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EFFECT OF NEODYMIUM AND ZIRCONIUM ON THE STRUCTURE OF CASTABLE MAGNESIUM ALLOY ML10 (NZ30K)

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Alloys of the Mg – Zn – Zr – Nd system with composition matching that of ML10 (NZ30K) and different contents of the main alloying components within the standardized range are studied. Four-component Mg – Zn – Zr – Nd phase diagrams are simulated, and the stages of crystallization of the alloys are considered. The structure of the alloys is determined in cast condition and after a T6 heat treatment. Fracture surfaces are analyzed. The distribution of the alloying elements in the structure is studied. The changes in the content of zirconium within the standardized range are shown to affect the grain size in the cast and heat treated states.

Key words: magnesium, magnesium alloys, crystallization, heat treatment, fracture, Themo-Calc, Mg – REM – Zr system.

INTRODUCTION

ML10 belongs to the group of refractory magnesium alloys of the Mg – Zn – Zr – REM system. The composition of ML10 is close to that of foreign alloy NZ30K but differs from the latter by a somewhat lower limiting content of neodymium (up to 3% in NZ30K) [1]. The chemical composition of alloy ML10 is presented in the Table 1 as standardized in GOST 2856–79.

The main alloying component of ML10 is neodymium with a purity of at least 87.5%; the other alloying elements are lanthanum, cerium, praseodymium and other REM [2], which places the alloy in the Mg – Nd – Zn – Zr system. Due to the presence of zirconium, the castings have a homogeneous fine-grained structure and good mechanical properties [2, 3]. Zirconium also possesses good refining properties, cleans the alloy from undesirable impurities and raises its corrosion resistance [4, 5]. The addition of zinc refines the grains in cast condition and thus raises the efficiency of the heat treatment, which elevates the yield strength and the creep resistance of the alloy [2, 3].

In cast condition, the structure of alloy ML10 is represented by grains of a solid solution of neodymium, zinc and zirconium in magnesium and a degenerated eutectic over grain boundaries, which has the form of veins of the intermetallic $Mg_{41}Nd_5$ phase [6, 7] sometimes identified as $Mg_{12}Nd$ [2, 3, 8, 9]. It should be noted that by the data of [10] both these phases may be detected in the structure of the alloy.

In cast condition, alloys of the Mg – REM – Zn – Zr system have low mechanical properties and corrosion resistance [5, 11]. For this reason, they are used as structural materials after a T4 or T6 treatment [12].

As a result of the heat treatment, the intermetallic phase first dissolves in the magnesium solid solution (Mg) and then precipitates in the form of fine particles as a result of artificial aging, which provides hardening. These particles are based on REM compounds with magnesium and other components of the alloy, and their distribution in the structure is not uniform [13].

Variation of the content of the main alloying elements in the alloy (within the standardized ranges) affects the structure and properties of articles in cast and heat treated states, which often causes their fracture under normal operating conditions. The causes responsible for fracture of cast articles due to reduced content of alloying elements have not been determined yet.

The aim of the present work was to study the effect of zirconium content on the process of crystallization, the cast structure and the distribution of alloying components in alloys of the Mg – Zn – Zr – Nd system of type ML10 (NZ30K) in cast and heat treated states and the effect of the content of neodymium and zirconium on the fracture behavior of the alloys.

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TABLE 1. Chemical Compositions of Magnesium Alloys

Alloy	Content of elements, wt.%									
	Main components			Impurities, at most						
	Nd	Zn	Zr	Al	Si	Fe	Ni	Cu	Be	Other
ML10[*]	2.2 – 2.8	0.1 – 0.7	0.4 – 1.0	0.020	0.030	0.010	0.005	0.030	0.001	0.12
0.3Zr	2.59	0.11	0.30	0.004	0.001	0.003	0.002	0.003	–	–
0.6Zr	2.73	0.38	0.59	0.004	0.002	0.004	0.001	0.003	–	–

[*] According to GOST 2856–79.

METHODS OF STUDY

We fabricated alloy ML10 from the following blend materials: alloy MTsr1N3 (Mg – 1% Zr – 3% Nd, GOST 2581–78), addition alloy MN (Mg – 25% Nd, TU 48-4-271–86), addition alloy L-4 (Mg – 15% Zr, TU 1714-002-00545484–99), and metallic zinc of grade Ts0 (99.98% Zn, GOST 3640–94).[2]

The metallographic analysis was performed with the help of a Carl Zeiss Axio Observer.D1m optical microscope (OM) and a Tescan Vega SBH3 scanning electron microscope (SEM) with an Oxford attachment for energy dispersive analysis. The grain structure of the alloy was uncovered by etching in a reagent consisting of 11 g picric acid, 11 ml acetic acid and 100 ml alcohol [14].

Polythermal sections were obtained with the help of the Thermo-Calc software by the CALPHAD method using the TTMG3 thermodynamic base.

RESULTS AND DISCUSSION

We studied two test alloys of the Mg – Nd – Zn – Zr system in cast condition and after a T6 heat treatment. The compositions of the alloys are given in Table 1.

Crystallization of Alloys of the Mg – Nd – Zn – Zr System

Figure 1 presents polythermal sections of the four-component Mg – Nd – Zn – Zr phase diagram in the region of existence of the alloys studied.

Alloy 0.3Zr (see the Table 1 and Fig. 1*a* and *b*) starts to crystallize upon precipitation of (Mg) solid solution from the melt at about 600°C; the crystallization finishes with formation of a binary (Mg) + $Mg_{41}Nd_5$ eutectic. A zirconium-base solid solution (Zr) appears in the alloy only in solid state as a result of decomposition of the magnesium-base solid solution.

Alloy 0.6Zr (see Table 1 and Fig. 1*c* and *d*) crystallizes in another way. At the liquidus temperature (about 710°C) primary crystals of (Zr) precipitate from the liquid. Crystals of a (Mg) solid solution start to form when the temperature attains 590°C. The crystallization finishes with precipitation of phase $Mg_{41}Nd_5$ by a eutectic reaction; the earlier precipitated zirconium should pass into the solution by a peritectic reaction and appear in the alloy only below 540°C as a result of decomposition of the magnesium-base solid solution. In the process of nonequilibrium crystallization, which accompanies the formation of the cast structure of the alloy, the peritectic reactions are suppressed completely or almost completely, which explains the presence of primary zirconium crystals in the cast structure.

When contained in the alloy in a concentration below 0.7%, zinc virtually does not affect the order of precipitation of phases in crystallization (Fig. 1*b* and *d*) but only widens insignificantly the equilibrium temperature range of the crystallization.

Formation of Cast Structure

Zirconium is one of the most effective elements refining grains of cast magnesium alloys due to restriction of grain growth [15, 16]. It is also known that the mechanism of formation of grains of magnesium-base solid solution in the process of solidification of the melt around primary crystals of the zirconium-base solid solution (Zr) intensifies the effect of grain refinement still more [17, 18]. A particle of (Zr) around which a crystal of a magnesium-base solid solution has grown in the cast structure of alloy 0.6Zr is presented in Fig. 2*a*. The occurrence of primary crystallization of the (Zr) solid solution during solidification should promote formation of a finer structure in alloy 0.6Zr than in alloy 0.3Zr.

Thus, the content of zirconium in the alloy (> 0.4%) enough for primary crystallization of phase (Zr) (Fig. 1*c*) should be a necessary condition for effective refinement of cast structure in alloys of the Mg – Nd – Zn – Zr system.

The distribution of elements in the structure of alloy 0.6Zr is presented in Fig. 2*b* – *e*. Like zirconium, neodymium is distributed in it nonuniformly and concentrates near grain boundaries, where phase $Mg_{41}Nd_5$ precipitates (Fig. 2*d*). Zinc behaves in a similar way and concentrates in the cast structure where neodymium does (Fig. 2*e*).

Metallographic Studies of the Alloys

Figure 3*a* and *b* present the structure of cast alloys. It can be seen that the casting produces similar structures, but the grains are finer in alloy 0.6Zr than in alloy 0.3Zr.

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[2] Here and below in the paper the content of elements is given in mass percent.

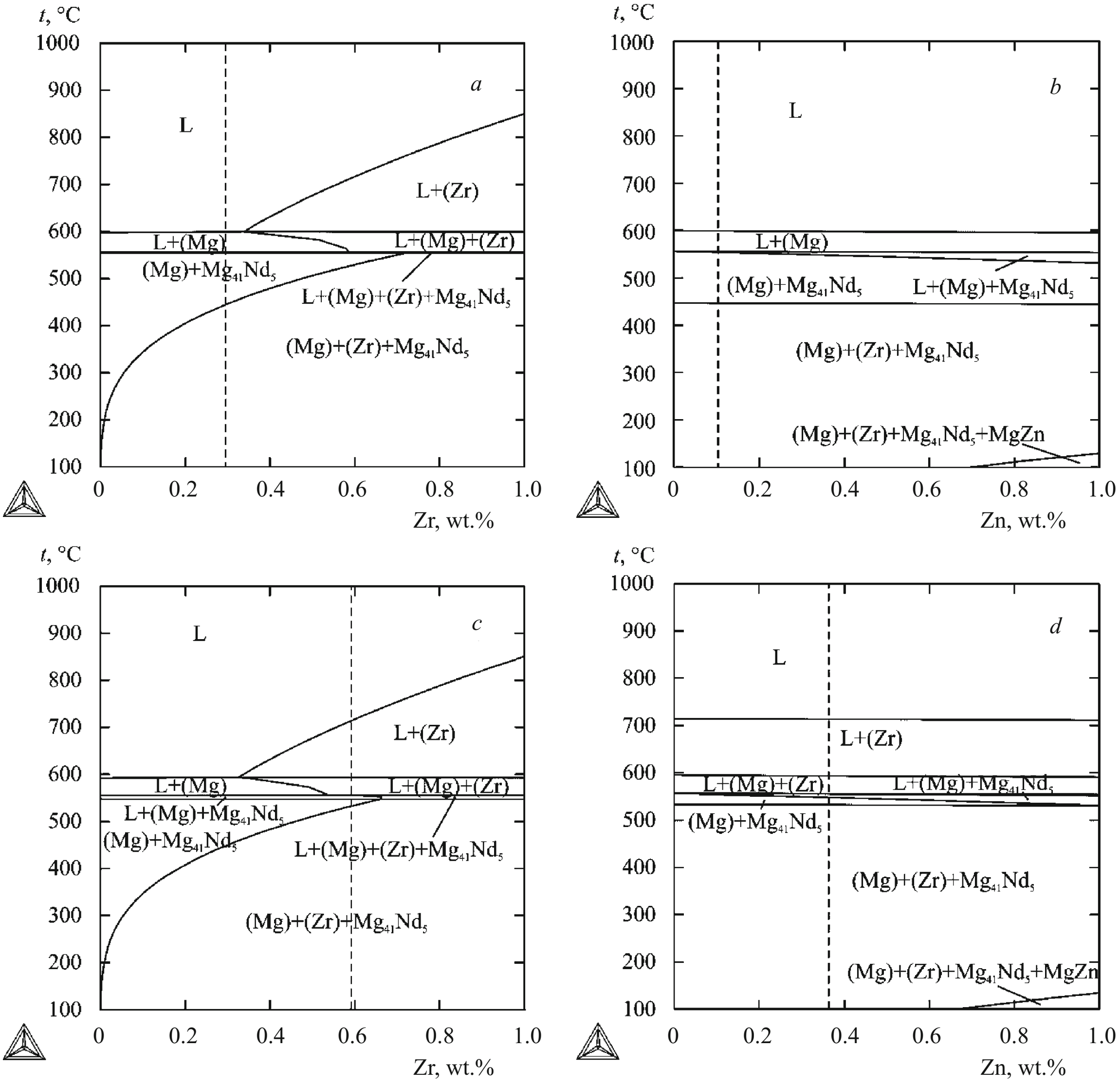

Fig. 1. Polythermal sections of the phase diagram of the Mg – Nd – Zn – Zr system (the vertical line presents the content of zirconium (*a, c*) and zinc (*b, d*) in the alloys): *a*) Mg – 2.59Nd – 0.11Zn – Zr; *b*) Mg – 2.59Nd – 0.3Zr – Zn; *c*) Mg – 2.73Nd – 0.38Zn – Zr; *d*) Mg – 2.73Nd – 0.59Zr – Zn.

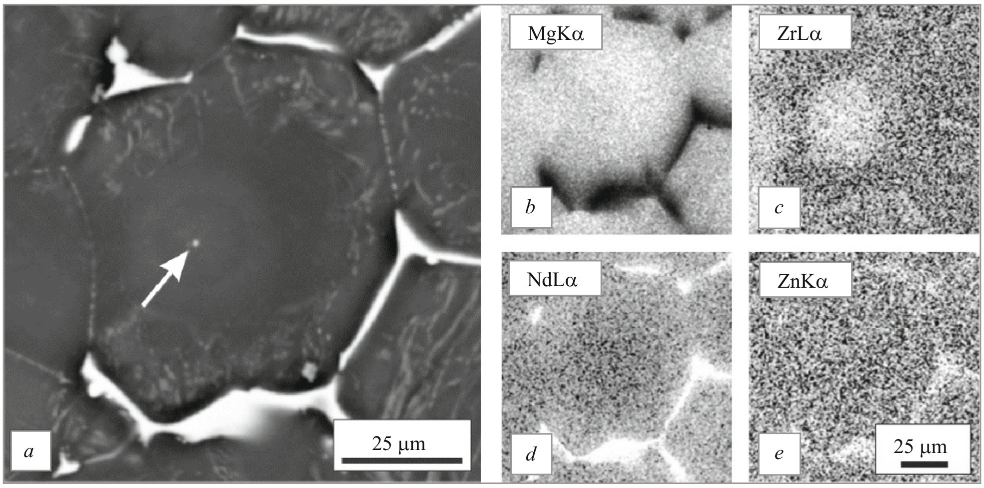

Fig. 2. Structure of alloy 0.6Zr in cast condition (SEM): *a*) zirconium particle in the center of a grain of magnesium-base solid solution (marked with the arrow); *b* – *e*) distribution of elements in the structure.

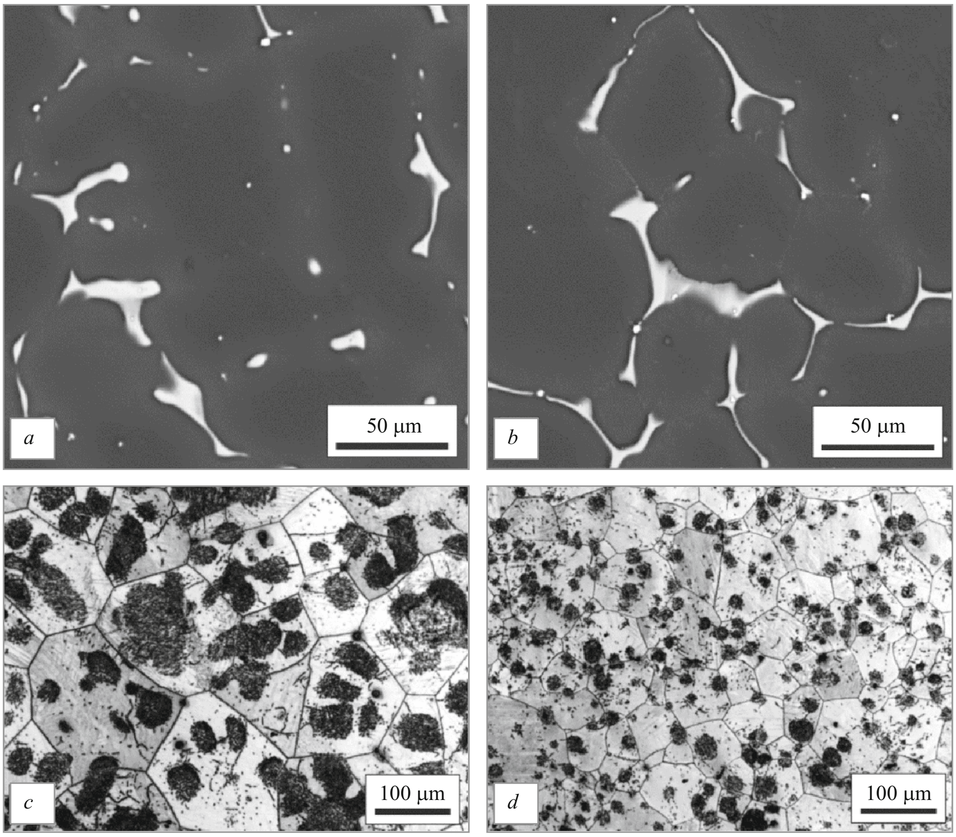

Fig. 3. Structure of magnesium alloys 0.3Zr (*a*, *c*) and 0.6Zr (*b*, *d*): *a*, *b*) in cast state (optical microscope): *c*, *d*) after a T6 heat treatment.

The microstructure of the magnesium alloys after a T6 heat treatment is presented in Fig. 3*c* and *d*. The mean grain size in alloy 0.3Zr is virtually twice larger than in alloy 0.6Zr (105 ± 10 μm and 51 ± 5 μm respectively). In addition, the structure of alloy 0.3Zr contains pores (Fig. 4) concentrated over grain boundaries, which are absent in alloy 0.6Zr. The heat treated alloys also differ in the kinds of precipitation of dispersoids. In alloy 0.3Zr they have a round shape partially repeating the configuration of cast grains. In alloy 0.6Zr dispersoids precipitate in the form of globular clusters randomly arranged in the structure. This is connected with the fact that the structure formed during the solidification of alloy 0.6Zr is finer than in alloy 0.3Zr with not developed dendrite arms. The grains of (Mg) have a more compact shape than in alloy 0.3Zr due to the limited possibility of growth.

Under a high magnification, we can observe colonies of particles of fine precipitates (Fig. 5*a* and *b*). In alloy 0.6Zr the size of the colonies of secondary precipitates and of the particles themselves is smaller than in 0.3Zr.

The microstructure of the specimens obtained by SEM is presented in Fig. 5*c* and *d*. The grain boundaries of the magnesium-base solid solution and the fields of fine precipitates formed as a result of the heat treatment are well discernible.

We performed a microscopic x-ray spectrum analysis (MXRSA) of different regions of the structures of the alloys with the aim to estimate the distribution of the alloying components in them (Fig. 6). It turned out that particles of zirconium-base solid solution (Zr) are often present in the center of dendrites (Fig. 6*b*) and grains (Fig. 6*d*) and are surrounded by a magnesium solid solution with an elevated content zirconium. This effect has been detected both in cast and in heat treated alloy 0.6Zr.

This phenomenon is not observed in alloy 0.3Zr, though particles rich with neodymium and, to a less degree, with zirconium are encountered in the volume of the (Mg) solid solution (Fig. 6*a*). In all probability, this is an effect of the presence of not fully dissolved particles of addition alloys in the alloy, because the composition of the alloy excludes precipitation of primary phases based on zirconium or neodymium (Fig. 1*a* and *b*). After the heat treatment, the structure of alloy 0.3Zr sometimes contains fine zirconium particles sur-

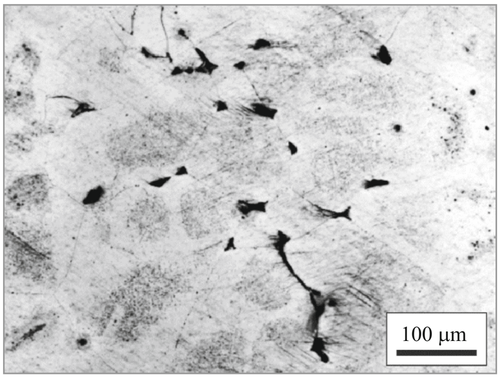

Fig. 4. Porosity over grain boundaries in alloy 0.3Zr (without etching).

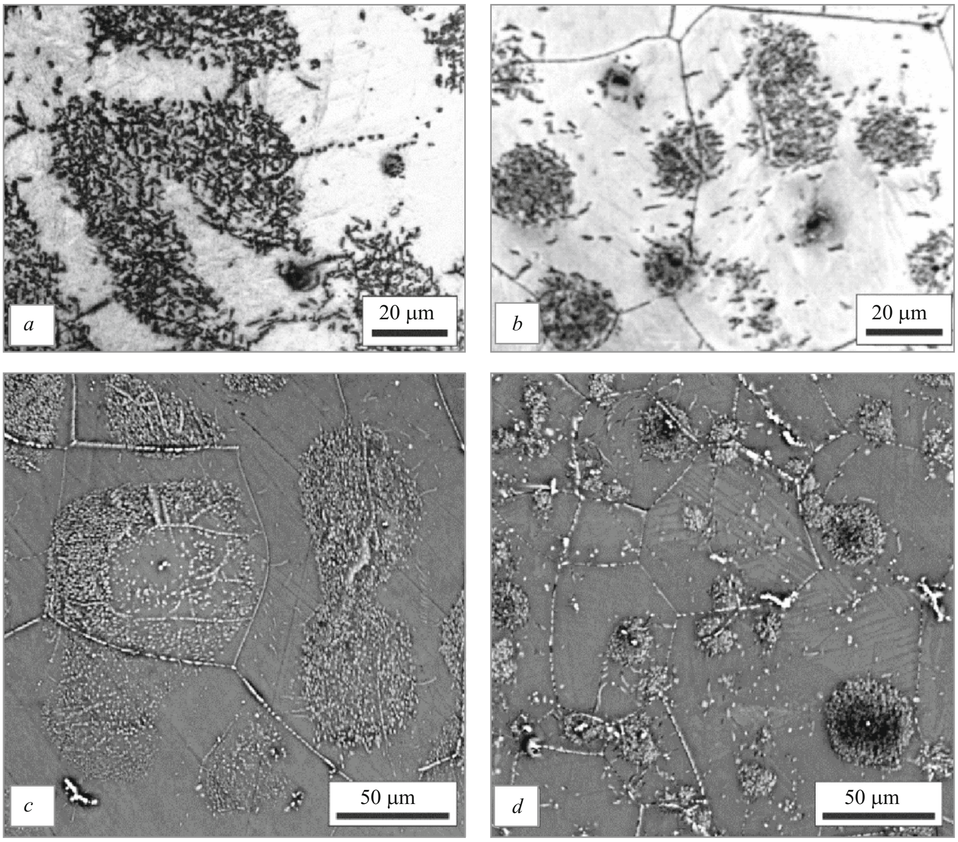

Fig. 5. Microstructure of magnesium alloys 0.3Zr (*a*, *c*) and 0.6Zr (*b*, *d*) after a T6 heat treatment.

rounded with precipitates of dispersoids but with a lower content of zirconium (Fig. 6*c*). Thus, we have not detected primary precipitates of zirconium in cast alloy 0.3Zr. In 0.6Zr zirconium was concentrated in the regions of precipitation of dispersoids; in the other parts of the structure its content was considerably lower.

In cast alloy 0.3Zr (Fig. 6*a*) neodymium and zinc are arranged at grain boundaries. In the cast specimen of 0.6Zr (Fig. 6*b*) neodymium is also present near grain boundaries in an amount exceeding considerably its average content in the alloy. In these regions the content of zinc is elevated. In the heat treated specimens zinc is distributed in the structure uniformly. In alloy 0.3Zr neodymium is chiefly concentrated in the zones of precipitation of dispersoids; in 0.6Zr it is distributed more uniformly, and its concentration near grain boundaries is elevated a bit (Fig. 6*c* and *d*).

Studies of Fractures

The specimens were fractured right before the study. A visual examination showed that the appearance of the fracture of alloy 0.3Zr was brittle and faceted; when rotated under a source of light the faces of the crystals produced numerous flares. The appearance of the fracture of alloy 0.6Zr was ductile. When rotated under a source of light, the visual picture was uniformly gray and lusterless.

The structures of the fractures studied by SEM are presented in Fig. 7. It can be seen that the fracture of alloy 0.3Zr has developed over grain boundaries (Fig. 7*a*). Alloy 0.6Zr has fractured partially over the bodies of grains (Fig. 7*b*).

We performed MXRSA of fracture surfaces of alloys 0.3Zr and 0.6Zr near grain boundaries. The content of neodymium over grain boundaries in alloy 0.6Zr was higher than the average, which was one of the causes of their strengthening.

CONCLUSIONS

1. Alloys of the Mg – Nd – Zn – Zr system fracture by the ductile mechanism at a specific content of zirconium and neodymium, which provides primary crystallization of the (Zr) solid solution and precipitation of an elevated content of neodymium over grain boundaries of the (Mg) solid solution. The presence of ≥ 0.4% Zr in the alloys promotes refinement of the structure and distribution of dispersoids about primary crystals of the (Zr) solid solution under aging.

2. The presence of zirconium exceptionally in the magnesium-base solid solution (Mg) does not provide good enough grain refinement. Only an alloy where primary crystals of zirconium-base solid solution (Zr) form during crystallization can have fine grains in cast and heat treated conditions.

3. When contained in the alloy in an amount less than 0.7%, zinc virtually does not affect the crystallization process and the precipitating phases; it only widens somewhat the equilibrium temperature range of the crystallization.

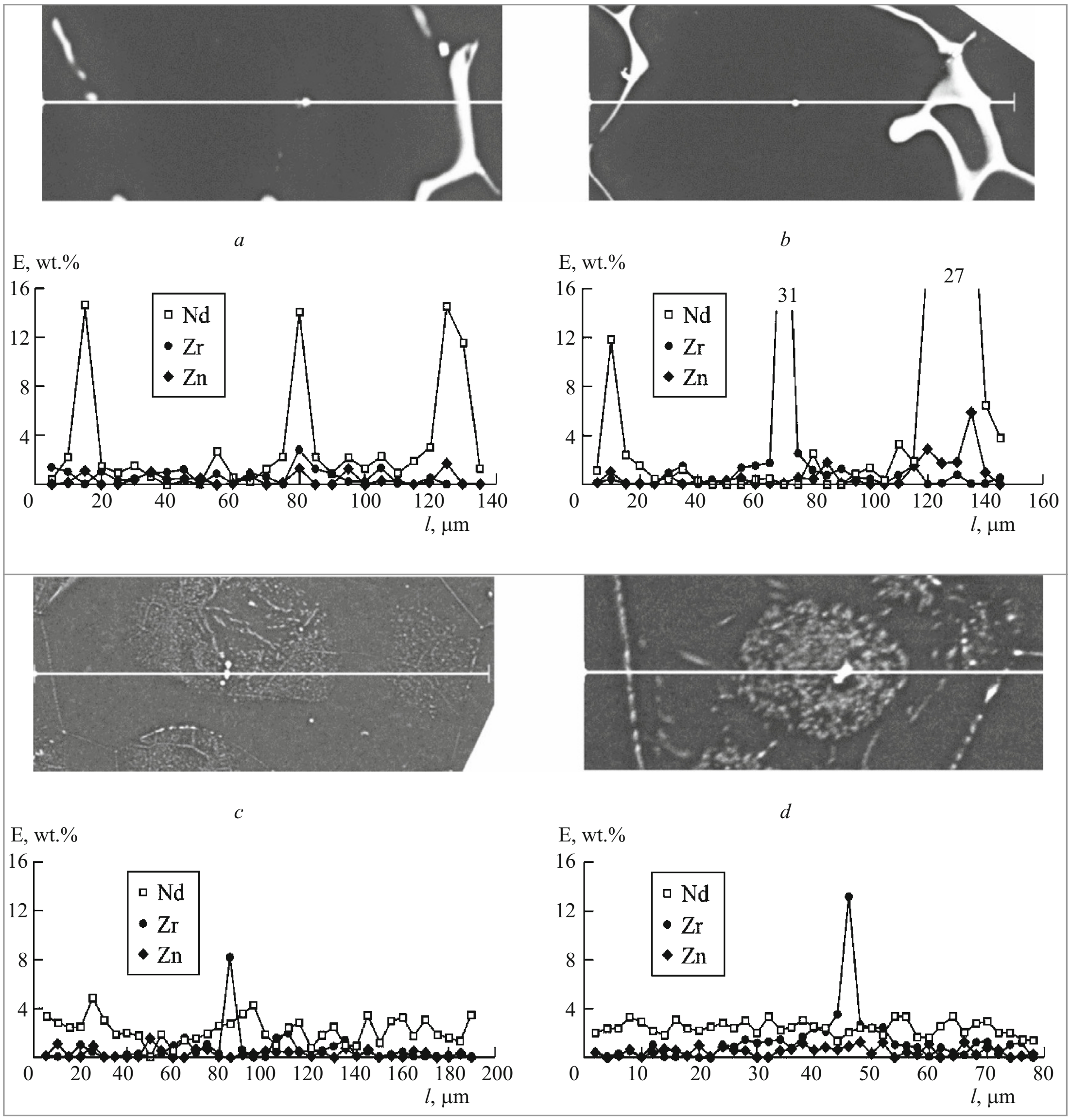

Fig. 6. Distribution of alloying elements in the structure of alloys 0.3Zr (*a*, *c*) and 0.6Zr (*b*, *d*) (over the light line, MXRSA): *a*, *b*) in cast condition; *c*, *d*) after a T6 heat treatment.

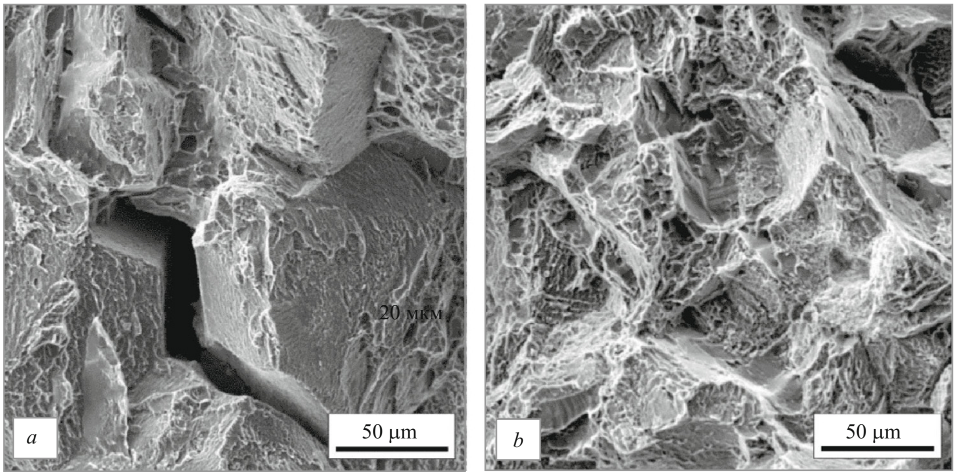

Fig. 7. Fractures of alloys 0.3Zr (*a*) and 0.6Zr (*b*) after a T6 treatment (SEM).

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