FOLIA 251

Annales Universitatis Paedagogicae Cracoviensis

Studia Technica 10 (2017)
ISSN 2081-5468
DOI 10.24917/20815468.10.18

Olena Shved, Stepan Mudry, Olga Zhak, Ivan Shcherba

X–ray diffraction studies of Al–Ni–Zr ternary alloy

Introduction

Aluminum – based alloys are of great importance due to their use in various areas of industry and first of all in aviation and rocketry. For instance, ternary Al–Ni–Zr alloys are perspective materials for steam turbine engines and corrosion resistant materials. From fundamental viewpoint alloys of this system as well as of Ni-Zr binary one attract the attention of researchers because its phase diagram reveals the concentration regions, within which the amorphous phase can be obtained by rapid cooling of melt. On that reason, Ni–Zr and Al-Ni-Zr systems due to their high glass forming ability are interesting not only from viewpoint of practical application but also fundamental one. The results on studying of such alloys help to attain a more deeper understanding the nature of amorphous state (Inoue, Takeuchi 2002; Wang, Shek, Qiang 2004).

Notably, that intermetallics are most attractive among various phases of this ternary system because most of them reveal the high melting temperature, good ductility, high corrosion resistance and high electroconductivity. Intermetallics of Ni-Al binary system also reveal high strength (Guo, Ohtera 1998), good corrosion and oxidation resistance, good resistance to rapture and creep at high temperatures. Moreover, when Zr is added to binary intermetallics these properties can be enhanced. At controlled thermal treatment the amorphous alloys of this system can be transformed into nanocrystals, owing to which many physical properties become more improved. Taking into account these facts one can conclude that structure studies of alloys of this system are very important for understanding of physical properties improving mechanism. Thus knowledge about high-temperature behavior of crystallographic structures of the Al–Ni–Zr ternary compounds is very important in materials science of aluminum-based alloys.

Most of available publications consist the results on investigation of Zr and Ni-enriched alloys, whereas an information on structure of Al-enriched alloys is poor. On that reason our attention was focused on studying of alloys from aluminum corner of Al-Ni-Zr ternary phase diagram. The Al–Ni–Zr system was repeatedly investigated by XRD and optical microscopy at 800°C (Markiv, Matushevskaya, Rozum, Kuz'ma 1966), and in Ni-enriched region of the phase diagram at 1000 and

1100°C (Jayanth 1983a, 1983b). Recently, phase equilibrium of the system at 850 and 1050°C were also published (Chen, Huang, Liu, Zheng, Jin 2013).

It is known about existence of two ternary compounds with permanent composition in Al-enriched part of isothermal section of the phase diagram – $Zr_6Ni_8Al_{15}$ (τ_5), $ZrNi_2Al_5$ (τ_6) and $ZrNi_{0,5}Al_{1,5}$ (λ_2) with significant homogeneity range. At first it was discovered by (Markiv, Matushevskaya, Rozum, Kuz'ma 1966; Ganglberger, Nowotny, Benesovsky 1966). It was established (Markiv, Krypyakevych, Belyavina 1982) tetragonal lattice with parameters: a = 0,4023 nm, c = 1,444 nm and composition described by formula $ZrNi_2Al_5$, despite published earlier (Markiv, Matushevskaya, Rozum, Kuz'ma 1966) $Zr_3Ni_6Al_{16}$. Recently crystal structure of τ_6 was refined by means of XRD and NPD and its composition was counted as $ZrNi_{2-x}Al_{5-x}$ (x = 0.4) (Khan, Bursik, Grytsiv, Pomjakushin, Effenberger, Rogl 2011).

It is shown (Inoue, Zhang, Masumoto 1990) by melt spinning two quit wide glass formation fields into ranges of Zr-rich and Al-rich composition, moreover Al-rich composition formed amorphous brittle phases. Mechanical alloying of elemental powders produced an amorphous phase having composition Al-12.5Ni25-Zr (at.%), which crystallizes into $ZrAl_3$ and τ_5 upon heating to 780°C (Desch, Schwarz, Nash 1991), which is not the equilibrium state (Markiv, Matushevskaya, Rozum, Kuz'ma 1966).

Experimental

The ingot sample was prepared from pieces of Zr, Ni and Al with stoichiometric ratio of 1:2:5, respectively, by arc melting on a water-cooled copper plate under argon atmosphere with titanium as getter material placed in the arc chamber.

Structural parameters were determined by least squares refinements of room temperature X-ray powder diffraction (XRD) data obtained from a STOE STADI P (Stoe WinXPOW) and DRON-3M devices equipped with a UVD-2000 high-temperature vacuum chamber employing monochromatic $CuK_{\alpha 1}$-radiation in both experiments. High-temperature study had been carried out on a cut and polished plate-shaped specimens 1mm in thickness in the temperature interval from room temperature to 973 K.

Also have been carried out X-ray diffraction studies on high temperature diffractometer ($MoK_{\alpha 1}$-radiation), which allowed to investigate solid and liquid materials up to 1800 K. Sample was placed in vacuum chamber filled with pure helium in order to prevent oxidation of sample. Temperature was controlled with accuracy ±2K.

Preliminary data processing and X-ray phase analysis were performed using PowderCell (Kraus, Nolze 2000) program. Crystal structure was refined by the Rietveld method with the program FullProf.2k (version 5.40) (Rodriguez-Carvajal 2001; Roisnel, Rodriguez-Carvajal 2001), applying a pseudo-Voigt profile function.

Metallographic qualitative and quantitative composition analyses of the polished samples were performed by EDX with REMMA-102-02 scanning electron microscope.

Results and discussion

X-ray investigation shown that $ZrNi_{2-x}Al_5$ is the main phase of the $Zr_{12.5}Ni_{25}Al_{62.5}$ alloy at room temperature (fig. 1*a*). We have obtained almost a single-phase sample with small amount of τ_5 phase (~10%). Crystal structure of τ_6 phase was refined by Rietveld method. Structural parameters of it are listed in table 1. Low values of residual factors obtained from Rietveld refinement and minor differences between observed and calculated intensities confirmed the structure as well. As one can see we described composition of τ_6 by formula $ZrNi_{2-x}Al_5$ (x = 0.24) unlike last literature data $ZrNi_{2-x}Al_{5-x}$ (x = 0.4) (Khan, Bursik, Grytsiv, Pomjakushin, Effenberger, Rogl 2011). It may indicate that this compound have a homogeneity range in respect of Ni positions occupation from 0.792(1) to 0.844(2) and Al *8g* positions from 0.90(2) to 0.98(1). Calculated interatomic distances for $ZrNi_{2-x}Al_{5-x}$ compound are listed in (tab. 2).

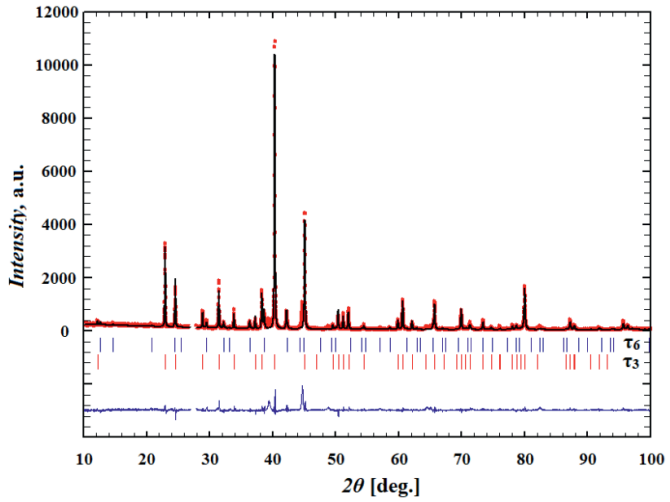


Figure 1. Rietveld refinement of the X-ray powder pattern for alloy $Zr_{12.5}Ni_{25}Al_{62.5}$ (composition of initial arc melted alloy) annealed at 1073 K (Cu $K\alpha_1$-radiation) (*a*) and X-ray diffraction pattern at 1773 K (Mo $K\alpha_1$-radiation) (*b*)

Table 1. Rietveld refinement data for compounds of the $Zr_{12.5}Ni_{25}Al_{62.5}$ alloy (from STOE STUDI P, $CuK_{\alpha1}$-radiation)

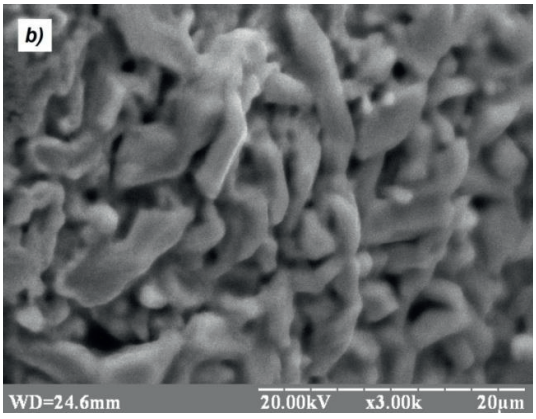
Parameter/Compound	$ZrNi_{2-x}Al_5$ (x=0.24)
Space group	*I*4/*mmm*; No.139
Structure type	$ZrNi_2Al_5$
Theta range	10°<2θ<110°
Number of atoms in cell	15.5
Calculated density (g/cm^3)	4.6945(2)
Cell parameters	

a [nm]	0.401529(6)
b [nm]	-
c [nm]	1.44669(3)
β [deg]	90
Reflections in refinement	67
Number of variables	24
Reliability factors Brag R-factor $R_f = \Sigma F_o - F_c / \Sigma F_o$	 0.0937 0.0788
Zr; Occ., U_{eq} (B_{iso})	***2a(0,0,0)***
	1.00(1) Zr, 1.183(9)
Ni1; Occ., U_{eq} (B_{iso})	***4e (0,0,z)***
	z=0.23842(21) 0.844(2) Ni, 0.452(9)
Al1; Occ., U_{eq} (B_{iso})	***8g (0,1/2,z)***
	z=0.14864(20) 0.982(8) Al, 1.001(9)
Al2; Occ., U_{eq} (B_{iso})	***2b (0,0,1/2)***
	1.00(1) Al, 1.239(9)

Table 2. Interatomic distances for $ZrNi_{2-x}Al_{5-x}$ compound, standard deviation ≤0.0002

Atom		*d,* **nm**
Zr – CN=16	4Al2 –8Al1 –2Ni –4Zr	0.28390 0.29423 0.34462 0.40153
Ni – CN=13	4Al1 –4Al1 –4Ni –Zr	0.23904 0.25879 0.28588 0.34462
Al1 – CN=13	2Ni –2Ni –4Al1 –1Al1 –2Al2 –2Zr	0.23904 0.25879 0.28390 0.29373 0.29423 0.29423
Al2 – CN=12	4Zr –8Al1	0.28390 0.29423

Ternary $Zr_{12.5}Ni_{25}Al_{62.5}$ alloy has been studied also in liquid state at temperature 1773 K. There is no information in literature about the melting temperature of ternary Al–Ni–Zr compounds, but we suppose that this temperature is close to the ones for the intermatallic compounds of Al–Ni–Hf system, which in many respects is similar to Al-Ni-Zr system and do not exceed 1773 K (Effenberg, Ilyenko 2005). To our great surprise we observed a crystalline-like peaks on the X-ray diffraction pattern at 1773 K (fig. 1*b*). Diffraction peaks have significantly different positions than ones, existed at room temperature. Comparing with the known reflexes for all ternary and binary Al–Ni, Ni–Zr and Al–Zr compounds did not allow to index the reflexes of unknown compound. And unfortunately we could not to determine what of intermetallic phases is dominating at formation of chemical ordering in liquid state due to possible formation of thin film on the surface of melt. It is also clear that alloy at such high temperature can not be considered as solution of Al, Ni and Zr – atoms as well as mixture of clusters on the base of these elements. Thus the tendency to chemical ordering exists over wide temperature range from room temperature up to melting point.



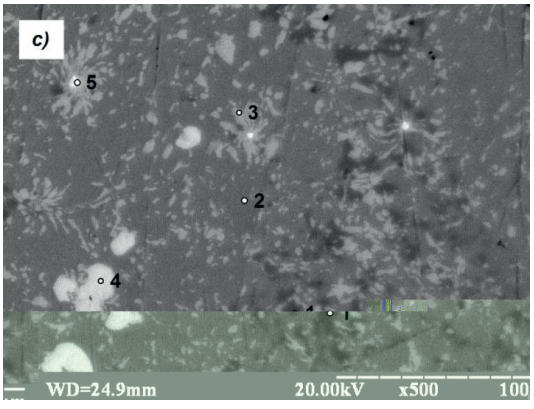


Figure 2. Metallographic analysis for different part of $Zr_{12.5}Ni_{25}Al_{62.5}$ sample: 1 – *a,b*; 2 – *c*

To make sure that the elemental and phase composition of the sample was unchanged further analysis after cooling the molten sample was performed. We mark the place on the surface of the sample as 1, middle point in vertical cross as 2 and powdered sample as 3.

SEM analysis shown (fig. 2c) the existence of five phases in bulk part of sample, and each of them contains the different content of Al, Ni and Zr-atoms (table 3). It should be noted that total content of elements does not coincide with initial one. Unfortunately the composition of aluminum may be determined with lower accuracy in comparison with other elements, due to aluminum oxide, which is the standard for measuring. On that reason content of Al is less than should be in alloy.

Table 3. Elemental analysis of volumetric part of the sample

Position	Content of elements, *at.%* (figure 2*c*)		
	Hf	Al	Ni
1	0,7012	40,379	58,9198
2	20,2104	47,4751	32,3145
3	29,8163	38,1118	32,0719
4	48,7759	38,5511	12,6731
5	87,3427	5,2933	7,3640
Total	20,4162	45,4716	34,1121

The results of X-ray phase analysis for different part of the sample shown the existence of $ZrNi_{2-x}Al_{5-x}$ and $Zr_6Ni_8Al_{15}$ in the sample (table 4) that is in agreement with other results on studying of Al-Ni-Zr phase diagram. However, the fraction of each compound in various parts of sample is different. On the surface part of sample the $ZrNi_{2-x}Al_{5-x}$ compound is the main phase (~65 at.%). For bulk part its content is significantly reduced (~25 at.%), and $Zr_6Ni_8Al_{15}$ intermetallics is the main phase (~65 at.%) in this case. It is also can be seen (fig. 2*c)* the largest area (dark gray phase with position 2), where the ratio of elements (20,2104-32,3145-47,4751) corresponds to stoichiometry of $Zr_6Ni_8Al_{15}$ phase. A good agreement between results of X-ray investigation and data on microscopy analysis for bulk part of sample is the evidence of the change in sample composition from top to bottom of sample cross section.

Table 4. Phase analyses (XRD) for different part of $Zr_{12.5}Ni_{25}Al_{62.5}$ sample, cooled to room temperature after heating up to 1773 K

Part of sample	Phase	Space group	Lattice parameters, nm		
			a	b	c
1	$ZrNi_{2-x}Al_{5-x}$ $Zr_6Ni_8Al_{15}$	$I4/mmm$ $Fm\bar{3}m$	0,403 1,212	– –	1,444
2	$Zr_6Ni_8Al_{15}$ $ZrNi_{2-x}Al_{5-x}$	$Fm\bar{3}m$ $I4/mmm$	1,210 0,403	– –	 1,454
3	$Zr_6Ni_8Al_{15}$ $ZrNi_{2-x}Al_{5-x}$ …	$I4/mmm$ $Fm\bar{3}m$ …	1,216	– – …	

Conclusions

X-ray investigation of the of τ_5 phase allowed to refine its crystalline structure and can be described by formula $ZrNi_{2-x}Al_{5-x}$ (x = 0.24). Intermetallics of different stoichiometry are not randomly distributed from the top of sample to bottom. Surface of sample is enriched with $ZrNi_{2-x}Al_{5-x}$ phase, whereas in bulk part the $Zr_6Ni_8Al_{15}$ phase is dominant. Tendency to chemical ordering exists over wide temperature region from room temperature up to melting point.

References

Chen Q., Huang H., Liu H.S., Zheng F., Jin Z.P., 2013. *Isothermal section of Al-Ni-Zr ternary system at 850 and 1050°C*. Journal of phase Equilibria and diffusion, 43(5), 390–402.

Desch P., Schwarz R.B., Nash P., 1991. *Formation of Metastable LI_2 Phases in Al_3Zr and Al-12% X-25% Zr (X=Li Cr, Fe, Ni, Cu)*. Journal of the Less Common Metals, 168, 69–80.

Effenberg G., Ilyenko S., 2005. *Ternary Alloy Systems: Phase Diagrams, Crystallographic and Thermodynamic Data Light Metal Systems. Part 3*, 11A3.

Ganglberger E., Nowotny H., Benesovsky F., 1966. *Monatshefte für Chemie (und verwandte Teile anderer Wissenschaften)*, 97, 219–220.

Guo J.Q., Ohtera K., 1998. *Microstructures and mechanical properties of rapidly solidified high strength Al–Ni based alloys*. Acta Materialia, 46(11), 3829–3838.

Inoue A., Takeuchi A., 2002. *Recent progress in bulk glassy alloys*. Materials Transactions, 43(8), 1892–1906.

Inoue A., Zhang T., Masumoto T., 1990. *Zr-Al-Ni Amorphous Alloys with High Glass Transition Temperature and Significant Supercooled Liquid Region*. Materials Transition, 31, 177–183.

Jayanth C.S., 1983. *Phase Equilibria in the Ni-Al-Zr and Ni-Al-V Systems. M.S. Thesis*, Illions Institut of Technology.

Jayanth C.S., Nash P., 1983. *Phase Equilibria in the Ni-rich region of the Ni-Al-Zr System*. Materials Research Society, 19, 395–398.

Khan U., Bursik J., Grytsiv A., Pomjakushin V., Effenberger H., Rogl P., 2011. *Effect of silicon on the formation of intermetallic phases in aluminide coating on mild steel*. Intermetallics, 19(10), 1340–1347.

Kraus W., Nolze G., 2000. *PowderCell for Windows (version 2.4)*, Berlin, Federal Institute for Materials Research and Testing.

Markiv V.Y., Krypyakevych P.I., Belyavina N.N., 1982. *Dopovidi Akademii Nauk Ukrains'koi RSR, Seriya A*, 3, 76–79.

Markiv V.Y., Matushevskaya N.F., Rozum S.N., Kuz'ma Y.B., 1966. *Inorganic Materials (translated from Neorganicheskie Materialy)*, 2, 1356–1359.

Rodriguez-Carvajal J., 2001. *Recent developments of the program FULLPROF, Commission on Powder Diffraction (IUCr)*. Newsletter, 26, 12–19.

Roisnel T., Rodriguez-Carvajal J., 2001. *WinPLOTR: a Windows tool for powder diffraction patterns analysis*, Materials Science Forum, 378–381, 118–123.

Stoe WinXPOW (version 3.03), Stoe & Cie GmbH, Darmstadt, Germany.

Wang Y., Shek C.H., Qiang J., 2004. *The e/a Criterion for the Largest Glass-forming Abilities of the Zr-Al-Ni(Co) Alloys*. Materials Transactions, 45(4), 1180–1183.

Tytuł

Abstract

Alloys of ternary Al-Zr-Ni ternary system of with stoichiometric ratio of Zr, Ni and Al 1:2:5 has been studied by X-ray diffraction method at room temperature and in the temperature region close to melting point. It is shown that within wide temperature region exists the tendency to chemical ordering. The results of investigation allowed refining the crystalline structure of ternary intermetallics to calculate an interatomic distances in $ZrNi_{2-x}Al_{5-x}$ phase.

Key words: Aluminum-based alloys, intermetalliics, cell parameter

O. Shved, S. Mudry, O. Zhak, I. Shcherba
Department of Physics of Metals,
Ivan Franko National University of Lviv,
Kyryla and Mefodiya Str. 8,
UA-79005 Lviv, Ukraine
E-mail: olenkawved01@gmail.com