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Effect of rapid quenching on phase formation of Zr–Al–Ni–Co–Cu high-entropy alloy

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In present work, the effect of rapid quenching on the phase formation process of high entropy Zr–Al–Ni–Co–Cu alloy was investigated. It is shown that the basis of the rapidly quenched alloy is the Laves phase ZrCoAl, the solid solution $Cu_{0.6}ZrCo_{0.4}$ and the ZrNiAl phase. The exothermic reaction in rapidly quenched sample was found to occur at 960–980 K. The activation energy of this reaction is 293 ± 6 kJ/mol. It is shown that rapid quenching leads to structural changes, thus changing the thermal stability of the Zr–Al–Ni–Co–Cu alloy.

Keywords: high-entropy alloys, Laves phase, zirconia, aluminum, transition metals.

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Owing to their mechanical properties (strength, microhardness, and plasticity) and high corrosion resistance, high-entropy alloys (HEAs) are being studied extensively in recent years [1]. A special place among HEAs is occupied by compositions containing transition metals and aluminum. For example, the structure and mechanical properties of multicomponent alloys $Al_{15}Zr_{40}Ti_{28}Nb_{12}Cr_5$, $Al_{15}Zr_{40}Ti_{28}Nb_{12}Mo_5$, and $Al_{15}Zr_{40}Ti_{28}Nb_{12}Si_5$ were examined in [2]. The formation of amorphous phases in the production of rapidly quenched high-entropy alloys in the form of ribbons and rods [3] is one of the promising research directions. High-entropy metallic glasses form a separate class of promising materials that potentially combine the advantages of amorphous alloys and HEAs [4–8]. Zhang et al. have demonstrated recently [4] that high-entropy alloys $(Al_{1/4}Ni_{1/4}Zr_{1/4}Co_{1/4})_{100-x}Y_x$ ($x = 16-28$ at.%) may be produced in the form of amorphous ribbons. The mechanical properties of amorphous zirconium alloys are also being studied extensively in recent years. Specifically, the authors of [9] have examined bulk amorphous alloy $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$. Thus, it can be concluded that alloys synthesized by rapid quenching and containing zirconium (40 at.% or more), aluminum (15–20 at.%), and transition metals are promising materials, and the investigation of phase formation processes in them is relevant. The aim of the present study is to produce Zr–Al–Ni–Co–Cu HEAs by electric arc melting and vacuum suction and assess the influence of quenching rate on phase formation and thermal stability of the alloy. The novelty of this study lies in the fact that the Zr–Al–Ni–Co–Cu composition has not been discussed yet, and its preparation, structure, and thermal reactions under heating are being examined for the first time.

The $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloy was produced by electric arc melting in a protective argon atmosphere from pure components (mass%): Zr (99.99), Al (99.95), Ni (99.9), Co (99.9), and Cu (99.95). It was remelted five times to ensure a uniform distribution of elements. The prepared samples in the form of ingots 20 mm in diameter and 12 mm in height were used to obtain rapidly quenched rods by vacuum suction into a copper mold. These rods were 3 mm in diameter and 50 mm in length. Following the preparation of samples of the initial alloy and rapidly quenched rods, their chemical composition was studied using a SpectroFlame Modula S atomic emission spectrometer with inductively coupled plasma. It was found in these experiments that the composition of the obtained samples differs by no more than 1 at.% from the nominal one in each component. The phase composition of samples was determined using a D8 ADVANCE diffractometer (CuK_α-radiation; 40 kV; 40 mA; Göbel parabolic mirror; VÅNTEC-1 position-sensitive detector; β-filter). The DIFFRACplus EVA package and the ICDD PDF4 (2021) database [10] were used in phase analysis. Full-profile Rietveld analysis was performed in TOPAS [11]. The morphology of the obtained samples was studied with a TESCAN Mira3 LMU transmission electron microscope. Differential scanning calorimetry (DSC) with a NETZSCH STA 409 PC analyzer was used to determine the characteristic temperatures of the alloy samples. Experiments for the initial alloy were carried out in the regime of heating with subsequent cooling at a rate of 10 K/min in a protective argon atmosphere in Al_2O_3 crucibles. Experiments for rapidly quenched rods were performed at heating rates of 10, 20, and 40 K/min. The analyzer was pre-calibrated against the melting points of pure indium, tin, aluminum, gold, and nickel.

The diffraction patterns of the initial and rapidly quenched $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloys are shown in Figs. 1, *a, b*, and the detected phases, their parameters, and the results of full-profile Rietveld analysis are listed in the table.

It was found that the initial alloy consists of two main phases based on solid solutions: ZrCoAl (Laves phase) and $Cu_{0.6}ZrCo_{0.4}$. This has never been reported before.

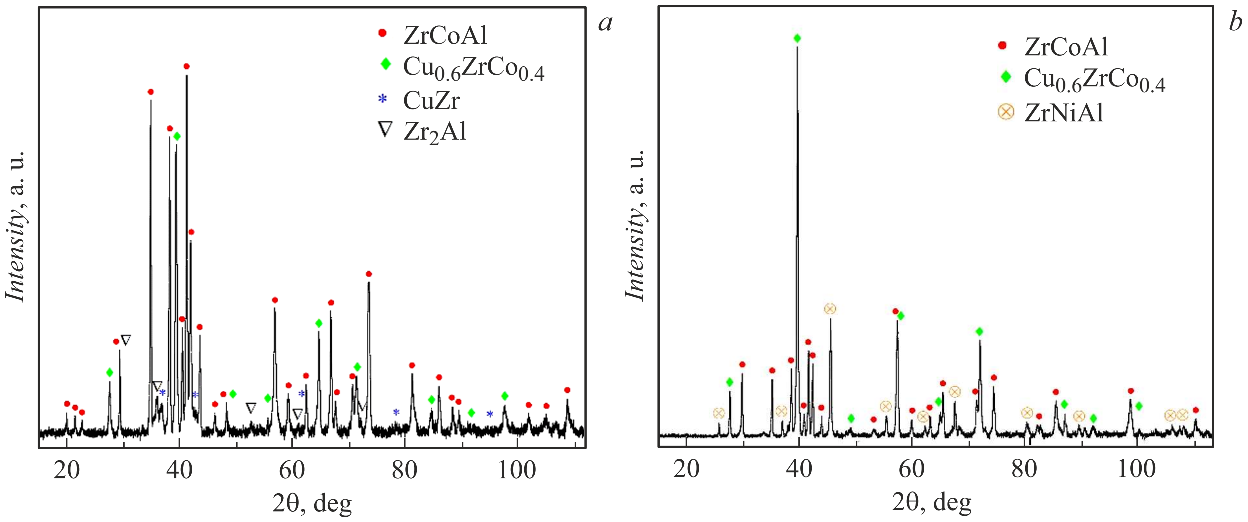

Figure 1. Diffraction patterns of initial (*a*) and rapidly quenched (*b*) $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloys.

Phase composition of the $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloy in its initial and rapidly quenched states

Phase	Space group	a, Å	c, Å	V, Å^3	Content, mass%
		Initial alloy			
ZrCoAl	$P6_3/mmc$	5.1496	8.3057	190.74	66.2
$Cu_{0.6}ZrCo_{0.4}$	Pm-$3m$	3.2361	–	33.89	23.3
$Cu_{1.74}Zr_{2.26}$	Fm-$3m$	4.2334	–	75.87	2.4
Ni	Im-$3m$	2.7769	–	21.41	2.8
Zr_2Al	$P6_3/mmc$	4.9000	6.2001	128.92	3.5
Zr_3Al	Pm-$3m$	4.3617	–	82.98	1.8
		Rapidly quenched alloy			
ZrCoAl	$P6_3/mmc$	5.1470	8.3216	190.92	35.9
$Cu_{0.6}ZrCo_{0.4}$	Pm-$3m$	3.2427	–	34.10	43.7
ZrNiAl	P-$62m$	6.9621	3.4632	145.37	20.4

An insignificant amount of binary intermetallic compounds of aluminum and copper with zirconium and a nickel-based solid solution were also detected. In its rapidly quenched state, the alloy has a significantly different phase composition: the ZrCoAl phase content is reduced almost twofold relative to the initial alloy, while the amount of the $Cu_{0.6}ZrCo_{0.4}$ solid solution phase increases. In addition, a solid solution based on the ZrNiAl phase forms during rapid quenching in the $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloy.

Figure 2 shows images of the surface of the obtained samples.

It was found that the main phases in the initial alloy form large dendrites up to 25–30 μm in size. Rapid heat removal, which was established in the process of vacuum suction of the melt into a copper mold, ensures a high rate of alloy crystallization, inhibiting the growth of dendrites. The obtained result is typical of rapidly quenched alloys, including zirconium-based ones [12].

DSC measurements were performed in order to determine the characteristic temperatures and the type of thermal reactions during heating of the obtained samples. In addition, special attention was paid to the analysis of DSC thermograms of the rapidly quenched $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ rod. Thermograms of the obtained samples are shown in Fig. 3.

It was found that melting of the initial alloy is accompanied by several thermal reactions, which may be associated with the processes of decomposition of formed solid solutions. It was established that the key differences between the thermograms of rapidly quenched and initial alloys consist in the emergence of an exothermic reaction at a temperature of 960–980 K, a slight reduction in the solidus temperature, and the lack of a second endothermic peak in the melting process ($T = 1350$–1400 K). The observed exothermic reaction may be associated with decomposition of the hexagonal phase of ZrNiAl into stable binary intermetallic compounds Zr_3Al, Zr_2Al and a nickel-based solid solution. The DSC data obtained at different heating rates (Fig. 3, *b*) were used to calculate the activation

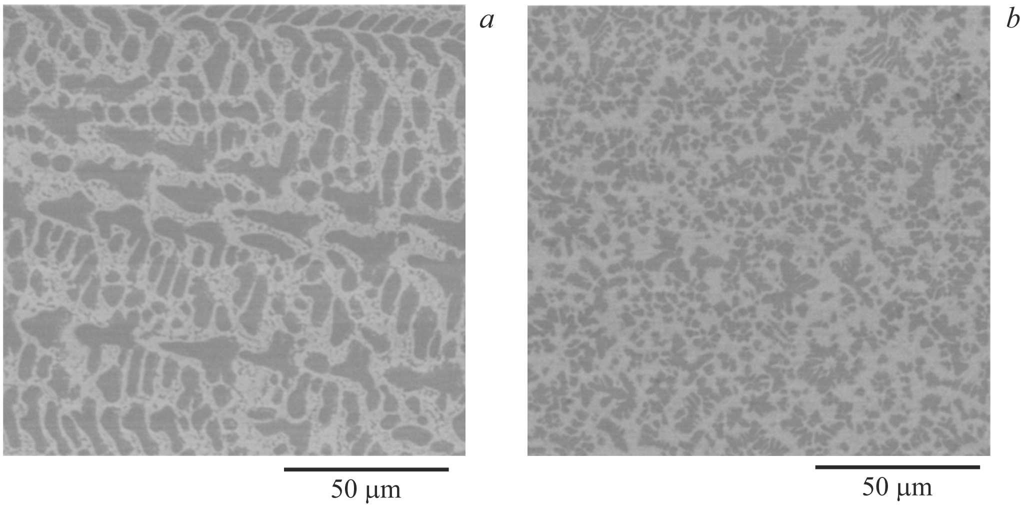

Figure 2. Morphology of the $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloy in its initial (*a*) and rapidly quenched (*b*) states.

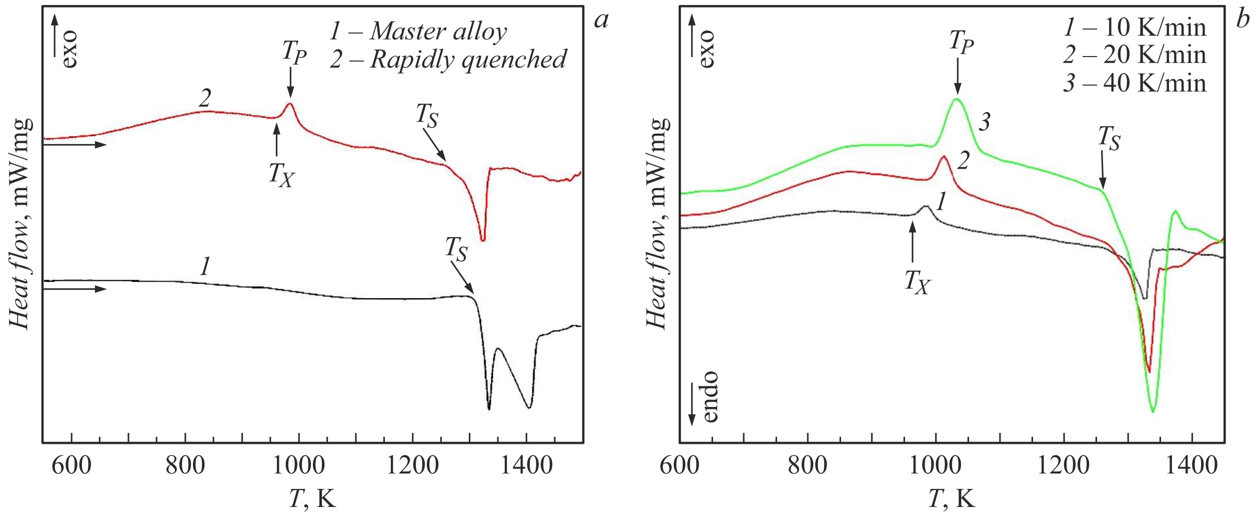

Figure 3. *a* — DSC thermograms of the initial and rapidly quenched $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloys under heating at a rate of 10 K/min; *b* — DSC thermogram of the rapidly quenched $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloy at various heating rates. T_S — solidus, T_X — exothermic reaction onset temperature, and T_P — reaction peak temperature.

energy by the Kissinger method:

$$\ln \frac{\beta}{T_P^2} = \frac{E}{RT_P} + \text{const},$$

where β is the heating rate, T_P is the peak temperature, and R is the universal gas constant.

The activation energy of the exothermic reaction is 293 ± 6 kJ/mol. The reproducibility of this reaction at different heating rates ($T_P = 984$, 1012, and 1032 K at $\beta = 10$, 20, and 40 K/min, respectively) was established. Thus, it was demonstrated that rapid quenching of the $Zr_{40}Al_{20}Ni_5Co_{15}Cu_{20}$ alloy leads to a significant change in its thermal stability, which may be associated with the decomposition of ZrNiAl. The obtained results may find application in the design of high-temperature sensors based on the Zr–Al–Ni–Co–Cu alloy and serve as a basis for further research into Zr-based HEAs.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] B.R. Gelchinski, I.A. Balyakin, A.A. Yuryev, A.A. Rempel, Russ. Chem. Rev., **91** (6), RCR5023 (2022). DOI: 10.1070/RCR5023.

[2] Y. Li, P.K. Liaw, Y. Zhang, Metals, **12** (3), 496 (2022). DOI: 10.3390/met12030496

[3] H. Ding, X. Bao, Z. Jamili-Shirvan, J. Jin, L. Deng, K. Yao, P. Gong, X. Wang, Mater. Des., **210**, 110108 (2021). DOI: 10.1016/j.matdes.2021.110108

[4] Z. Zhang, S. Zhang, Z. Jing, C. Chen, X. Liang, Intermetallics, **165**, 108164 (2024). DOI: 10.1016/j.intermet.2023.108164

[5] H. Sonomura, K. Katagiri, T. Ozaki, Y. Hasegawa, T. Tanaka, A. Kakitsuji, Mater. Lett., **353**, 135264 (2023). DOI: 10.1016/j.matlet.2023.135264

[6] J. Chi, H. Hu, H. Jin, Y. Ma, X. Su, J. Non-Cryst. Solids, **625**, 122777 (2024). DOI: 10.1016/j.jnoncrysol.2023.122777

[7] J.S.C. Jang, L.J. Chang, T.H. Hung, J.C. Huang, C.T. Liu, Intermetallics, **14** (8-9), 951 (2006). DOI: 10.1016/j.intermet.2006.01.012

[8] H.-R. Wang, Y.-L. Gao, Y.-F. Ye, G.-H. Min, Y. Chen, X.-Y. Teng, J. Alloys Compd., **353** (1-2), 200 (2003). DOI: 10.1016/S0925-8388(02)01208-2

[9] C. Liu, V. Roddatis, P. Kenesei, R. Maaß, Acta Mater., **140**, 206 (2017). DOI: 10.1016/j.actamat.2017.08.032

[10] S. Gates-Rector, T. Blanton, Powder Diffr., **34** (4), 352 (2019). DOI: 10.1017/S0885715619000812

[11] A.A. Coelho, J. Appl. Cryst., **51** (1), 210 (2018). DOI: 10.1107/S1600576718000183

[12] Q. Jing, Y. Zhang, D. Wang, Y. Li, Mater. Sci. Eng. A, **441** (1-2), 106 (2006). DOI: 10.1016/j.msea.2006.08.109

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