

THE PHENOMENON OF REVERSION IN AGING MAGNESIUM ALLOYS WITH THE RARE-EARTH METALS

Prof. Rokhlin L.L., PhD. Dobatkina T.V., Tarytina I.E., PhD. Lukyanova E.A.
Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, Russia

rokhlin@imet.ac.ru

Abstract: The reversion in magnesium binary alloys with rare-earth metals (Nd, Sm, Y, Gd, Tb, Dy, Ho) at a temperature of 300°C has been studied. The phenomenon of the reverse dissolution of rare-earth metals in solid magnesium has been established to begin in all alloys under study already after short-term annealing at 300°C for 15 min. As the annealing time at 300°C further increases, the reverse dissolution of rare-earth metals in solid magnesium first continues and then the magnesium solid solution becomes again depleted of rare-earth metals because of their precipitation. The degree of reversion has been found to generally increase with an increase in the atomic number of the yttrium-group rare-earth metal in accordance with its position in the lanthanum row: Gd, Tb, Dy, and Ho. The degree of reversion in the alloys with cerium-group metals (Nd, Sm) with atomic numbers below those of Gd, Tb, Dy, and Ho is substantially smaller than that is in the alloys with yttrium-group metals.

Keywords: MAGNESIUM ALLOYS, RARE-EARTH METALS, REVERSION, SOLID SOLUTION DECOMPOSITION, STRUCTURE.

1. Introduction

Magnesium alloys are used in modern industry as light structural materials. The addition of rare-earth metals to magnesium can substantially improve their strength characteristics at both ambient and elevated (200-300°C) temperatures [1 - 4]. However, upon short-term holdings at not-too-high temperatures, the magnesium alloys age-hardened to high strength exhibit the phenomenon of reversion, which can lead to weakening because the REM-containing hardening particles precipitated upon aging undergo a reverse dissolution in the magnesium solid solution [5 - 7]. The reversion process should lead to a decrease in strength properties, especially at elevated temperatures. The paper presents the results of the study of reversion at a temperature of 300°C in the magnesium alloys containing rare-earth metals of cerium (Nd, Sm) and yttrium groups (Y, Ho, Dy, Tb) after age hardening at 200°C for the maximum strength.

2. Experimental

The alloys for the study were prepared by melting in an electric resistance furnace in iron crucibles under the standard VI2 flux containing 38-46% MgCl₂, 32-40% KCl, 5-8% BaCl₂, 3-5% CaF₂, which was used for the protection of the molten magnesium from ignition. Magnesium Mg95 (>99.95% Mg) and rare-earth metals such as ItM-1 yttrium, NM-1 neodymium, SmM-1 samarium, GdM-1 gadolinium, TbM-1 terbium, DiM-1 dysprosium, and GoM-1 holmium at least 99.83% pure (hereinafter, the compositions are given in wt.%) were used as the starting materials. The rare-earth metals were added into the Mg melt upon melting as master alloys. The rare-earth metals for the study were chosen because, in binary magnesium alloys, they provide a substantial strengthening effect caused by the decomposition of the supersaturated magnesium solid solution upon aging [3]. The alloy compositions were chosen with allowance for the binary phase diagrams in such a way that the content of each rare-earth metal was somewhat below its solubility in solid magnesium at the homogenization temperature. Table 1 shows the alloy chemical compositions analyzed by inductively coupled plasma atomic emission spectroscopy with an Ultima 2C Jobin-Yvon instrument.

The alloys were cast into a stainless steel mold heated to ~300°C to obtain cylindrical ingots of 15 mm in diameter and 90 mm long. The ingots were cut into blanks, which were subjected to homogenization annealing for 6 hours at temperatures given in Table 1. The blanks after homogenization annealing were quenched in room-temperature water in order to obtain a supersaturated magnesium solid solution.

Table 1: Alloys compositions, homogenization temperatures, and aging time at 200°C for achievement of the maximum hardness

Alloy composition	Homogenization temperature, °C	Aging time at 200°C for the achievement of maximum hardness
Mg-8.3% Y	540	128
Mg-2.2% Nd	530	4
Mg-3.5% Sm	520	16
Mg-15.5% Gd	520	32
Mg-17.7% Tb	540	32
Mg-19.5% Dy	540	128
Mg-21.4% Ho	540	128

Samples for the hardness and electrical resistivity measurements were made from the quenched blanks of the alloys.

The hardness was tested by the Brinell method with a TSH-2M tester using a ball of 5 mm in diameter at a load of 2500 N. Electrical resistivity of the samples of 6 mm in gage diameter and 23.7 mm in gage length was measured with a unit based on the BSZ-010-2 microohmmeter. The error of the electrical resistivity measurement was about 0.7%. The microstructure of the alloys was examined with an M 24 Reichert metallographic microscope. The polished samples were etched with 0.5% nitric acid solution in ethanol or 30% orthophosphoric acid solution in ethanol.

3. Results and discussion

At the first stage of the study, the alloy samples after homogenization and quenching were subjected to isothermal aging at 200°C for up to 128 hours with the view to follow the process of age hardening upon decomposition of the supersaturated magnesium solid solution by measuring hardness and to establish the aging time, at which the maximum hardness is reached. The established aging times required to achieve the maximum hardening at 200°C in the alloys are given in Table 1. Then the alloys were subjected to isothermal annealing at 300°C for 0.25 - 128 hours to detect reversion. The results of the hardness and resistivity measurements for the alloys aged for maximum hardening at 200°C and then annealed at 300°C for the study of the reversion are shown in Figs. 1 and 2.

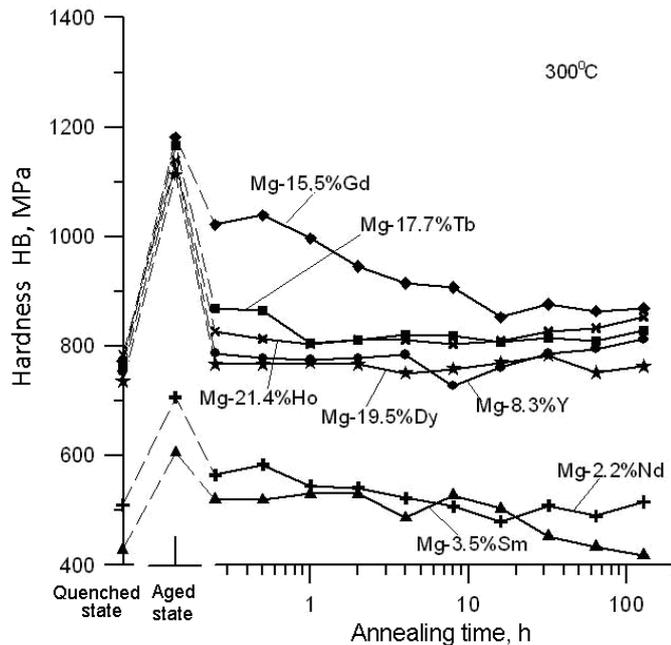


Fig. 1. Hardness of the REM-containing magnesium alloys quenched and aged at 200°C for the maximum hardening as a function of time of subsequent isothermal annealing at 300°C.

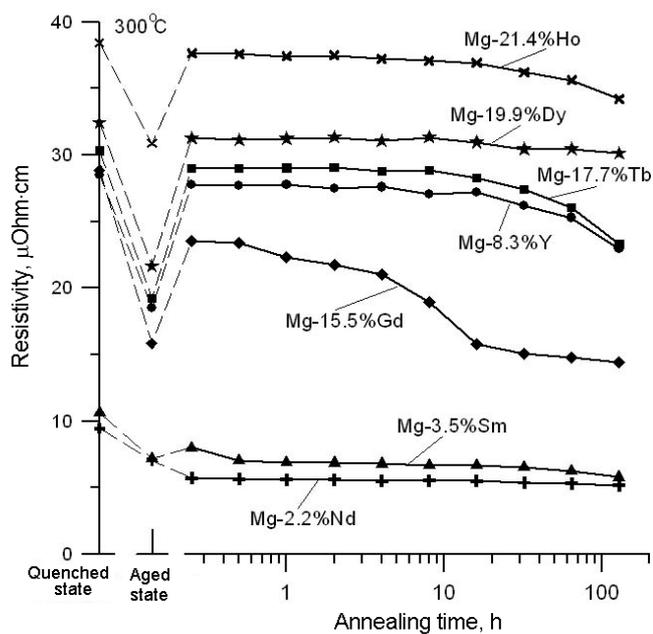


Fig. 2. Electrical resistivity of the REM-containing magnesium alloys quenched and aged at 200°C for the maximum hardening as a function of time of subsequent isothermal annealing at 300°C.

According to the data presented in Fig. 1, the hardness of the aged magnesium alloys with rare-earth metals is abruptly reduced even after the shortest (15 min) annealing at 300°C, especially in the alloys with yttrium group rare-earth metals (Y, Gd, Tb, Dy, Ho). This suggests the possibility of the reversion phenomenon, i.e., the reverse dissolution of rare-earth metals in solid magnesium. Such reversion effect presumed according to change in hardness becomes proven by the observed increase in resistivity after annealing by the same regime (Fig. 2). The resistivity data show that, with a further increase in the annealing time at 300°C, first the reverse dissolution of rare-earth metals in solid magnesium remains unchanged, and then the magnesium solid solution becomes again depleted because of the precipitation of rare-earth metals. The degree of reversion is substantially smaller in the magnesium alloys with cerium-group

rare-earth metals, which have been studied for comparison, and can be even absent in the magnesium alloy with neodymium.

The degree of reversion was evaluated by the formula: $S = (\rho_{\text{ann}} - \rho_{\text{ag}}) / (\rho_{\text{q}} - \rho_{\text{ag}})$, where S is the degree of reversion, and ρ_{ann} , ρ_{ag} , and ρ_{q} are the resistivities of the alloy in the states after annealing at 300°C for the maximum reversion, after aging to the highest hardening at 200°C, and after quenching, respectively. The results obtained are given in Table 2. Note that the degree of reversion in the magnesium alloys with yttrium group rare-earth metals of the lanthanum row (Gd, Tb, Dy, Ho) increases with increasing their atomic number. The degree of reversion of magnesium alloy with yttrium, which does not belong to the lanthanum row, is close to that of the magnesium alloys with the lanthanum row metals such as dysprosium and holmium. The reversion after aging in the alloys with cerium group metals is substantially smaller than in the alloys with yttrium group metals and can be even absent, as in the alloy with neodymium. An increase in the degree of reversion with increasing atomic number of yttrium group rare-earth metals of the lanthanum row (Gd, Tb, Dy, Ho) was also observed in the same alloys upon annealing at a temperature of 250°C [7].

Table 2: Degree of reversion in aged magnesium alloys with rare-earth metals after annealing at 300°C.

Atomic number of REM	Alloy	Degree of reversion, %
60	Mg - 2.2% Nd	0
62	Mg - 3.5% Sm	24.1
64	Mg - 15.5% Gd	58.8
65	Mg - 17.7% Tb	88.8
66	Mg - 19.5% Dy	89.9
67	Mg - 21.4% Ho	89.5
39	Mg - 8.3% Y	92.3

The microstructure examination of the alloys by optical microscopy did not reveal any signs of the decomposition of the supersaturated magnesium solid solution after aging to the maximum hardness and after reversion after short-term annealing at 300°C. This can be explained by very fine precipitates from the magnesium solid solution and by the retention of the coherence between the crystal lattices of the precipitates and the magnesium solid solution. However, after long-term annealing following the reversion at 300°C, optical microscopy revealed the decomposition of the magnesium solid solution in the structure of the alloys in the form of the particles precipitated at three planes of the crystal lattice of the magnesium solid solution and at grain boundaries (Fig. 3). With allowance for the results reported in [3, 8, 9], we can assume that the increase in hardness up to the stage of the maximum strengthening is due to the formation of a metastable β' phase, which is typical for the decomposition of the magnesium solid solution in the magnesium alloys with yttrium group rare-earth metals. This phase has a base-centered orthorhombic crystal lattice.

4. Conclusions

1. It is established that the binary magnesium alloys with yttrium group rare-earth metals (yttrium, gadolinium, terbium, dysprosium, and holmium) after age hardening can undergo a substantial reversion with the reverse dissolution of the particles precipitated upon the decomposition of the supersaturated solid solution.

2. The degree of reversion sequentially increases with increasing atomic number of the rare-earth metals belonging to

yttrium group of the lanthanum row from Gd to Tb, Dy, and Ho. The degree of reversion of the magnesium alloy with yttrium, which does not belong to the lanthanum group, is close to those of the alloy with holmium and dysprosium. The reversion in the magnesium alloys with cerium group rare-earth metals is substantially smaller than that in the magnesium alloys with yttrium group metals and can be even virtually absent.

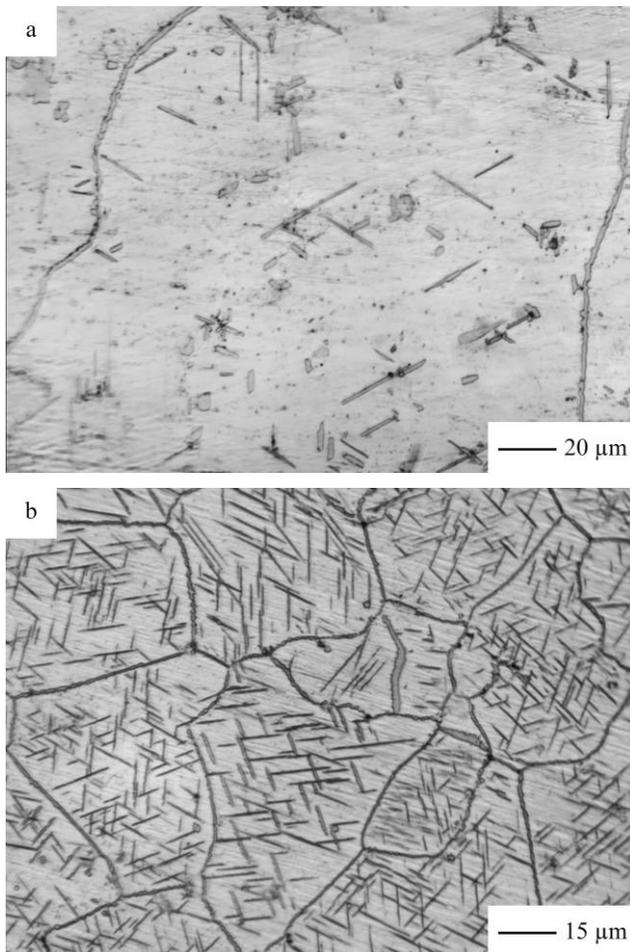


Fig.3 Typical microstructures of the alloys: Mg - 8.3% Y (a), and Mg - 17.7% Tb (b) after quenching + aging at 200°C + annealing at 300°C for 128 h.

5. References

1. Bohlen J., Letzig D., Kainer K. U. New perspectives for wrought magnesium alloys // *Mater. Sci. Forum.* 2007. V. 546-549. p. 1-10.
2. Kablov E.N., Volkova E.F., Filonova E.V. Effect of REE on the phase composition and properties of new refractory magnesium alloy of the Mg - Zn - Zr- REE system // *Metallovedenie i termicheskaya obrabotka metallov.* 2017. No. 7. p. 19-26. (in Russian)
3. Rokhlin L.L. *Magnesium Alloys Containing Rare-Earth Metals.* London - NewYork: Taylor and Francis. 2003. 245 p.
4. Li H., Lv F., Liang X., Qi Y., Zhu Z., Zhang K. Effect of heat treatment on microstructures and mechanical properties of a cast Mg-Y-Nd-Zr alloy // *Materials Science and Engineering A.* 2016. V. 667. p. 409-416.
5. Rokhlin L.L., Nikitina N.I. Recovery after aging of Mg-Y and Mg-Gd alloys // *Journal of Alloys and Compounds,* 1998, V. 279, p. 166-170.
6. Rokhlin L.L., Dobatkina T.V., Tabachkova N.Yu., Lukyanova E.A., Tarytina I.E. Aging-Induced Recovery of Magnesium Alloys with Various Rare-Earth Metals // *Russian Metallurgy (Metally).* 2019. №5. p.511-516.
7. Rokhlin L.L., Dobatkina T.V., Lukyanova E.A., Tarytina I.E., Dobatkin S.V. Studies to develop new structural magnesium alloys doped with REM // *Technology of light alloys.* 2018. №4. p.44-53. (in Russian)
8. Nie J.F. Precipitation and Hardening in Magnesium Alloys. // *Metallurgical and Materials Transactions A.* 2012. V. 43A. No11. p. 3891 -3939 .
9. Kawabata T., Matsuda K., Kamado S., Kojima Y., Ikeno S. HRTEM observation of the precipitates in Mg-Gd-Y-Zr alloy // *Mater. Sci. Forum.* 2003. V. 419 - 422. p. 303-306.

The work was supported by the Russian Foundation for Basic Research (project no. 18-03-00223-A) and was carried out within the Governmental task number 075-00746-19-00.