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Recovery after ageing of Mg–Y and Mg–Gd alloys

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Abstract

Using electrical resistivity and hardness measurements the recovery after ageing in two alloys of magnesium with rare-earth metals (Mg–12 wt.% Y and Mg–24 wt.% Gd) was investigated. The alloys were solution treated and aged up to the hardness maximum. The following treatment included isothermal annealing for different times at some temperatures higher than the ageing temperatures. The investigation revealed similar and different features of the recovery behaviour in the two alloys with different rare-earth metals. In both alloys a similar dependence of the recovery on the annealing temperature and time was established. The dissolution of the precipitate into the Mg matrix increased with increasing annealing temperature and passed through a maximum as the annealing time became longer. The increase of the annealing temperature and time promoted only softening of the alloys. Meanwhile, in Mg–24 wt.% Gd the recovery effect was significantly smaller than in Mg–12 wt.% Y. This fact is ascribed to the higher decomposition rate of the Mg–Gd solid solution at the annealing temperatures.

Keywords: Mg alloys; Rare-earth metals; Recovery; Solid solution decomposition

1. Introduction

The Mg–Y-base alloys are interesting as light structural materials with high strength properties at ambient and elevated (up to 300°C) temperatures [1,2]. One of the outstanding features of the Mg–Y alloys is their possibility to show a substantial strengthening effect during decomposition of the magnesium supersaturated solid solution [3]. This effect is connected with the Mg–Y phase diagram showing limited solubility of Y in solid Mg. This solubility decreases with decreasing temperature [4]. Gd belongs to the same subgroup of the rare-earth metals as Y. Accordingly, the magnesium rich Mg–Gd alloys are similar to the Mg–Y alloys. The Mg–Gd phase diagram shows also a limited Mg solid solution field, opening the possibility to the Mg supersaturated solid solution formation [4]. Also in Mg–Gd alloys a high strengthening effect takes place during the decomposition of the solid solution with a kinetic character and with phase transformations that are in general the same as in the Mg–Y alloys [5]. Mg–Gd alloys as well as Mg–Y alloys show high strength properties [5]. Nevertheless, there are certain differences between the alloys of both systems. The solubility of Gd in solid Mg is higher than that of Y. Besides, in Mg–Gd alloys the decomposition of the solid solution is accompanied by strengthening up to higher ageing temperatures than that in Mg–Y alloys [5]. When studying the decomposition of the solid solution in Mg–Y alloys, a recovery after ageing was discovered [6,7]. It was observed, however, only at two heat treatment regimes (260°C, 1 h and 315°C, 2 h). Meanwhile, recovery after ageing is expected to occur quite often in practice and at different heating conditions and it may significantly affect the strength and other important properties of the alloys. In this study the recovery after aging in Mg–Y alloys was investigated more in detail. In addition, the possibility of this process in Mg–Gd alloys and its characteristics were investigated.

2. Experimental details

The alloys for the investigation were prepared from Mg of 99.96 wt.% purity, Y of 99.83 wt.% purity, and Gd of 99.85 wt.% purity by melting in a resistivity furnace in iron crucibles under a flux. The flux contained 38–46 wt.% $MgCl_2$, 32–40 wt.% KCl, 3–5 wt.% CaF_2, 5–8 wt.% $BaCl_2$, 1.5 wt.% MgO, <8 wt.% ($NaCl+CaCl_2$) and was used in order to preserve the melts from burning. During melting the rare-earth metals were added into melted Mg using Mg–40 wt.% Y and Mg–50 wt.% Gd master alloys prepared before. The ingots of the alloys were homogenized at 500°C for 12 h and then hot extruded into rods of

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about 11 mm in diameter with area reduction of 88%. The rods were cut into pieces which were solution treated at 540°C for 2 h (Mg–Y alloys) or at 520°C for 2 h (Mg–Gd alloys) followed by quenching into cold water. Then the samples were aged at 200°C for 100 h. This regime was used for the alloys of both systems and corresponded the hardness maximum during solid solution decomposition. The aged samples were isothermally annealed at four temperatures, 225, 250, 275, and 300°C, in order to have recovery after ageing. The duration of the annealing was from 15 min to 64 h. The recovery was investigated by electrical resistivity measurements using a compensation method with an error of ±0.7%. Simultaneously, the hardness of the alloys was determined by the Brinell method using a load of 250 kg and a ball of 5 mm in diameter. The electrical resistivity is quite sensitive to the solid solution concentration. It decreases significantly when the solid solution depletion takes place during decomposition and it increases when the solid solution dissolves alloying elements. Therefore, the electrical resistivity measurements were chosen to check directly and reliably the rare-earth metal dissolution into and its precipitation from the solid magnesium during experiments. The microstructure of the alloys was analyzed by transmission electron microscopy. The foils for this study were prepared by thinning in 20% nitric acid in ethyl alcohol and rinsed in clean ethyl alcohol. A JEM-200A transmission electron microscope operating at 150 kV was used. Several binary Mg–Y and Mg–Gd alloys were prepared for the investigation. In this article the results of the experiments made on one alloy of each system are presented only. These alloys are Mg–12 wt.% Y (3.6 at.% Y) and Mg–24 wt.% Gd (4.6 at.% Gd). The compositions of the alloys are close to the maximum solubility of Y or Gd in solid Mg [4].

3. Results

Fig. 1 shows results of the resistivity measurements of the Mg–12 wt.% Y alloy. At all annealing temperatures (225, 250, 275, and 300°C) an increase of the resistivity was observed, showing dissolution of the precipitates into the Mg solid solution. The resistivity curves show that the recovery effect increases and reaches its maximum at times that are the shorter the higher the annealing temperatures. The resistivity falls gradually beyond the maximum as the annealing time increases, which shows that the decomposition of the magnesium solid solution takes place. As the decreasing resistivity at 225°C shows, after the longest exposure of 64 h the magnesium solid solution becomes even more depleted than after the primary ageing at 200°C for 100 h. After recovery the solid solution concentration does not reach the same level as after the solution treatment, although at the highest annealing temperature, 300°C, the former turns out to be close the later. The

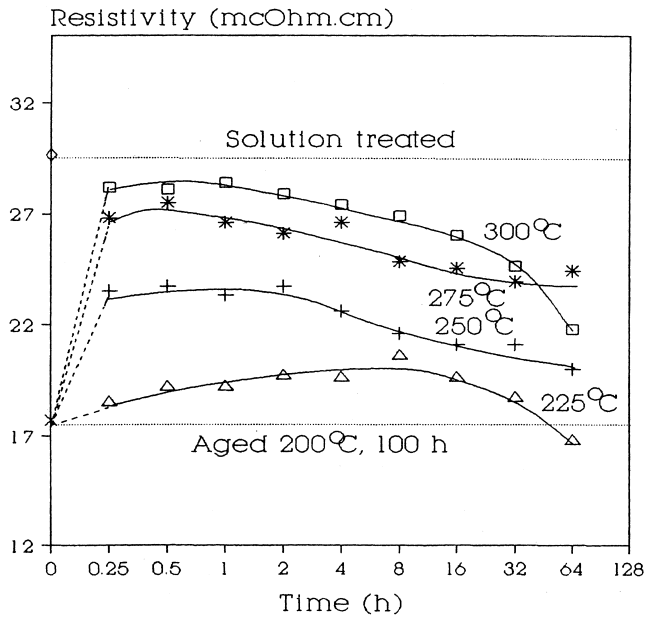

Fig. 1. Resistivity of the Mg–12 wt.% Y alloy versus the annealing time.

hardness measurements (Fig. 2) show only softening of the alloy at all annealing temperatures as the time increases. As the annealing temperature increases, the hardness becomes significantly lower. There are 'plateaus' on all hardness curves in their middle parts.

Fig. 3 shows the results of the resistivity measurements of the Mg–24 wt.% Gd alloy. They show that also in Mg–24 wt.% Gd, as in Mg–12 wt.% Y, the recovery after ageing takes place at all used annealing temperatures. The recovery effect increases similarly and reaches a maximum after shorter times with increasing annealing temperatures.

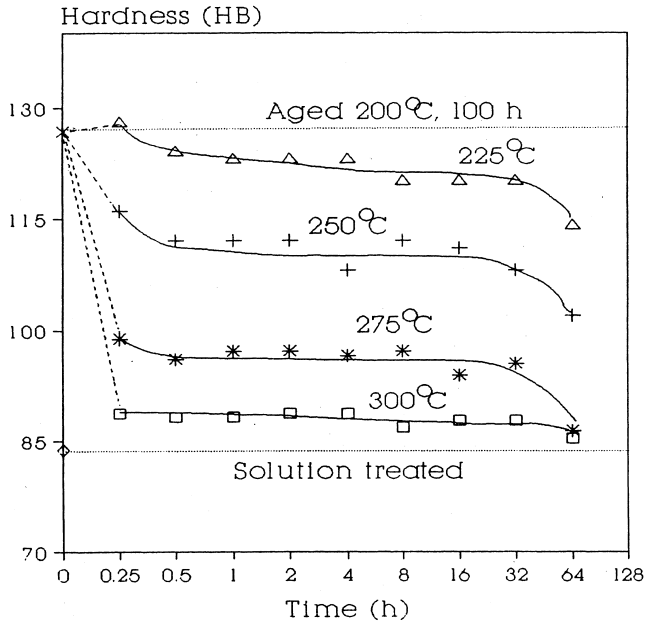

Fig. 2. Hardness of the Mg–12 wt.% Y alloy versus the annealing time.

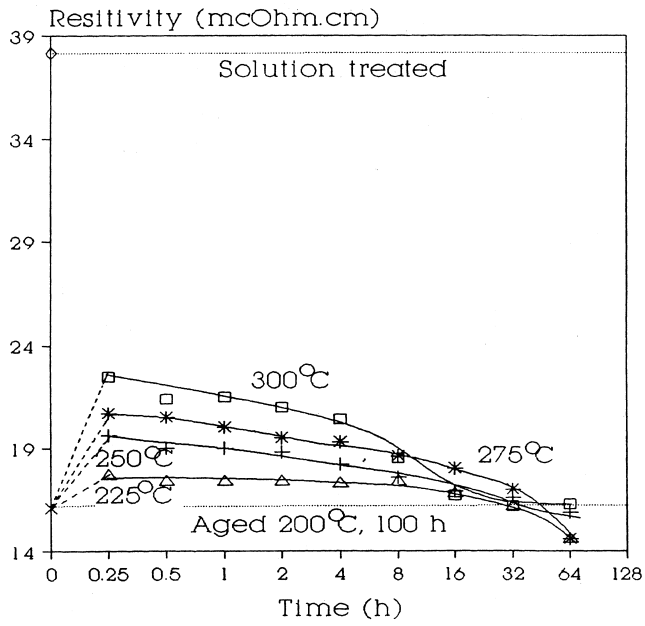

Fig. 3. Resistivity of the Mg–24 wt.% Gd alloy versus the annealing time.

With increasing annealing time the resistivity falls showing that precipitation from the magnesium solid solution has taken place after recovery at all temperatures. After the long annealing times the solid solution concentration approximates that of the primary aged alloy and may become even lower. The hardness of the Mg–24 wt.% Gd decreases after recovery at all annealing temperatures (Fig. 4). It continues to decrease gradually as the annealing time increases. Unlike in Mg–12 wt.% Y, the 'plateau' on the hardness curve of Mg–24 wt.% Gd is displayed only at the lowest temperature, 225°C. The higher annealing temperature, the lower is the hardness of the alloy. It does not reach, however, the value of the solution treated condition.

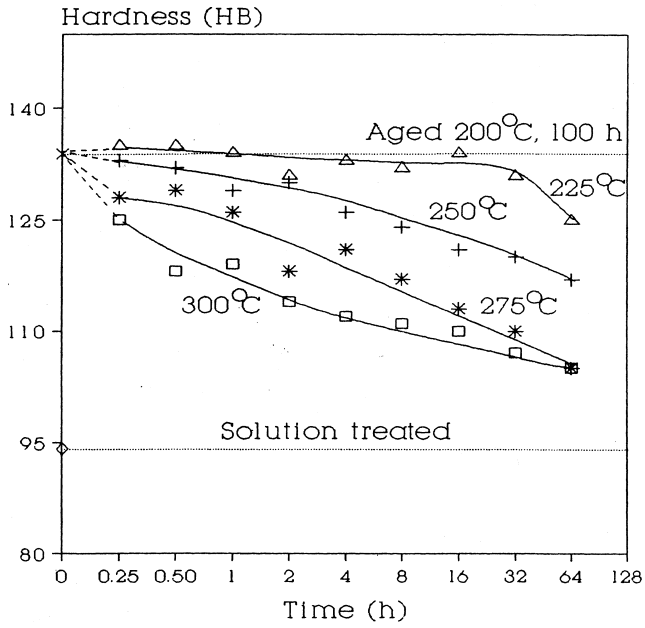

Fig. 4. Hardness of the Mg–24 wt.% Gd alloy versus the annealing time.

The transmission electron microscopy investigation showed the same kinds of the precipitates in the microstructure of both alloys after ageing, as in [5,7]. In accordance with [8], these are the particles of the metastable orthorhombic phase, which is coherently connected with the Mg solid solution matrix. The particles are of platelike form and are arranged along three symmetry planes of the Mg solid solution lattice. A typical microstructure of the alloys with precipitates after ageing is shown in Fig. 5a. It displays the ripple contrast which is a common feature for oriented and coherent precipitates. A typical electron diffraction pattern of the aged alloys is shown in Fig. 6. The characteristic features of the pattern are three superstructure reflexions between the reflexions of the Mg solid solution along each $\mathbf{g}_{100}$-type radius-vector. There are also pairs of superstructure reflexions lying along the same $\mathbf{g}_{100}$-directions without the corresponding Mg solid solution reflexions. The disposition of the superstructure reflexions along $\mathbf{g}_{100}$-directions conforms the tracks of the Mg reciprocal lattice basis-planes. So all visible superstructure reflexions lie on these reciprocal lattice planes. The pattern shows also small arcs from the thin MgO film formed on the foil at air. They are clear visible between second and third rows of the superstructure reflexions along $\mathbf{g}_{100}$-directions. The arcs do not hamper the analysis of the pattern. Moreover, they may be

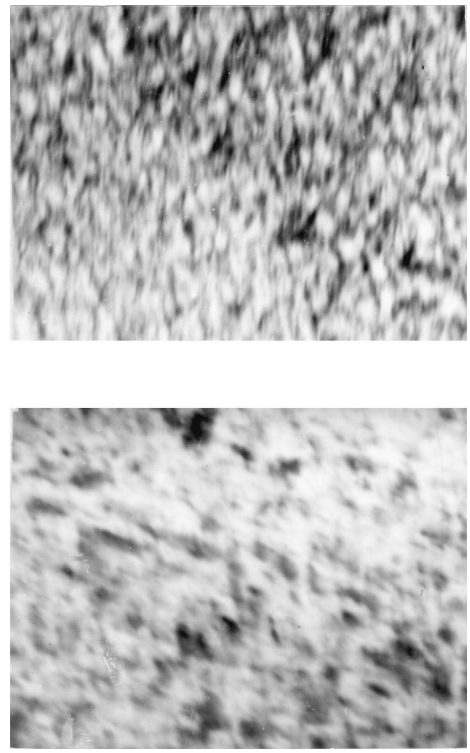

Fig. 5. Electron micrographs of the alloys: (a) Mg–24 wt.% Gd after ageing 200°C, 100 h (100 000×), (b) Mg–12 wt.% Y after recovery annealing 250°C, 1 h (43 000×).

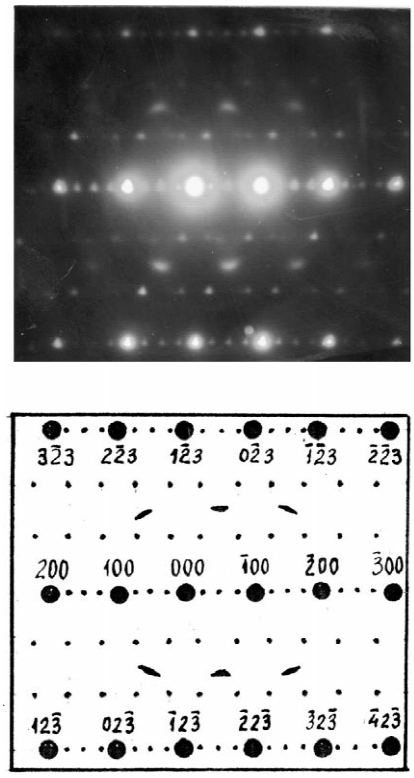

Fig. 6. Electron diffraction pattern of the Mg– 24 wt.% Gd alloy and its scheme, [032] zone. Ageing 200°C, 100 h.

useful for it for the exact calculation of the interplanar distances. The treatment of this pattern from the Mg solid solution decomposed and other patterns from it confirmed the structure of the precipitates and their connection with the matrix described above. As the electron diffraction pattern showed, the precipitates retained their crystal structure after recovery. The particles disappeared partly after recovery. The above-mentioned ripple contrast became weaker after recovery suggesting a loss in coherency between precipitates and matrix. A typical micrograph of the alloy after recovery is shown in Fig. 5b. The long time annealing after recovery has led to a structure close that formed after the heating and exposure at the same temperature without primary ageing.

4. Discussion

The results presented show the degree of the recovery after ageing in the alloys and its dependence on the annealing temperature and time.

The resistivity method used in this investigation may be considered as more reliable than the hardness measurements used in [6], because hardness may decrease as a result of not only recovery, but also as a result of coalescence of the precipitates. This is confirmed to a certain extent by the experiments of this work. The hardness of the alloys continues to decrease as the annealing time increases at each temperature even after recovery is completed and the solid solution begins to decompose. The 'plateau' on the hardness curves may be explained therefore by two processes which promote decrease and increase of the alloy hardness simultaneously: dissolution of the precipitates into solid Mg and continuation of the precipitation from it.

The results of the experiments showed at first that the recovery after ageing takes place in Mg–Gd alloys. This might be expected taking into consideration the similarity of the Mg–Gd and Mg–Y systems. The recovery in the Mg–Gd alloy displayed also a number of similar features as compared with the Mg–Y alloy. The recovery effect continuously increases in both alloys as the annealing temperature increases within the same temperature range. There is no additional hardening of both alloys when annealing is continued at all temperatures after the recovery is completed. Both alloys show the same phase transformations during recovery and the following solid solution decomposition. All these facts confirm the similarity of the Mg–Y and Mg–Gd alloys, as is known for several other characteristics [5].

According to modern theories [9], the recovery after ageing takes place as result of the precipitate instability at a higher temperatures. The instability is connected with the surface energy of the precipitates and is determined by the elastic stresses arisen as result of coherency between them and the matrix. In general, electron microscopy investigations support this viewpoint, suggesting a loss of coherency between the retained precipitates and the matrix after recovery.

Nevertheless, there are differences between the Mg–Y and Mg–Gd alloys in the recovery process. The most important one is the substantially smaller recovery effect in the Mg–Gd alloys. The resistivity method makes it possible to estimate quantitatively the recovery assuming that it is a measure of the ratio $R=(\rho_r-\rho_{ag})/(\rho_{st}-\rho_{ag})$, where ρ_{st}, ρ_{ag}, and ρ_r are the resistivities of the alloy after solution treatment, after ageing at 200°C for 100 h, and after recovery annealing, respectively. This ratio may be considered as 'recovery fraction'. The maximum recovery fraction of Mg–12 wt.% Y and Mg–24 wt.% Gd at each temperature calculated from the resistivity values is shown in Table 1. The significantly smaller recovery in Mg–24 wt.% Gd is evident. In this alloy the recovery fraction reaches only 26.9% at the highest annealing temperature as compared with 88.8% in Mg–12 wt.% Y.

The smaller recovery effect in the Mg–Gd alloy as

Table 1
Maximum recovery fraction (%) of the alloys at different temperatures

Alloy	Recovery temperature, °C			
	225	250	275	300
Mg–12 wt.% Y	20.8	50.0	80.8	88.8
Mg–24 wt.% Gd	6.7	15.8	20.7	26.9

compared with the Mg–Y alloy might be explained by a difference in the solid solution decomposition rate at the annealing temperature. At the same temperature the decomposition in Mg–24 wt.% Gd proceeds in a shorter time. This fact is illustrated in Fig. 7 which displays the curves showing the time dependence of the solid solution decomposition in both alloys at one of the annealing temperatures. The samples of the alloys were commonly solution treated and then annealed at 300°C without primary ageing at 200°C, 100 h. For better comparison the solid solution decomposition was characterized by a similar quantity as calculated for the recovery fraction. This quantity is the ratio $S=(\rho_{an}-\rho_{ag})/(\rho_{st}-\rho_{ag})$, where ρ_{st}, ρ_{ag}, and ρ_{an} are the resistivities after solution treatment, after ageing at 200°C for 100 h, and after annealing at 300°C for different times, respectively. In fact, this ratio represents the part of the solid solution that was not transformed at 300°C as compared with the total part of the solid solution that could have been transformed during ageing at 200°C for 100 h. It might be regarded as the 'supersaturation fraction' of the magnesium solid solution retained after the heat treatment. As Fig. 7 shows, there are several stages of the solid solution decomposition in both alloys. The first of them is accompanied by a drastic decrease of the solid solution concentration followed by a gradual one. Later a second strong decrease of the concentration takes place. The kinetic character of the solid solution decomposition for both alloys is identical, in general, but this process is significantly more rapid in Mg–24 wt.% Gd and the supersaturated fraction becomes lower at all times. As recovery begins, the solid solution decomposition begins, too, and the later process should restrain the former. Therefore, the more rapid decomposition of the solid solution in Mg–24 wt.% Gd may be assumed to be responsible for the smaller recovery in this alloy, as compared with Mg–12 wt.% Y.

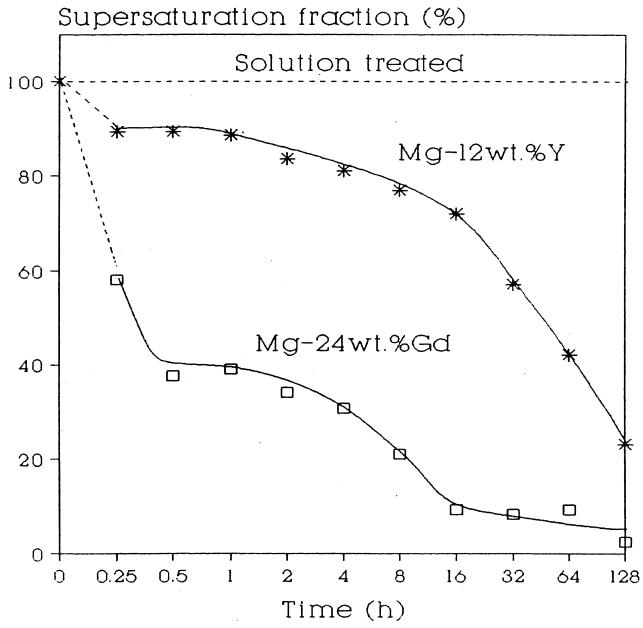

Fig. 7. Kinetics of the solid solution decomposition of the alloys at 300°C.

It is reasonable to suppose that the higher decomposition rate in Mg–24 wt.% Gd is also responsible for the earlier softening which causes the continuous hardness decrease without 'plateau' on the curve, and which is not found in Mg–12 wt.% Y.

5. Conclusion

Using resistivity measurements the recovery after ageing up to the hardness maximum was investigated in Mg–Y alloys during isothermal annealing in the 225–300°C temperature range. The recovery effect in the alloy passes through a maximum as the annealing time becomes longer and increases continuously with increasing annealing temperature, so that at 300°C the Mg solid solution concentration turns out to be close to that after the solution treatment. Recovery after ageing under similar conditions was also observed at first in Mg–Gd alloys. In the Mg–Gd alloys the recovery dependence on the annealing time and temperature is the same as in Mg–Y alloys, but the recovery effect is significantly less. In both alloys there is no hardness increase during isothermal annealing after ageing. Also in other respects, the Mg–Y and Mg–Gd alloys behave similarly, but there are some differences in the recovery behaviour.

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