Changes in the phase composition depending on the sizes of Zr–based bulk alloys

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Abstract. The crystalline phases formed during quenching of Zr–based amorphizing alloy; depending on the sample, sizes and position in it, have been identified. The samples of amorphous, partially crystalline, and crystalline alloys have been obtained by levitation melting and quenching into a copper mould of variable diameter.

1. Introduction
The studies of bulk amorphous alloys are relevant since these alloys have a number of unique properties, such as high strength, high elastic limit, good corrosion resistance and wear resistance [1, 2]. Zr–based bulk amorphous alloys are interesting in that they have high glass–forming ability and thermal stability, which has been known long since [3, 4]. The high degree of Zr oxidation, the required high cooling rate, and a number of other reasons significantly complicate the process of obtaining bulk amorphous alloys. Therefore, the creation and development of a method for obtaining such samples with an amorphous structure is a very laborious task. Upon obtainment at a rate insufficient for complete amorphization, crystalline phases may be formed that differ from the phases formed during decomposition of the amorphous phase. The present work describes the method of manufacturing zirconium bulk amorphous alloys, as well as the analysis of the crystalline phases arising at cooling rates insufficient for complete amorphization.

2. Experimental
The samples of a bulk alloy of Zr_{55}Cu_{30}Al_{10}Ni_{5} were obtained by levitation melting and quenching into a copper mould of variable diameter in a levitation melting unit. The melting and casting were carried out in ultrapure argon atmosphere. We used moulds with a hole in the form of a 8 mm diameter rod and with a channel in the form of a cone. After smelting, the samples were cut into disks with a thickness of 1 mm using an electrical discharge machine. The position of the samples selected for the analysis is demonstrated in Figure 1. After cutting, the samples were ground and examined by X–ray diffraction (XRD) on a Siemens D–500 diffractometer using CoKα radiation. The crystalline phases were analyzed using the JCPDS database.

3. Results and discussion
Figure 1 shows the view of the sample and indicates the position of the sections whose structure was analyzed. The corresponding X–ray diffraction patterns of the samples from these sections are presented in Figure 1 b, c, d, e, f. In the obtained X–ray diffraction patterns it can be seen
that the structure is amorphous in a disk with a diameter of 3 and 4.8 mm. The corresponding X–ray diffraction pattern contains only a diffuse halo, no peaks from the crystalline phases are observed. In the X–ray diffraction pattern of the sample with a diameter of 5 mm, peaks of the crystalline phase in the background of an amorphous halo were detected. In the X–ray diffraction patterns of samples with diameters of 8 and 11 mm, there are only peaks from the crystalline phases.

The phase analysis for X–ray diffraction patterns of cross–sections of 8 and 11 mm was performed using the JCPDS database.

![Figure 1. View and cross–sections of cone; a) appearance of a cone; b) X–ray diffraction pattern, cross–section Ø is 3 mm; c) X–ray diffraction pattern, cross–section Ø is 4,8 mm; d) X–ray diffraction pattern, cross–section Ø is 5 mm; e) X–ray diffraction pattern, cross–section Ø is 8 mm; f) X–ray diffraction pattern cross–section Ø is 11 mm](image-url)
The phases were identified in the X-ray diffraction patterns. It was found that crystalline phases are present in the 5 mm diameter sample along with the amorphous matrix: orthorhombic Cu$_{10}$Zr$_7$ (Aba2a(41)) $a=9.347$, $b=9.322$, $c=12.67$) and tetragonal CuZr$_2$ ((I 4/m 2/m 2/m) $a=b=3.22$, $c=11.13$). The same crystalline phases are observed in the samples with a diameter of 8 and 11 mm, the same. The amorphous phase is not detected. In orthorhombic Cu$_{10}$Zr$_7$ phase, small deviations of interplanar spacing relative to the tabular values were observed. Such deviations may be due to the fact that Al atoms which are present in the alloy can partially replace Cu atoms. Their arrangement in the lattice can be carried out in a certain way and lead to anisotropic deformation of the lattice. The sizes of Ni and Cu atoms are close to each other, that is why their substitution does not affect the lattice parameters.

It should be noted that the XRD showed no presence of NiZr$_2$ phase, which is formed as a result of heat treatment of an amorphous alloy of the same composition [5]. This fact is the further evidence of that the identified crystalline phases were formed during quenching, not during heating of the amorphous phase.

The similar changes in the phase composition were observed in rod-like samples depending on the location (Fig. 2, 3).

![Figure 2](image)

**Figure 2.** a) View of a rod; b) Disk Ø is 8 mm; c) X-ray diffraction pattern

Figure 2 shows X-ray diffraction patterns of the start tip, middle, and end tip of the smelted rod. They demonstrate that at the start tip of the rod – the structure is mainly amorphous, but there is a weak peak in the amorphous halo. In the middle the structure also corresponds to the amorphous one, however, the peak at the top of the halo becomes wider. In the end tip there is the crystal structure. Two phases were also determined using the phase analysis: orthorhombic Cu$_{10}$Zr$_7$ and tetragonal CuZr$_2$. The reason for this might seem to be quite obvious it is insufficient cooling during quenching into the mould, due to the large diameter of the latter. However, some interesting results were obtained during the work. The structure of one of the smelted rods was different from that of the others. Figure 3 shows X-ray diffraction patterns
of this rod, from which it follows that the smelted rod is amorphous throughout the volume. Apparently, this was due to a different melt temperature, which is difficult to regulate during levitation melting.

![Figure 3. a) View of a rod; b) Disk Ø is 8 mm; c) X-ray diffraction pattern](image)

Thus, the samples of amorphizing Zr_{55}Cu_{30}Al_{10}Ni_{5} alloy have been obtained by quenching the melt into copper molds. The crystalline phases formed during quenching have been identified. The dependence of the phase composition on the position in the sample has been found. It has been assumed that the presence of NiZr_{2} phase may serve as an indicator of the decomposition of the amorphous phase.

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