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THE REGULARITIES IN THE Mg-RICH PARTS OF THE PHASE DIAGRAMS, PHASE TRANSFORMATIONS AND MECHANICAL PROPERTIES OF MAGNESIUM ALLOYS WITH INDIVIDUAL RARE EARTH METALS [1)]

PRAWIDŁOWOŚCI BOGATYCH W Mg FRAGMENTÓW UKŁADÓW RÓWNOWAGI, PRZEMIAN FAZOWYCH I WŁASNOŚCI MECHANICZNYCH STOPÓW MAGNEZU I POSZCZEGÓLNYCH METALI ZIEM RZADKICH

Magnesium alloys containing individual rare-earth metals (RE) are interesting due their high strength properties. The strengthening effect of the RE added to Mg alloys is connected with respective phase diagrams, especially solubility of RE in solid Mg which changes regularly with increasing RE atomic number. This regularity is caused by favourable differences between atomic radii of individual RE and Mg. The higher solubility corresponds to less difference between atomic radii of RE and Mg. Nevertheless, solubility of RE of the yttrium subgroup in solid Mg is significantly more than that of RE of the cerium subgroup suggesting different electron interaction between Mg and RE of different subgroups when Mg solid solutions are formed. Decrease of the RE solubility in solid Mg with lowering temperature creates a possibility of Mg supersaturated solid solution decomposition accompanied by strengthening effect, which depends regularly on solubility value. Solubility of RE in solid Mg and Mg supersaturated solid solution decomposition are responsible for different strength properties of Mg alloys with different RE.

Keywords: Magnesium alloys. Rare-earth metals. Phase diagrams. Decomposition of supersaturated solid solution. Mechanical properties.

Stopy magnezu zawierające poszczególne metale ziem rzadkich (RE) są interesujące ze względu na ich wysokie własności wytrzymałościowe. Efekt umocnienia metali RE dodanych do Mg jest związany z odpowiednimi diagramami fazowymi, w szczególności rozpuszczalnością RE w stałym Mg, która zmienia się proporcjonalnie ze wzrostem liczby atomowej RE. Ta prawidłowość jest spowodowana korzystną różnicą pomiędzy promieniami atomowymi poszczególnych RE i Mg. Większa rozpuszczalność odpowiada mniejszej różnicy pomiędzy promieniami atomowymi RE i Mg. Niemniej jednak, rozpuszczalność RE z podgrupy itru w stałym Mg jest znacznie większa niż dla RE należących do podgrupy ceru wskazując na odmienne oddziaływania elektronowe pomiędzy Mg i RE w różnych podgrupach podczas tworzenia się roztworu stałego Mg. Obniżenie się rozpuszczalności RE w stałym Mg przy obniżaniu temperatury stwarza możliwość rozpadu przesyconego roztworu stałego Mg towarzyszącego efektowi umocnienia, który zmienia się proporcjonalnie do wielkości rozpuszczalności. Rozpuszczalność RE w stałym Mg i w rozpadzie przesyconego roztworu stałego Mg jest odpowiedzialna za różne własności wytrzymałościowe stopów Mg z poszczególnymi RE.

Magnesium alloys are widely used in industry as light structural materials where requirements of high strength combining with low density are of great importance. These requirements can be realized at most by using the individual rare-earth metals as alloying additives.

The individual rare-earth metals are used as an alloying additive for magnesium alloys for a long time. Initially they were used together in form of mishmetal with typical composition (in mass %): 50% Ce, 25% La, 15% Nd, 5% Pr and 1% of other RE [1, 2]. However, in fifties-sixties the different effects of La, Ce, Pr, and Nd on Mg was reliably established [1–3]. As a result, the special cast and wrought commercial magnesium alloys with neodymium were developed. These are the West alloy QE22A [4] and Russian alloys ML9, ML10, MA11, MA12 [5].

Some time later, the high strengthening effect of yttrium added to magnesium was discovered. This fact promoted investigations directed to develop-

ment of commercial magnesium alloys containing yttrium [6].

Taking into consideration tendency of significant improvement of magnesium alloys by individual rare-earth metals a number of investigations of them were conducted in Baikov Institute of Metallurgy and Materials Science (Moscow, Russia). The investigations included a study of the nature of strengthening effect of individual rare earth metals when they are added to magnesium and connecting the strengthening effect with the respective phase diagrams. The results of the investigations established regularities in the Mg-rich parts of the Mg-RE phase diagrams, the behaviour of the Mg-RE supersaturated solid solutions during decomposition, the connection between Mg-RE phase diagrams and the mechanical properties of the alloys. In this article the main results of these investigations combining with results of the investigations of other authors in the same directions are reviewed.

1. Phase diagrams

Nature of different influence of individual rare-earth metals on strength properties of magnesium was revealed in investigations of the Mg-RE binary phase diagrams. The investigations showed that the Mg sides of the Mg-RE phase diagrams are of the eutectic type with certain RE solubility in solid magnesium. There is only one exception of this rule for Mg-Sc system. The Mg-Sc phase diagram is of peritectic type in the Mg side, but the solubility of Sc in solid magnesium exists. The solubility of the rare-earth metals in solid Mg attracted the main attention in the investigations because it was considered to be responsible at most for strength properties and plasticity of the alloys.

Results of the solid solubility determination in the binary systems of magnesium with individual rare-earth metals are presented in Fig. 1 [7–9]. They enable us to note the following features.

1. The solubility of all rare-earth metals in solid magnesium decreases with lowering temperature suggesting the possibility of a Mg supersaturated solid solution and the decomposition of it during aging at lower temperatures.
2. The solubility of individual rare-earth metals in solid Mg turned out to be substantially different. The solubility of Eu and La is essentially zero whereas the solubility of Lu reaches about 40 mass % or about 9 at.%. But it is not the highest solubility in at. %. The highest solubility in at. % is shown by Sc, which is about 15%.

3. There is the certain regularity in the solubility change of the rare-earth metals of the lanthanide series with increasing their atomic number. With increasing atomic number the solubility of the RE of the lanthanide series successively increase with two exceptions for Eu and Yb which show significantly smaller solubility than their neighbours in the lanthanide series. The solubility of Y in solid magnesium is intermediate between that of Sm of the cerium subgroup and Gd of the yttrium subgroup of the rare-earth metals of the lanthanide series in mass and at. %. Solubility of Sc is in limits of that of the elements of yttrium subgroup in mass %, although it is the highest one in at. %.
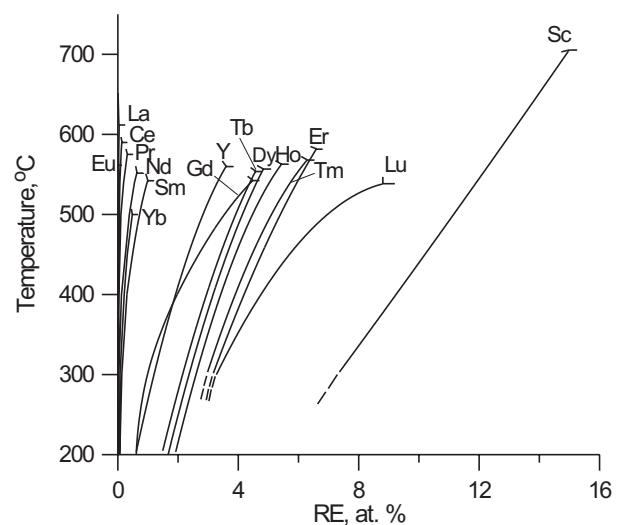

Fig. 1. Solubility of the individual rare-earth metals in solid magnesium

The above mentioned character of the solubility change with increasing atomic number of the rare-earth metals of the lanthanide series confirms the theory of solid solution formation between metals. According to the theory, the important factors for the solid solution formations are the difference between the atomic sizes of the components and lattice rigidity of them [10]. In the considered case the solubility correlates with change of the atomic size of the rare-earth metals [11]. The smaller the atomic size of the rare-earth metal, the higher the solubility in solid Mg. The correlation is justified also for Eu and Yb showing significantly less solubility in solid Mg that their neighbours in the lanthanide series because of their larger atomic sizes, and for Y with Sc which do not belong to the lanthanide series at all. The atomic radii of all the rare-earth metals (0.1640–0.2042 nm) are larger than that of Mg (0.1602 nm) (Table 1) and, therefore, decrease of the RE atomic radius results in a decrease of the difference between the lanthanide atomic radii and Mg, which promotes the increase of the

solubility in accordance with theory of the solid solution formation. The RE atomic radii decrease with increasing atomic number for the elements of the lanthanide series (lanthanide contraction) with exceptions for Eu and Yb which have larger atomic radii than their neighbours in the lanthanide series.

TABLE 1

Metallic radii of rare earth metals and magnesium [12]

Metal	Atomic number	Metallic radius, nm	Metal	Atomic number	Metallic radius, nm
Mg	12	0.1602	Eu	63	0.2042
Sc	21	0.1641	Gd	64	0.1802
Y	39	0.1801	Tb	65	0.1782
La	57	0.1877	Dy	66	0.1773
Ce	58	0.1825	Ho	67	0.1766
Pr	59	0.1828	Er	68	0.1757
Nd	60	0.1821	Tm	69	0.1746
Pm	61	0.1810	Yb	70	0.1940
Sm	62	0.1802	Lu	71	0.1734

Nevertheless, there is a peculiarity in solubility of the rare-earth metals in solid Mg which can not be explained by their atomic sizes. It is the steep increase of the solubility at the transition from the rare-earth elements of the cerium subgroup to the elements of the yttrium subgroup. This fact can be seen in significantly higher solubility of Gd (yttrium subgroup) as compared with solubility of Sm (cerium subgroup) although their atomic radii are actually the same (0.1802 nm) or in unusual high solubility of Yb (yttrium subgroup) having atomic radius 0.1940 nm as compared with solubility of La, Ce, Pr and Nd (cerium subgroup) having smaller atomic radii (in limits 0.1821–0.1877 nm)[2]. The steep increase of the RE solubility in solid Mg in the case of the elements of yttrium subgroup as compared with elements of the cerium subgroup can be explained by different electron interaction between RE atoms and Mg lattice during Mg solid solution formation with rare-earth metals of different subgroups. This explanation does not contradict, in general, the theory of the solid solution formation between metals, as well.

So, the solubility of the rare-earth metals in solid Mg show the certain similarity amongst the alloys with the RE of the same subgroup and difference amongst the alloys with RE of different subgroups. Such a kind of similarity and difference is observed also in behaviour of Mg-RE alloys during solid solution decomposition.

2. Decomposition of supersaturated solid solutions

The similarity and difference amongst the Mg-RE alloys of the same and different subgroups of the rare-earth metals are most clearly revealed in the kinetics of the solid solution decomposition. It is characterised in Fig. 2 by results of the hardness measurements of the alloys during aging at 200°C. They were obtained using binary alloys with RE contents shown on the hardness curves. The RE contents in the alloys were chosen to be near maximum solubility in solid Mg. The alloys were quenched after annealing near the eutectic temperatures near and simultaneously aged.
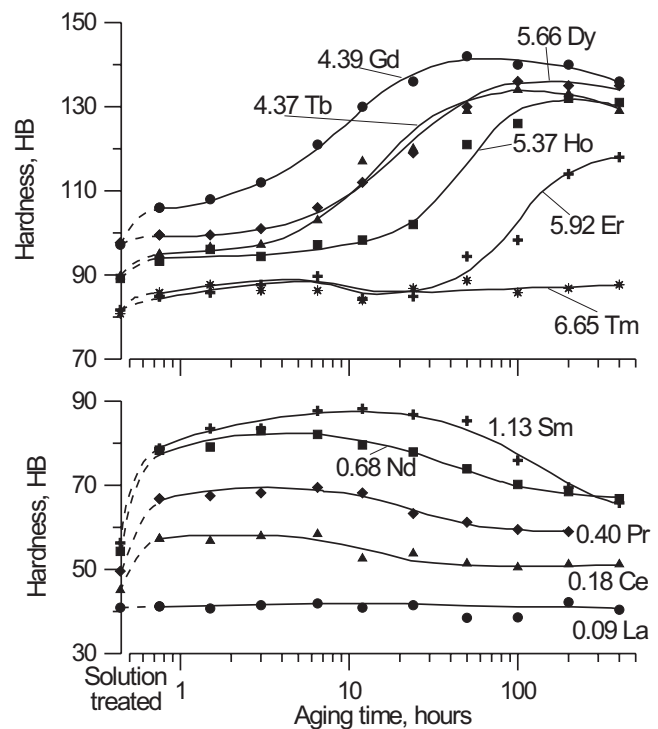
Fig. 2. Hardness change of Mg-RE alloys with increasing aging time at 200°C

The hardness curves show strengthening of the alloys during aging if the RE solubility in solid Mg is not very small, as in the lanthanum alloy. For the alloys with elements of the same subgroup, either the cerium or yttrium one, the character of the hardness change during aging is the same, but for the alloys with elements of different subgroups character of the hardness change during aging is different. For the alloys with elements of cerium subgroup (Ce, Pr, Nd, Sm) a steep hardness increase is observed after short aging times without a visible latent period. Hardness at any aging time and hardness maximum of the alloys increase with increasing solubility of the rare-earth metals of this subgroup in solid Mg (from

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[2] The high solid solubility of Yb in Mg compared with solubilities of La-Nd metals could also be due to the valence of Yb which is 2+, and the same as Mg.

Ce to Pr, Nd and Sm). In the alloys with the elements of the yttrium subgroup (Gd, Dy, Ho) a latent period of the solid solution decomposition is observed. For this initial period hardness increases insignificantly. After the latent period the hardness begins to grow steeply and reaches a maximum. Hardness maximum in the alloys with yttrium subgroup is reached after longer aging time as compared with the alloys with elements of cerium subgroup. No tangible increase of hardness maximum with increasing RE solubility in solid Mg (from Gd to Dy and Ho) is observed. Moreover it decreases for Er and Tm.

There is also difference in decomposition kinetics amongst the alloys with the elements of the same subgroup of the rare-earth metals. It consists of deceleration of the solid solution decomposition with increasing atomic number of the rare-earth metals and is revealed by the shift of critical points on the hardness curves (kink at the end of the latent period or the hardness maximum) to the longer aging time. The effect is revealed more clearly in the alloys with elements of yttrium subgroup, but it is seen also in the alloys with elements of cerium subgroup, as well.

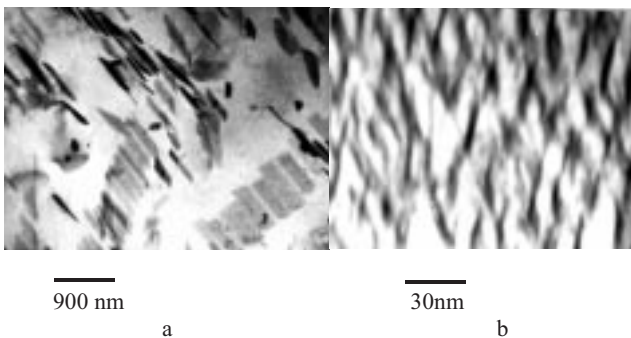900 nm   30nm
a   b

Fig. 3. Typical microstructure of the Mg-RE alloys after aging obtained by transmission electron microscopy [9]. a – Mg-0.12 at. % Sm, aging 250°C, 6 h. b – Mg-4.18 at. % Gd, aging 250°C, 50 h

Investigation of the phase transformations during the decomposition of Mg-RE supersaturated solid solutions showed the complicated nature of it. The phase transformations turned out to be, in general, the same in the alloys with elements of one of the subgroups of the rare-earth metals and different in the alloys of different subgroups. In the alloys with elements of cerium subgroup the succession of the phase transformations during solid solution decomposition includes GP-zones formation, two metastable phases formation of a plate-like form and, at the end, the formation of the equiaxial crystals of the equilibrium phase. In the alloys with all elements of yttrium subgroup, except Yb, ordering in Mg solid solution takes place in quenched state and during latent period. The steep increase of hardness and hardness maximum corresponds to formation of base-centred orthorhombic metastable phase in form of plates on

the prismatic planes of Mg solid solution lattice with three-fold symmetry. At higher aging temperatures the plates of the equilibrium phase are formed. They are arranged in Mg solid solution lattice also along the prismatic planes with three-fold symmetry, but these prismatic planes are other than the prismatic planes with precipitates of the orthorhombic phase. Two typical microstructures of the alloys with rare-earth metals of cerium and yttrium subgroups are shown in Fig. 3 [9].

3. Mechanical properties

The mechanical strength properties of the alloys with respective binary Mg-RE alloys increase with increasing RE contents to limits of the Mg solid solution regions. In the alloys with elements of cerium subgroup, such dependence of the strength properties on RE concentration is clearly manifested if the tensile tests are conducted at elevated temperatures. As an example of such a regularity is shown in Fig. 4 where the tensile tests of cast alloys of the Mg-La, Mg-Ce and Mg-Nd systems are presented [1].
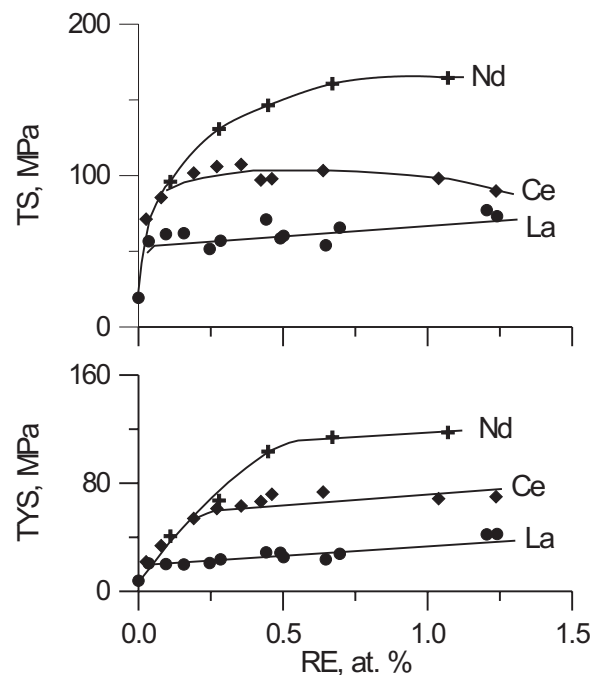

Fig. 4. Strength properties of binary Mg cast alloys with La, Ce and Nd at 260°C. Solution treatment + aging (T6)

The tested alloys were solution treated with quenching and then aged to hardness maximum (T6 temper). As one can see, tensile strength and tensile yield strength of them increase with increasing RE contents. The kinks in the curves correspond approximately to the RE solubility at quenching temperature. As a result, the highest strength properties are reached in the alloys with neodymium and the lowest strength properties are

reached in the alloys with lanthanum. In the alloys with cerium showing intermediate solubility in solid Mg the intermediate level of the strength properties is reached.

In the alloys with the elements of yttrium subgroup the correlation between strength properties and solubility in solid Mg is also observed, although its character is some different. The typical change of mechanical properties of the binary Mg alloys with Gd, an element of the yttrium subgroup, is shown in Fig. 5 [13]. At small Gd concentrations when a supersaturated solid solution can not be formed the tensile strength and tensile yield strength at room and elevated temperature slowly increase with increasing Gd content. At higher Gd contents the strength properties increase more rapidly with increasing Gd up to about its solubility limit in solid Mg at the quenching temperature. At these concentrations a supersaturated solid solution is formed during heat treatment and additional strengthening results from its decomposition. At even higher concentration, corresponding to the two-phase area in the phase diagram, the formation of coarse eutectic crystals of the Mg-Gd compound, no increases of the tensile strength and tensile yield strength take place at room temperature and there is an actual decrease, and even the elongation drops to very low values. At elevated temperatures the strength properties continue to increase in two-phase region, but slower than in the single phase Mg solid solution region.
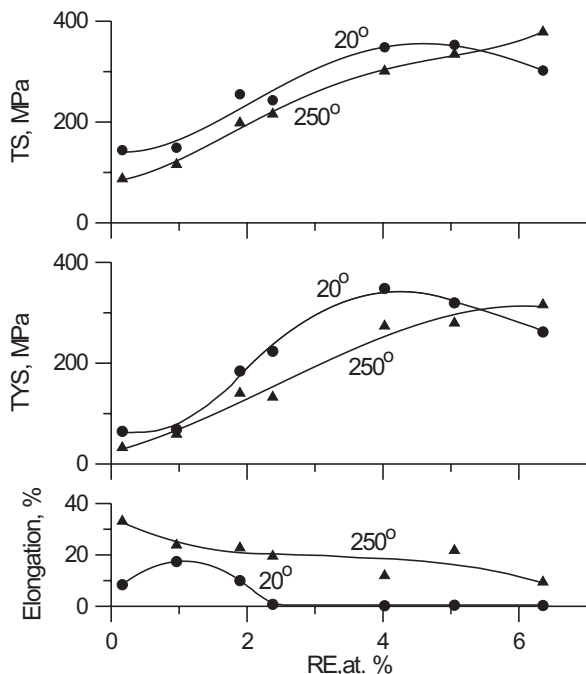

Fig. 5. Mechanical properties of Mg-Gd alloys at 20°C and 250°C. Solution treatment + aging (T6)

The considered dependence of the strength properties of Mg alloys on RE concentration enables one to conclude that the different solubilities of the rare-earth metals in solid Mg are responsible for the different level of strength reached when the individual rare-earth metals are added. Respectively, the higher strength properties should be expected on the alloys of the systems with a greater RE solubility in solid Mg. Nevertheless, such regularity is justified only in certain limits, i.e. as observed in the alloys with elements of cerium subgroup which show small solubilities. The alloys with elements of yttrium subgroup show also the higher strength properties than those with elements of cerium subgroups in accordance with this regularity since the solubility of the rare-earth metals of yttrium subgroup is higher. However, amongst the alloys with elements of yttrium subgroup the increase of the strength with increasing RE solubility in solid Mg was not observed. The highest strength properties at approximately the same level were observed for the alloys Gd, Tb and Dy, which have the less solubility in solid Mg than other elements of the lanthanide series, which have higher atomic numbers, i.e. Ho and Er. This can be seen in Fig. 6, where results of tensile tests of the Mg-RE alloys with elements of yttrium subgroup at room temperature are presented. The tests were conducted on the round rods of 11 mm in diameter obtained by hot extrusion of ingots with cross section reduction 88%. The rods were aged up to the maximum hardness maximum immediately after hot extrusion (T5 temper). For comparison, the results of tensile tests of the Mg-Sm alloys hot extruded and aged then up to hardness maximum are presented, too.
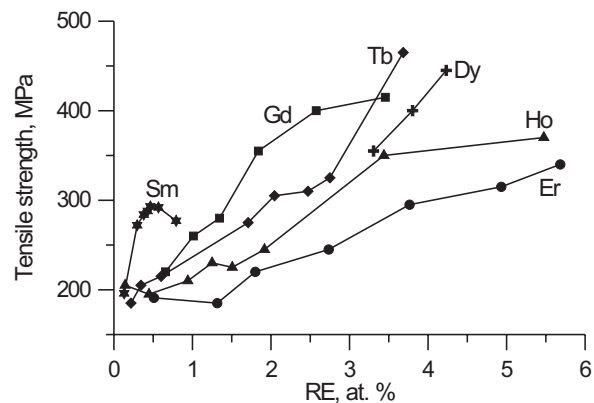

Fig. 6. Tensile strength of Mg alloys with rare-earth metals versus composition. Aging after hot extrusion (T5)

Data presented in Fig. 6 show, that the highest tensile strength of the alloys with Gd, Tb and Dy is more than 400 MPa at room temperature are reached at high alloying contents of them of about 4 at. %. These alloys also have the highest strengths at 250 and 300°C of more than 320 and 250 MPa, respectively.

Amongst the rare-earth metals only some of them are used currently in industry as alloying additives for Mg-base alloys. They are La, Ce, Nd and Y. Other

rare-earth metals may be present in commercial alloys, but only as components in mixtures. An assessment of binary Mg alloys with all rare-earth metals suggests that some of the other rare-earth metals may be useful additives to Mg alloys for improvement of their strength: these are Gd, Tb and Dy. The alloys with them have the highest strength properties at room and elevated temperatures. In addition to Gd, Tb and Dy, Sm can be also considered as useful element for alloying of Mg-base alloys because the alloys with Sm exhibit excellent strength at lower concentrations of Sm than the alloys with Gd, Tb and Dy. The rare-earth metals, especially those belonging to the yttrium subgroup, are quite expensive. Therefore, diminution of their concentrations in commercial alloys is of a great importance.

Although the above mentioned binary Mg alloys with Gd, Tb and Dy show the highest strength properties, these properties are reached at too high a concentration. Therefore, because of their high cost, it is most unlikely that the application of Gd, Tb and Dy for alloying of commercial Mg alloys can be justified. However, there is another way for utilization of these rare-earth metals. They can be added to Mg alloys in small concentrations, but together with other rare-earth metals which are cheaper and used already in commercial alloys. An example of such a possibility is demonstrated by tensile tests of a Mg-Gd-Y-Mn alloy with lower Gd contents, see Table 2 [13].

TABLE 2

Mechanical properties of the alloy Mg-1.67 at.% Gd-1.49 at.% Y-0.3 at.% Mn after hot extrusion and aging

Product	Property	Test temperature, °C			
		20	250	300	350
Rod, diam. 20 mm	σ_B, MPa	400-435	365-375	270-285	110-160
	$\sigma_{0,2}$, MPa	345-385	285	230	105-135
	δ, %	4,0	7,0	18-21	25-28
Bar, 12.5 × 65 mm²	σ_B, MPa	$\frac{385-390}{370-380}$	$\frac{355-360}{340-350}$	$\frac{235-265}{240}$	$\frac{90-140}{75-115}$
	$\sigma_{0,2}$, MPa	$\frac{335-340}{295-310}$	$\frac{330-335}{290-320}$	$\frac{220}{210}$	$\frac{85-125}{70-100}$
	δ, %	$\frac{5.0}{4.0}$	$\frac{9.0}{11-12}$	$\frac{17-18}{16-22}$	$\frac{11-25}{22-30}$

Comments: for the bar: the longitudinal properties are given in numerator and the transverse properties are given in denominator.

The tested alloy was prepared by melting under Ar+SO$_2$ atmosphere. Weight of melt was 45 kg. The round ingot of 118 mm in diameter was obtained by continuous casting. The ingot was homogenized at 490°C for 12 hours and cut then into parts which were hot extruded into either a round rod of 20 mm in diameter or a bar with cross section 12×65 mm. Hot extrusion was followed by aging at 200°C for 24 hours which resulted

in the maximum hardness (T5 temper). Table 2 shows that the strength properties of the alloy at room and elevated temperatures at low gadolinium contents are quite high, with a small anisotropy of strength properties and a reasonable plasticity.

In Fig. 7 the tensile strength of a Mg-Gd-Y-Mn alloy are compared with the tensile strength values of several main wrought commercial magnesium alloys produced in Russia [14]. Similar alloys are produced also in Western world. The tensile strength values of all of the alloys correspond to heat treatment regimes which provide the highest levels. The advantage of the improved strength of the Mg-Gd-Y-Mn alloy at room and elevated temperatures as compared to the commercial alloys is evident.
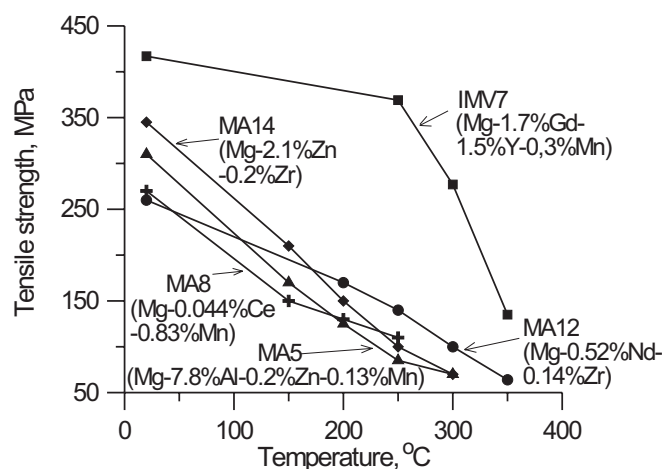

Fig. 7. Comparison of the tensile strength at room and elevated temperatures of the Mg-1.67 at.% Gd-1.49 at.%Y-0.3 at.% Mn alloy (IMV7) with several Russian wrought commercial alloys. Composition of the commercial alloys are given in at. %

4. Summary

1. The binary Mg-RE phase diagrams are characterised by the existence of limited Mg solid solutions.
2. The solubility of the individual rare-earth metals in solid Mg is different and changes regularly with increasing RE atomic number in accordance with the change of the RE atomic size.
3. The decomposition of Mg-RE supersaturated solid solutions is accompanied by a strengthening effect. The kinetics and phase transformations of this process are similar for Mg alloys with elements of the same subgroup, and different for the alloys with elements of different subgroups of the rare-earth metals.
4. The strength properties of the Mg-RE alloys depend on solubility of the rare-earth metals in solid Mg and possibility of the decomposition of the Mg solid solution.

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