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Phase equilibria and crystal structures in the Zr–Ru–Al system at 900°C

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The Zr–Ru–Al system was studied at 900 °C by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A number of phase equilibria were established for the system with an Al content ≤ 55 at. %. The existence of two ternary compounds was confirmed: $ZrRu_xAl_{2-x}$ with a hexagonal structure of the $MgZn_2$ type (space group $P6_3/mmc$): a = 5.2225(5), c = 8.1980(8) Å and cubic $Zr_6Ru_{7+x}Al_{16-x}$ (x = 0.58) with the Th_6Mn_{23} type of structure: a = 12.27655(8) Å. Continuous solid solution based on binary compounds RuAl and ZrRu with a CsCl type (PG $Pm\bar{3}m$) was found along the isoconcentrate at 50 at. % Ru.

Keywords: phase equilibria, crystal structure, X-ray diffraction, Zirconium with transition metals alloys

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Introduction

Zirconium alloys with transition metals have attracted considerable scientific interest due to their broad application potential from the nuclear industry to sporting goods and medical implants [1–2]. Among this class of materials, alloys based on the Zr–Ni–(Cu)–Al systems are the most extensively investigated because of their high glass-forming ability and capacity to bulk amorphous alloys producing [3,4].

Recently, increasing attention has been paid to alloys based on the Zr–Ru–Al system in the form of thin films [5–6], which are considered promising ultrathin coatings for microelectromechanical systems, gas turbines, and equipment used in nuclear power plants. Despite this, the Zr–Ru–Al system hadn't been the subject of systematic investigation. In particular, there is a lack of information regarding its phase diagram, the crystal structures of its compounds, and the glass-forming ability of alloys based on this system. To date, only limited data are available on the formation of two ternary phases, published a considerable time ago. Specifically, in 1966, the formation of a ternary phase of the G-type structural type (ST) Th_6Mn_{23} was reported in the Zr–Ru–Al system [7]. Later, a hexagonal Laves phase of the $MgZn_2$ structural type was described in [8]. However, structural information for both phases is restricted to the values of their unit cell parameters.

Thus, the investigation of phase equilibria and crystal structures of compounds in the Zr–Ru–Al system represents a relevant scientific task. This work presents the results of a study of phase equilibria in the central region of the isothermal section of the Zr–Ru–Al phase diagram at 900 °C, as well as the crystal structures of the ternary phases formed within this compositional range.

I. Experimental

The ternary alloys of the system were prepared from ingots of metals with a purity of 99.98 at. % in a high-frequency induction furnace under purified argon atmosphere. To ensure better homogeneity, the alloy samples were re-melted for five times. High-temperature annealing at 900 °C was performed in vacuum-sealed quartz ampoules for 336 hours.

The phase composition of the alloys was studied using X-ray diffraction data (XRD) obtained with an Aeris diffractometer (Cu–Kα radiation). Data analysis was carried out using the PowderCell program. The crystal structures of the compounds were refined using the

Rietveld full-profile analysis method, employing the FullProf2k software.

Microstructural investigations and composition control of the alloys were carried out using a Zeiss Evo 10 scanning electron microscope (SEM) with a tungsten cathode, utilizing energy-dispersive X-ray spectroscopy (EDX).

II. Results

According to the results of the analysis using XRD and EDX spectroscopy of the samples annealed at 900 °C, several phase equilibria were identified, and a partial isothermal section of the Zr–Ru–Al phase diagram was constructed in the concentration range corresponding to Zr_5Al_4–Zr–Ru–RuAl (Fig. 1). The study is limited to compositions with up to 55 at. % of Al.

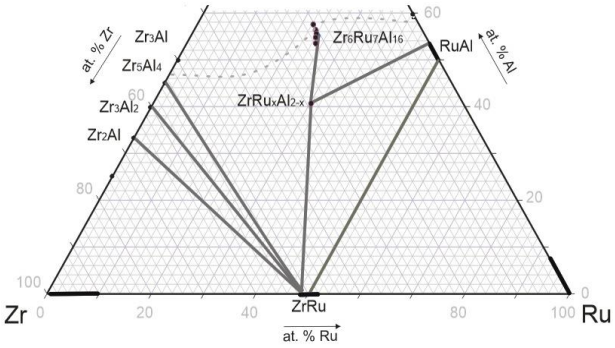


Fig. 1. Partial isothermal section of the phase diagram of the Zr–Ru–Al system at 900 °C.

The existence of continuous solid solution phase based on the binary compounds CsCl-type ZrRu and RuAl was identified along isoconcentrates at 50 at. % of Ru. The experimental and calculated patterns of the alloy of composition $Zr_{25}Ru_{50}Al_{25}$ are presented in Fig. 2. It was determined that the alloy is single-phase at 900°C. Further refinement revealed partial occupation of the 1*a* site by Zr and Al atoms. The other site is fully occupied by Ru atoms. The lattice parameter of the ternary phase was calculated as a = 3.09778(7) Å, and the composition of this solution, $Zr_{24.8}Ru_{50}Al_{25.2}$, differs slightly from the initial charge composition and can be represented by the formula Zr_xRuAl_{1-x} (where x = 0.504). The refinement was carried out to low discrepancy factors (R_f = 4.26).

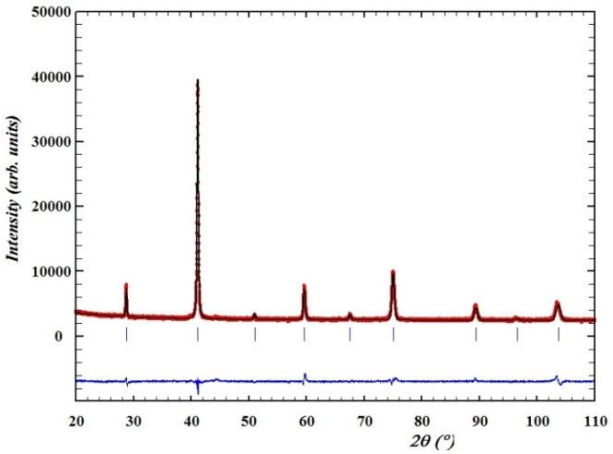
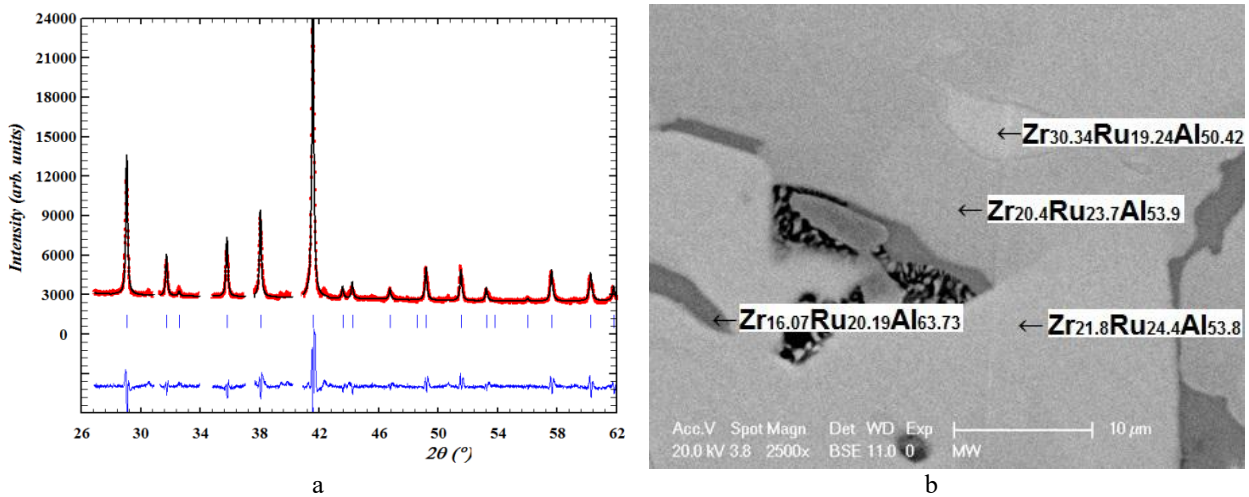


Fig. 2. Experimental, calculated and differential XRD data of the $Zr_{25}Ru_{50}Al_{25}$ alloy annealed at 900 °C.

The structural parameters of the G-phase (ST Th_6Mn_{23}) were refined based on diffraction data (Fig. 3) for the alloy with the composition $Zr_{20.7}Ru_{24.2}Al_{55.1}$ (with the composition ratio 6:7:16). The results of full-profile refinement of the 900 °C annealed alloy are presented in Table 1. The calculated unit cell parameter a = 1.227655(8) nm was found to be smaller than the previously reported value (1.240 nm [7]). This could be due to partial occupancy of both positions by Ru atoms instead of Al. The phase composition (Table 1) deviates slightly from the initial charge composition and can be represented by the formula $Zr_6Ru_{7+x}Al_{16-x}$ (x = 0.58). It is worth noting that SEM data (Fig. 4*b*) and elemental analysis revealed minor differences in the composition of the alloy in regions corresponding to this phase. Furthermore, the composition of this phase, in equilibrium with the hexagonal Laves phase in the alloy, differs. This suggests the possible existence of a homogeneity range, which can also be inferred from the broadening of the



a b

Fig. 3. Experimental, calculated and differential XRD data (*a*) and the microstructure and EDX analysis data (*b*) of the $Zr_{20.7}Ru_{24.2}Al_{55.1}$ alloy, annealed at 900°C.

Table 1.

Crystallographic data of the ternary phases of the Zr–Ru–Al at 900 °C

Initial alloy composition	$Zr_{30}Ru_{30}Al_{40}$	$Zr_{20.7}Ru_{24.2}Al_{55.1}$
Calculated composition	$Zr_{33.3}Ru_{27.4}Al_{39.3}$	$Zr_{20.7}Ru_{26.2}Al_{53.1}$
Space group	$P6_3mmc$; № 194	$Fm\bar{3}m$; № 225
ST	$MgZn_2$	Th_6Mn_{23}
Cell parameters		
a [Å]	5.2225(1)	12.27655(8)
c [Å]	8.1980(8)	-
Reliability factors - $R_F = \Sigma \lvert F_o - F_c \rvert / \Sigma F_o$ - $R_{exp} = [(N-P+C)/\Sigma w_i y^2_{oi})]^{1/2}$ GOF : - $\chi^2 = (R_{wP}/R_e)^2$	 0.0244 0.0798 25.11	 0.0476 0.0179 14.3
Zr; Occ., U_{eq} (B_{iso})	***4f (1/3,2/3,x)*** x = 0.43606(28) 1.00 Zr, 0.30(6)	***24b (x,0,0)*** x = 0.28765(28) 1.00 Zr, 0.585(9)
Al1; Occ., U_{eq} (B_{iso})	–	***32f (x,x,x)*** *x* = 0.12309(24) 0.987 (7) Al, 0.633(15) 0.013(7) Ru, 0.633(15)
Al2; Occ., U_{eq} (B_{iso})	–	***32f (x,x,x)*** *x* = 0.33700(25) 0.939(9) Al, 1.43(15) 0.061(9) Ru, 1.43(15)
Ru1; Occ., U_{eq} (B_{iso})	***2a (0,0,0)*** 0.395(6) Ru, 1.0(8) 0.605(6) Al, 1.0(8)	***24d (0,1/4,1/4)*** 1.00 Ru, 0.44(9)
Ru2; Occ., U_{eq} (B_{iso})	***6h (x,y,1/4)*** x = 0.8300 ; y = 0.6600 0.416(6) Ru, 0.5 0.584(6) Al, 0.5	***4a (0,0,0)*** 1.00 Ru, 0.23(10)

main phase maxima in the diffraction pattern at high diffraction angles.

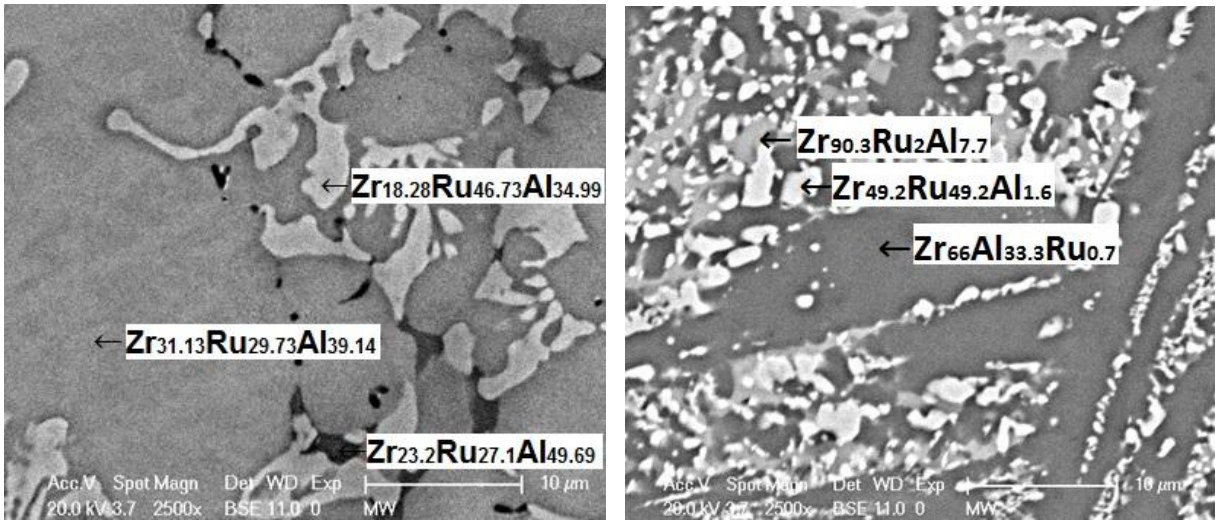
The structural parameters of the phase were refined for a sample of the same alloy obtained immediately after induction melting. The calculated cell parameter is equal *a* = 1.227107(11) nm. Similar to the annealed alloy, partial occupation of the Al atomic positions with Ru atoms resulted in a slight deviation from the initial stoichiometric ratio.

In the initial alloy, the diffraction peaks demonstrate the almost identical intensity ratio of the reflections as in the annealed alloy at 900 °C. The phase density does not significantly differ before and after annealing, with values of 6.251 and 6.211 g/cm³, respectively. This indicates to sufficiently high phase stability and the absence of structural transformations in the studied temperature range.

The structural parameters of the phase with $MgZn_2$ type of structure were refined based on the annealed alloy with the composition $Zr_{30}Ru_{30}Al_{40}$. The alloy was obtained as a three-phase system at 900 °C. In addition to the main phase, corresponding to the phase with $MgZn_2$ ST (Table 1), an amorphous halo and peaks from an unidentified crystalline phase were also present in the diffraction pattern. SEM analysis results (Fig. 4*b*) are in agreement with the XRD data. It indicates that the alloy consists of three phases. According to the data, the main phase has an integral elemental composition of ($Zr_{31.13}Ru_{29.73}Al_{39.14}$), which is close to the initial composition of the alloy. However, it should be noted that this phase is inhomogeneous throughout the volume of the investigated alloy, which may indicate the presence of a homogeneity region.

Thus, the cell parameters of the phases we have established differ significantly from those reported previously. Moreover, based on the observed splitting of the peaks and the visual inhomogeneity of the areas corresponding to these ternary phases in the micrographs, it can be suggested that both phases exist in the homogeneity regions. Literature data indicate that these types of phases indeed tend to exhibit extended homogeneity regions. Additionally, SEM and elemental analysis of the $Zr_{66.6}Ru_{11.1}Al_{22.3}$ alloy (Fig. 4*b*), which shows equilibrium in the Zr-rich region of the phase diagram between the solid solution Zr, the Zr_2Al compound, and the ZrRu phase, always shows the presence of an additional third component. For instance, Zr_2Al was obtained with the composition $Zr_{66}Al_{33.3}Ru_{0.7}$, and ZrRu, instead of the 50:50 ratio, contains an additional 1.6 at. % Al. Based on these results, it can be assumed that atoms of all three elements of this system are capable to substituting of each other in the crystalline lattices.

Similar crystal structures and phase formation patterns to those we identified have also been observed in systematic studies of the Zr–Ru–Ga system [9]. In this system, three ternary phases were identified, isostructural



a b

Fig. 4. Microstructure and EDX analysis data of the $Zr_{30}Ru_{30}Al_{40}$ (*a*) and $Zr_{66.6}Ru_{11.1}Al_{22.3}$ (*b*) alloys annealed at 900 °C.

to the structural types $MgZn_2$ and Th_6Mn_{23}, which form significant homogeneity regions. It is worth noting that in the $MgZn_2$ structure type, two compounds crystallise: with Ru/Ga substitution $ZrRu_xGa_{2-x}$ ($0.60 < x < 0.96$) [9] and Zr/Ga $Zr_{1-x}Ga_xRu_2$ ($x = 0.18$) [10]. Additionally, the binary phase of the CsCl structure type in the Zr–Ru–Ga system is characterised by its own homogeneity region. In contrast, in the Zr–Ru–Al system, the CsCl phase structure forms continuous solid solutions along an isoconcentrate at 50 at. % of Ru. This may be related to the identical structure types of compounds. This distinction from the Zr–Ru–Ga system (where the ZrGa phase ST is MoB) allows for complete mutual substitution of Al and Zr atoms, despite the relatively large difference in their atomic radii.

Comparing the obtained results with literature data, as well as observing the splitting of diffraction maxima, some chemical inhomogeneity in microsections corresponding to these phases, and deviations of the calculated phase composition from the nominal values, indicate the presence of homogeneity regions in both phases — Th_6Mn_{23} and $MgZn_2$. This assumption aligns with reported homogeneity regions for the corresponding structures in related systems [9-11].

Conclusions

Based on X-ray diffraction and EDXS data, a partial isothermal section of the phase diagram for the Zr–Ru–Al system at 900°C was constructed.

The existence of a continuous solid solution based on binary phases of the CsCl structure type (ZrRu-RuAl) was established, forming along isoconcentrate of 50 at. % Ru.

Structural parameters for the Th_6Mn_{23} and $MgZn_2$ phases were clarified.

Deviations of the calculated compositions from the nominal ones and the cell parameters from those previously reported, as well as the explored microstructural inhomogeneities, suggest the possibility of the existence of homogeneity regions.

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О. Швед, С. Мудрий

Фазові рівноваги та кристалічні структури фаз у системі Zr-Ru-Al за 900°C

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Систему Zr–Ru–Al досліджено за 900 °C методами X-променевої дифракції та скануючої електронної мікроскопії. Встановлено низку фазових рівноваг в цій системі за вмісту Al ≤ 55 ат. %. Підтверджено існування двох тернарних сполук: $ZrRu_xAl_{2-x}$ з гексагональною структурою типу $MgZn_2$ (просторова група (ПГ) *P6₃/mmc*): a = 5,2225(5), c = 8.1980(8) Å та кубічної $Zr_6Ru_{7+x}Al_{16-x}$ (x = 0.58) структурного типу Th_6Mn_{23}: a = 12,27655(8) Å. Вздовж ізоконцентрати за 50 ат. % Ru виявлено неперервний твердий розчин на основі бінарних сполук RuAl та ZrRu зі структурою типу CsCl (ПГ $Pm\bar{3}m$).

Ключові слова: фазові рівноваги, кристалічна структура, X-променева дифракція, сплави цирконію з перехідними металами.