that last of these temperatures is close to the melting point. X-ray diffraction investigation has been carried out for crystalline alloy, annealed before experiment. It should be noted that concentration of this alloy corresponds to the region of easy amorphysation and on that reason it can exist in amorphous phase upon rapid cooling from liquid state [6].

Analysis of diffraction patterns (Fig. 1) shown that at room temperature alloy consists the two ternary compounds $HfNi_{2-x}Al_{5-x}$ (which corresponds to the alloy composition $Hf_{12,5}Ni_{25}Al_{62,5}$), $Hf_6Ni_8Al_{15}$ and binary one Al_3Ni_2. Structure, parameters and contents of each intermetallics are listed in table 1. At T = 1725 K diffraction peaks have significantly different positions than ones, existed at room temperature. Therefore tendency to chemical ordering exists over wide temperature range, and before melting the formation of intermetallic phase with more symmetric crystalline structure occurs as well as it was observed early for other metals and alloys, revealing structure transformations in solid state. Unfortunately it is difficult to determine what of intermetallic phases is more dominant at formation of

chemical ordering in liquid state due to formation of thin film on the surface of melt. To avoid the formation of this film, which distorts the diffraction data and is formed on the reason of high chemical activity of Al and Hf–atoms at elevated temperatures, is related with some troubles. Nevertheless, analyzing the diffraction pattern for such temperature we can conclude that no atomic solution of Al, Ni and Hf-atoms exist at near melting point temperatures as well as there are no facts to consider this alloy as consisting of mixture of Al, Ni and Hf-based clusters.
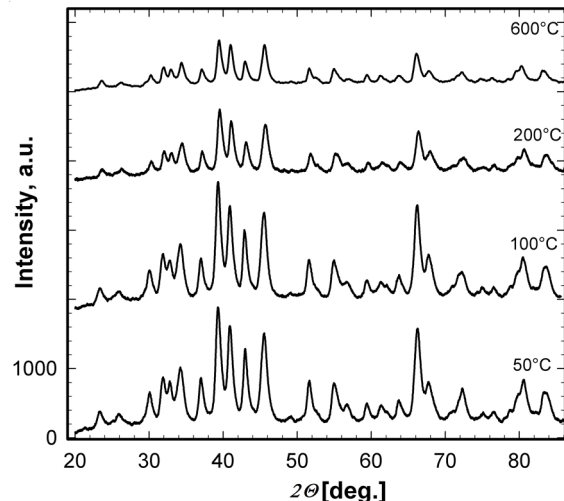
More detailed studies of structure variation with

Fig. 2. Diffraction patterns for $Hf_{12,5}Ni_{25}Al_{62,5}$ alloy at different temperatures.
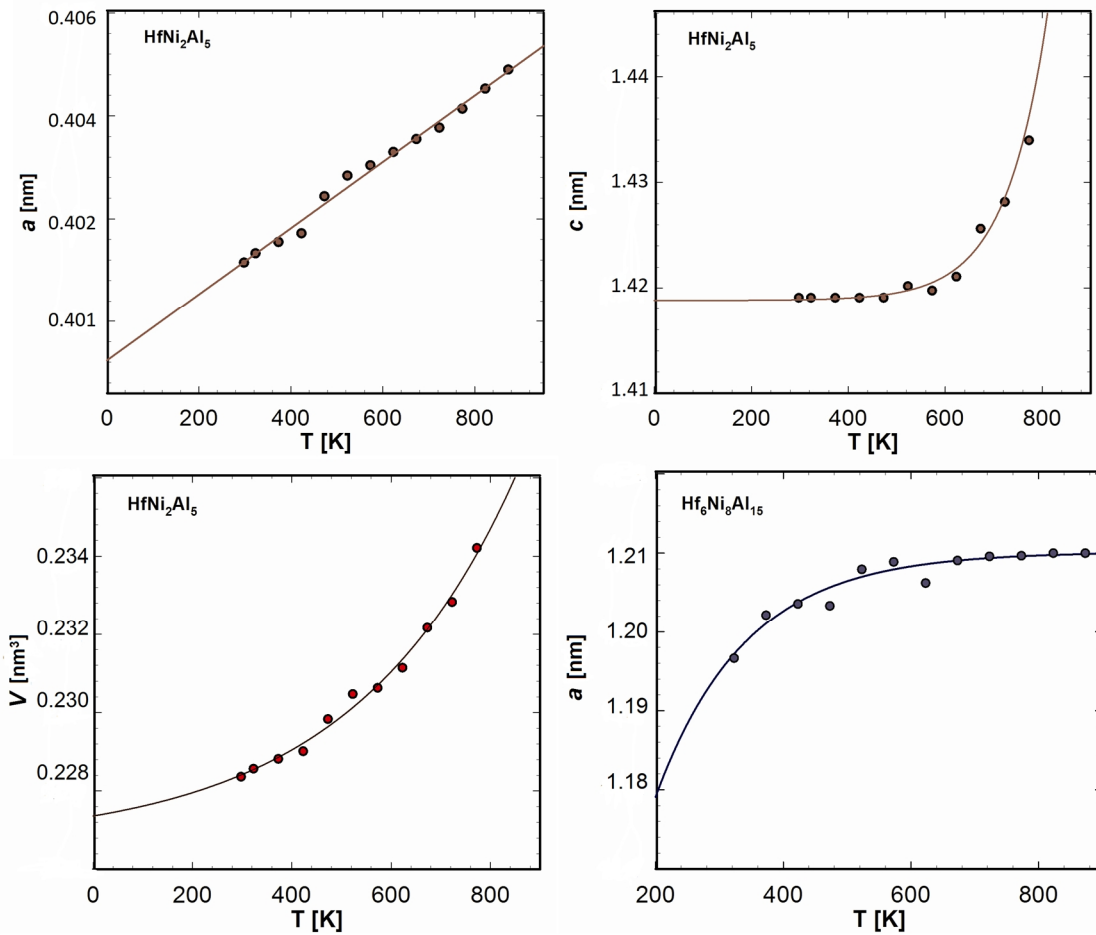
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Fig. 3. Temperature dependences of cell parameters and cell volumes for ternary intermetallics.

temperature was carried out within temperature range 323 – 873 K. Diffraction patterns obtained at different temperatures indicates some temperature stability of structure (Fig. 2).

One can see that peak positions and their heights show slight variation with temperature and phase content ($HfNi_2Al_5$, $Hf_6Ni_8Al_{15}$ та Ni_2Al_3) within this temperature range is the same. Diffraction data have been to calculate the temperature dependences of cell parameters for three intermetallics (Fig. 3). These dependences allowed us to calculate thermal expansion coefficients and their temperature dependences (Fig. 4).

As it can be seen the cell parameter a for tetragonal intermetallic phase $HfNi_2Al_5$ increases linearly, whereas parameter c shows more complicated dependence. With temperature increasing up to about 500 K it is almost unchangeable, but at higher temperatures it increases according to parabolic dependence. Such behavior of this parameter leads to similar dependence of elementary cell volume. For analytical approximation of these dependences we obtain such formulas:

$$a(T) = 3.9924 + 6.4454 \times 10^{-5}T \quad R = 0.99697,$$

$$c(T) = 14.1883 + 6.1656 \times 10^{-5} e^{0.0101T} \quad R = 0.9981,$$

$$V(T) = 226.6456 + 0.7138T + 3.0289T^2 \quad R = 0.99879$$

Temperature dependence of cell parameter and volume for $Hf_6Ni_8Al_{15}$ intermetallic phase we the such expressions:

$$a(T) = \frac{2,236\,T}{1+0,1857T} \quad R = 0.99999$$

$$V(T) = \frac{109,3\,T}{1+0,0604\,T} \quad R = 0.99991,$$

R is a correlation coefficient..

We suppose that these expressions can be used for estimation of cell parameters at another temperatures within larger temperature interval than 323 - 873 K.

One can see that peak positions and their heights show slight variation with temperature and phase content ($HfNi_2Al_5$, $Hf_6Ni_8Al_{15}$ та Ni_2Al_3) within this temperature range is the same. Diffraction data have been used to
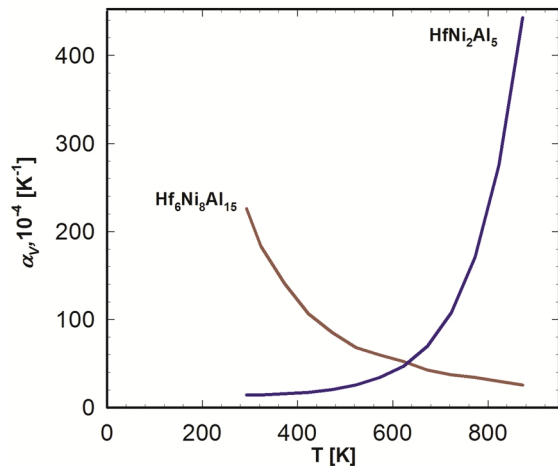

Fig. 4. Temperature dependence of thermal expansion coefficient for $HfNi_2Al_5$ and $Hf_6Ni_8Al_{15}$ intermetallics.

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One can see the different behavior of this characteristics. For $Hf_6Ni_8Al_{15}$ intermetallics thermal expansion coefficient decreases with temperature according to exponential law, whereas for $HfNi_2Al_5$ intermetallic phase this parameter varies proportionally to $1/T$. Features of such behavior most probably are attributed to more complicated bounding between atoms in tetragonal $HfNi_2Al_5$ comparatively to cubic structure of $Hf_6Ni_8Al_{15}$ intermetallic phase.

Conclusions

Ternary chemical compounds $HfNi_2Al_5$, $Hf_6Ni_8Al_{15}$ and Ni_2Al_3 determine the phase content of alloy, containing 62.5 at.% Al, 25 at.% Ni and 12.5 at.% of Hf not only at room temperature but also at elevated temperatures. Tendency to chemical ordering is observed at temperatures close to melting point. Temperature dependences of thermal expansion coefficients, calculated from experimental values of cell parameters reveal different behavior for each ternary intermetallics that is supposed to be features of chemical bonding between constituent atoms.

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Високотемпературні рентгенівські дифракційні дослідження тернарних сплавів Al-Ni-Hf

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Методом дифракції Х- променів досліджено фазовий склад і температурну залежність параметрів гратки інтерметалідів $HfNi_2Al_5$, $Hf_6Ni_8Al_{15}$ і Ni_2Al_3 потрійної системи Al-Ni-Hf. Експериментальні значення параметрів гратки при різних температурах використовувались для розрахунку коефіцієнтів термічного розширення та їх температурної залежності. Показано що для інтерметаліда з кубічною структурою температурна залежність коефіцієнта термічного розширення суттєво відрізняється від аналогічної залежності для інтерметаліда з тетрагональною структурою.

Ключові слова: параметри комірки, алюмінієві сплави, коефіцієнт теплового розширення.