The strength increase by nano-scale particles precipitated during magnesium solid solution decomposition in magnesium alloys with the rare-earth metals of the yttrium group

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Abstract. Magnesium-base alloys attract a great attention as light structural materials, where economy of weight is of great importance. According to the last investigations, the highest strength properties of these alloys, can be obtained, when they contain some of the rare-earth metals. All of them belong to the yttrium group. Existence of the rare-earth metals in magnesium alloys enable to form in their structures small hard particles, which increase significantly strength of the alloys. The hard particles appear after the special heat treatments and should have the certain measurement and amounts. In this article the main results of some investigations are described, where the best conditions for the heat treatments of the magnesium alloys with high strength were established. The highest strength in the alloys was observed, when the hard particles were nano-scale in them with certain disposition in the structure.

1. Introduction.
Magnesium-base alloys are used successfully in various areas of modern technique. However, the most important applications of them are as light structural materials. Magnesium and its alloys have low density at enough high strength properties. Therefore, various constructions made of them are characterized by lower weight, as compared with those made of other well known metal materials, such as steels, copper, titanium and aluminum alloys. Application of magnesium alloys for constructions enable to decrease their weight and that can be very important. Especially, light magnesium alloys are attractive for aviation and space technique and now also for automobiles and other machines for overland transport. As all other structural materials, magnesium alloys should have as high as possible strength properties, which are commonly reached by using various alloying additives. Investigations performed last time indicated, that the highest strength properties in magnesium alloys at near room and elevated temperatures can be obtained, if the alloying additives for them are the certain rare-earth metals [1-3]. The rare-earth metals consist of 17 metals disposed in the same IIIB group of the Periodical table of chemical elements with
close chemical properties. In accordance with this, their actions on Mg demonstrate a number of the similar features. However, effects of each of the individual rare-earth metals on structure, behavior during heat treatment and properties of Mg can be quite different [4-6]. Especially, there is the apparent difference in action of them on magnesium between the rare-earth metals belonging to two parts of them, the cerium group including elements from La to Eu of the lanthanum row and the yttrium group consisting of Y and the next elements of the lanthanum row from Gd to Lu. There are also the established certain regularities in the solubility of the individual rare-earth metals in solid Mg, in decomposition rates of the Mg supersaturated solid solutions in the binary alloys with the different rare-earth metals and difference in hardening during decomposition of Mg supersaturated solid solutions with different rare-earth metals. In general, the binary Mg alloys with the rare-earth metals of yttrium group demonstrate the more solubility in solid magnesium, the slower Mg supersaturated solid solutions decompositions and the higher hardening during these processes in them. The main features of the binary Mg alloys containing individual rare-earth metals of the lanthanum row change successively with increase of their atomic numbers, but commonly there are the sharp transitions of them between the end of the cerium group and beginning of the yttrium one. Besides, the alloys with europium (cerium group) and ytterbium (yttrium group) do not conform to the overall regularities. The main features of yttrium are close to them of the other metals of yttrium group of the lanthanum row, except ytterbium. Investigations of Mg alloys with individual rare-earth metals indicated, that the alloys with the rare-earth metals of yttrium group can demonstrate the higher strength properties, than the alloys with the rare-earth metals of cerium group. Among the Mg alloys with rare-earth metals of yttrium group the highest strength properties were observed in those with gadolinium, terbium, dysprosium and yttrium [7].

The highest strength properties of Mg alloys with the rare-earth metals are achieved after the heat treatment intending for decomposition of the Mg supersaturated solid solutions in them up to the certain degrees. In this case the small hard particles, containing rare-earth metals are arisen in structures of the alloys, increasing their strength. In the performed works the size of these hard particles precipitated from Mg solid solutions up to maximum strengthening was determined. Along with this, the dispositions of these particles in structures of the alloys were considered, as well.

2. Experimental Procedure

Investigations were performed using several binary Mg alloys with rare-earth metals of yttrium group, Y, Gd, Tb and Dy. These rare-earth metals were selected, because in Mg alloys with them the highest strengthening effects were observed during Mg supersaturated solid solution decomposition. The contents of every rare-earth metals in the alloys were closed to most solubility of each metal among them in magnesium solid solution.

The initial materials in the investigations were metals, Mg of 99.96% purity, and Y, Gd, Tb and Dy of 99.83% purity (herein and after in mass.%). The alloys were prepared by melting the initial metals in the certain proportions in the electrical resistance furnace in crucibles of low-carbon steel under flux preventing Mg melts from burning at air. The flux consisted of mix with 38-46% MgCl2, 32-40% KCl, 3-5% CaF2, 5-8% BaCl2, 1.5% MgO, < 8% (NaCl+CaCl2). The prepared melts of the alloys were poured into mould of stainless steel obtaining ingots of 15 mm in diameter and 90 mm in length. They were solution treated by annealing at temperatures near the maximal solubility of rare-earth metals in solid Mg: 520-540ºC, for 6 hours followed by quenching into water of the room temperature aiming to obtain in the alloys the Mg supersaturated solid solutions. The ingots were then cut into specimens for heat treatment at various regimes at 200-250 ºC (ageing). The specimens after the heat treatment were used to establish properties and structures of the studied alloys and change of them depending on the ageing regimes.

The strength of the alloys was estimated by the hardness measurements and, respectively, strengthening of them during Mg solid solution decomposition was characterized by hardening. The hardness of the alloy specimens was measured by the Brinell method using the TSh-2M equipment (Russia) at a load of 250 kg
with a steel ball of 5 mm in diameter. The structure of the alloys after ageing was studied by optical microscopy (OM) with observation on optical microscope Reichert MeF (Austria) and by transmission electron microscopy (TEM) on the JEM-2100 microscope acting at accelerative tension of 200kV.

3. Results and discussion.

The typical changes of the alloy hardness during Mg solid solution decomposition in the studied alloys are presented in figure 1. The figure shows, that character of the hardness change with increase of ageing time is the same for the alloys of every system. At first, after short ageing time, the hardness of the alloys increases insignificantly. It is seen for the all alloys, but length of this initial stage of decomposition is different for different alloy systems and grows in order: Gd, Tb, Dy according to increase of their atomic numbers and Y after them. The next increase of the hardness during decomposition (the second stage) is steeper and continues up to the hardness maximum with softening then.

At these two stages of the Mg solid solution decomposition optical microscopy did not indicate any change in structures of the alloys, in spite of evident hardness increase of the alloys. The change in structures of the alloys at these stages of Mg solid solution decomposition could be recognized by transmission electron microscopy. At the first decomposition stage with insignificant hardening the precipitated particles enriched by rare-earth metals were not recognized actually, but appearance of decomposition was confirmed by the electron patterns. Typical one of them is presented in figure 2a. In this pattern along with the main round reflexes from Mg crystal lattice there are between them the weaker elongated superstructure reflexes. Disposition of the superstructure reflexes indicates ordering of the Mg crystal lattice of the Mg3Cd type [8].

At the second stage with the steeper hardening increase, the Mg solid solution decomposition could be recognized already in transition electron observation certainly. Existence of the precipitated hard particles containing rare-earth metals in this case in the alloys was established by pitted view of the Mg solid solution field in the electron microscope. The respective imagination at common magnification is presented in figure 2b. The higher magnification presented in figure 2c enables to see existence of the precipitated particles in Mg solid solution more in detail. The precipitated particles here are dark and of plate-like form. They are disposed by big planes along approximately three directions with three order symmetry in accordance with the symmetry of Mg crystal lattice. As one can see, the precipitated particles at this stage of the Mg solid solution decomposition are of nano-scale measurements, as example, for figure 2c about 20 nm. Figure 2d indicates electron pattern from the alloy structure presented in figure 2c. It shows the crystal lattice of the alloy to be oriented with its base plane being parallel to the big specimen surface. This is confirmed by the six order symmetry of the main Mg solid solution reflexes. Besides, electron pattern contains also a lot of small round substructure reflexes from precipitated particles disposed by certain order, which is typical for the solid solution decomposition in the binary Mg alloys with rare-earth metals of yttrium group at high hardening [5]. The strict dispositions between both reflex systems, from Mg solid solution and from precipitated particles, confirm coherency between their crystal lattices.
Figure 1. Hardness of Mg alloys with the rare-earth metals versus ageing time at 200 °C

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According to the electron patterns, the nano-scale precipitated particles formed at steep hardening stage of the Mg solid solution decomposition belong to metastable phase with the base-centred orthorhombic crystal lattice [5]. This was observed in every four mentioned binary Mg alloys with the rare-earth metals of yttrium group.

The next stages of the Mg solid solution decomposition after the hardening maximum were accompanied with increase of the measurements of the precipitated particles enriched by the rare-earth metals. Besides, along with the particles of the mentioned metastable phase in structures of the alloys the bigger particles were appeared. The large measurements and electron patterns enable to assume them to be the equilibrium phases. The bigger particles were also of the plate form and disposed in the alloy structures with the three-order symmetry, but at certain turn relative to plates of the metastable phases. The bigger particles of the equilibrium phase could be observed together with the increased particles of the metastable
phase with less measurement or after ageing at more long times and at more elevated temperatures without them. The typical structures of the alloys with the precipitated particles of the equilibrium phases are presented in figure 3. These particles could be observed as with transmission electron microscopy (figures 3a and 3b) and with optical microscopy (figure 3c).

![Electron pattern from Mg-22%Gd alloy, ageing 200 ºC, 1.5 h Zone [1-10]](image1)

![Microstructure of the Mg-24.0%Tb alloy, ageing 200 ºC, 32 h](image2)

![Microstructure of the Mg-24.0%Tb alloy, ageing 200 ºC, 32 h More magnification](image3)

![Electron pattern from Mg-24.0%Tb alloy, ageing 200 ºC, 32 h Zone [001]](image4)

**Figure 2.** Electron patterns and microstructures of the Mg alloys with the rare-earth metals after ageing before the hardness maximum TEM
4. Conclusions.
1. The performed investigations indicated, that the hardening effects during solid solution decomposition in Mg-base alloys with the rare-earth metals of yttrium group is connected with successive phase transformations in their structures.
2. There are three types of these phase transformations during the solid solution decomposition corresponded to the certain hardening stages. The first of them consists of the ordering of the Mg₃Cd type without clear precipitated particles accompanied with insignificant hardening. The second one is precipitation of the very small hard particles enriched with the rare-earth metals accompanied with steep hardening up to maximum. The precipitated particles at this stage belong to the metastable phases. At last, the third type of the phase transformation in Mg solid solution decomposition consists of precipitation of the biggest particles belonging to the equilibria phases with replacement of the small particles of the metastable phases at the third stage of the Mg solid solution decomposition after the hardening maxima.
3. The most strength increase of the Mg alloys with the rare-earth metals of yttrium group is achieved after precipitation from Mg supersaturated solid solutions of the alloys the nano-scale particles of the metastable phases (about 20 nm).

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