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Deviations from Matthiessen's rule in some magnesium-based alloys

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Abstract. Electrical resistivity measurements have been made on dilute and concentrated binary magnesium alloys containing Ag, Zn, Al, Nd, Pb, Sn and Th over the temperature range 77–320 K. Small deviations occur from Matthiessen's rule for alloys that have been solution treated and quenched to retain the solid solution. Much larger deviations occur when the alloys are heat treated to precipitate the solute atoms from the solid solution. Possible causes of this effect are discussed.

1. Introduction

The electrical resistivities of pure metals and dilute alloys are usually described in terms of Matthiessen's rule, which states that the total resistivity is the sum of two independent contributions, the residual resistivity ρ_0 caused by scattering of electrons from impurities and structural imperfections, and the thermal resistivity ρ_i produced by scattering from phonons. Under most experimental conditions the electrical resistance arising from structural imperfections, e.g. dislocations and grain boundaries, is small compared with that produced by phonons and a concentration c of solute atoms. Matthiessen's rule may therefore be written

$$\rho(T, c) = \rho_i(T) + \rho_0(c).$$

This expression is only approximate and in practice deviations from Matthiessen's rule (DMR) occur (e.g. see Dugdale 1977). The DMR are approximately linear with temperature at temperatures exceeding $\theta/4$ where θ is the Debye temperature of the matrix ($\theta/4 \sim 80$ K for magnesium). The deviation may be either positive or negative depending on the alloy system.

In the present work the resistivity characteristics, including the change in DMR over the temperature range 77–320 K, of various magnesium alloys have been studied with two objectives in mind. Firstly, in recent reviews of DMR (Bass 1972, Cimberle *et al* 1974) it is apparent that relatively little work has been carried out on the effect of the metallurgical condition of an alloy on DMR. The present measurements have therefore been carried out on alloys that have been heat treated to produce a variety of metallurgical structures.

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The second objective concerns the use of resistivity measurements in the study of the kinetics of solid state precipitation. Here it is normally assumed that the fall in resistivity at a given temperature is due to the removal of solute atoms from the solid solution, and further that the magnitude of the decrement is directly proportional to the number of solute atoms contained in the precipitates. However, this simple relationship does not occur in some alloy systems (e.g. see Thompson and Noble 1973) and DMR may be of significance in explaining anomalies in the resistivity characteristics. The current study has therefore also been concerned with establishing the resistivity-temperature and resistivity-concentration relations of a number of alloys that undergo solid state precipitation reactions and in particular how these relations are modified by the metallurgical condition of the alloys.

The alloys studied are all precipitation hardening systems based on magnesium, involving a variety of solutes at several levels of concentration.

2. Experimental procedure

Samples of pure magnesium (99.998%) and a wide range of binary alloys containing the solutes Ag, Zn, Al, Nd, Pb, Sn and Th were prepared by induction melting and chill casting in an argon atmosphere. The solidus temperature of all samples was then established by quenching small samples from various temperatures followed by micro-examination to detect signs of grain boundary melting. The ingots were scalped, extruded and homogenised for several days by heating to a temperature 20 °C below the solidus. Finally the material was cold rolled to a 0.5 mm thick strip with interposed annealing periods at the homogenisation temperature. The compositions, determined by chemical analysis, are given in table 1.

Specimens for electrical resistivity measurements had dimensions of 150 mm × 3 mm × 0.5 mm and these were cut from the rolled strip, the ends slit, and wires of pure magnesium welded on for current and potential connections. Owing to the reactive nature of some of the solutes, and of magnesium itself, solution treatment was carried out in a dichromate salt bath. The heat treatment temperature was again 20 °C below the solidus and was followed by a rapid quench into water at 293 K, the cooling rate being typically about 10000 degs⁻¹. The constancy of the quenched resistivity of a single specimen after repeated solution treatments and quenches indicated the suitability of the heat treatment schedule.

Table 1. Chemical composition of magnesium alloys used in the investigation.

Alloy designation	Composition (at%)	Alloy designation	Composition (at%)
Zn 1	1.05	Nd 0.1	0.08
Zn 1.5	1.53	Nd 0.15	0.13
Zn 2	2.25	Nd 0.3	0.27
Pb 0.5	0.47	Nd 0.5	0.43
Pb 2	1.76	Sn 2	1.98
Pb 3.5	3.35	Ag 2.5	2.46
Th 0.1	0.10	Al 8	8.07
Th 0.3	0.31		
Th 0.5	0.44		

Resistivity measurements were made at a variety of temperatures from 77–320 K using standard potentiometric techniques. The largest errors occurred in measuring the specimen dimensions, and were less than $\frac{1}{2}\%$. The specimen measurement error will have the largest effect on the DMR for dilute alloys held at the higher temperatures. However, since the resistivity data were always found to be linear with no significant scatter over the temperature range 77–320 K for both dilute and concentrated alloys, it is apparent that measurement errors are not having a significant effect on the final result.

3. Results

3.1. Solid solution alloys

Solution treatment followed by water quenching produces an alloy with all the solute in solid solution, this being confirmed by optical and thin film electron microscopy. For alloys containing Zn, Pb, Nd and Th where a range of compositions were available, the resistivity increment due to the presence of the solute in solid solution was determined and this is shown as a function of composition in figure 1. In the figure the quantity $\Delta\rho(77)$ is the resistivity increment at 77 K as defined by the expression:

$$\Delta\rho(77) = \rho_{\text{alloy}}(77) - \rho_{\text{Mg}}(77).$$

The variation of the resistivity quotient $\Delta\rho(T)/\rho(77)$ of the quenched alloys with measuring temperature T is shown in figure 2. A linear dependence of the resistivity quotient on the measuring temperature was found for all alloys. Where this line is horizontal, i.e.

$$\frac{d}{dT}(\Delta\rho(T)/\rho(77)) = \alpha = 0$$

Matthiessen's rule is being followed, e.g. dilute Mg–Th alloys. A negative value of α was observed for Mg–Zn, Mg–Pb, Mg–Sn and Mg–Nd indicating that DMR is occurring. The negative values of α for these dilute alloys are in the range $0.2\text{--}2.0 \times 10^{-4} \text{ K}^{-1}$ and compare favourably with the values that can be derived from

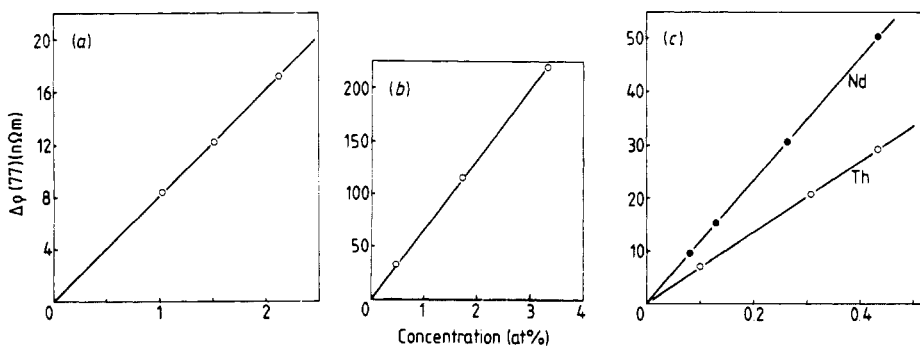


Figure 1. Variation of resistivity increment with concentration of (a) zinc, (b) lead and (c) thorium (○) and neodymium (●) dissolved in magnesium. $d\Delta\rho(77)/dc$ (in $\text{n}\Omega\text{m}$ per at%) has values of (a) 8.05, (b) 65.8 and (c) 67.0 and 115.0 respectively.

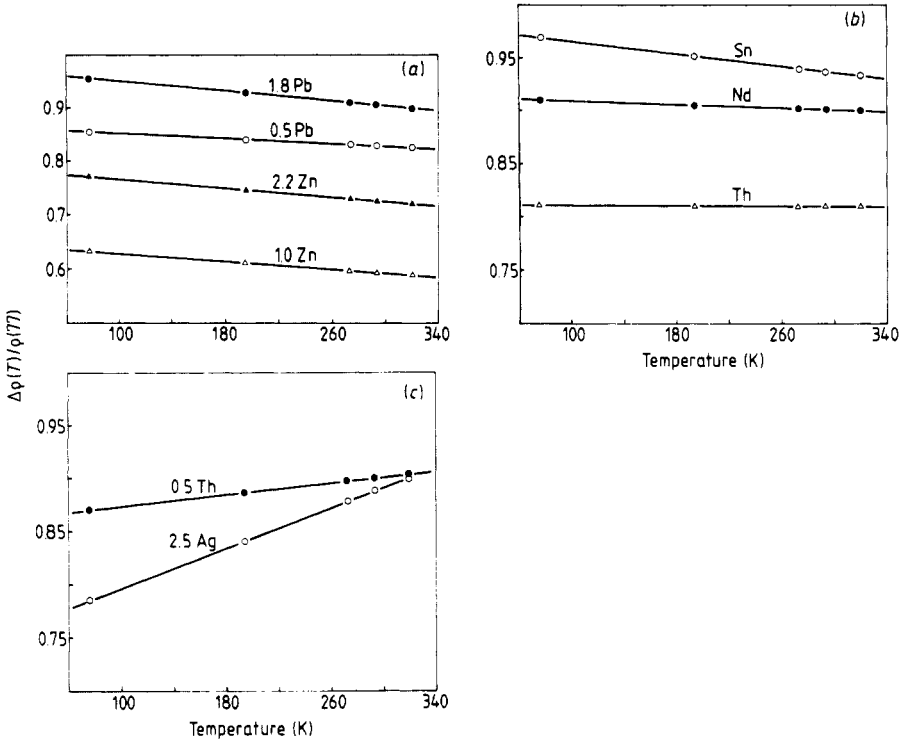


Figure 2. Variation of impurity resistivity quotient with measuring temperature. (a) Data for solid solutions of Mg-0.5, 1.8% Pb (O, ●) and Mg-1.0, 2.2% Zn (Δ , \blacktriangle). (b) Data for solid solutions of Mg-2.0% Sn (O), Mg-0.5% Nd (●) and Mg-0.3% Th (Δ). (c) Data for Mg-2.5% Ag (O) and Mg-0.5% Th (●).

the results of previous workers (e.g. see Bass 1972). For the more concentrated alloys (e.g. Mg-2.5% Ag and Mg-0.5% Th) the temperature variation of DMR is now found to be positive, a result that compares only with that reported for a concentrated Mg-4.4% Li alloy (Salkovitz *et al* 1957, Hedgcock and Muir 1964).

3.2. Aged alloys

Heating the quenched alloys to a temperature below the equilibrium solvus temperature produces controlled precipitation of a small volume fraction of solute-rich second phases, the precise nature of the phase depending on the heat treatment (ageing) temperature. The resistivity-temperature relationships were redetermined after this heat treatment, and again a linear dependence of $\Delta\rho(T)/\rho(77)$ on temperature was observed. In all cases the slope of the line (α) has increased compared to the solution treated condition, and has changed sign to become positive. The value of α in the aged (precipitated) alloy is typically of the order of $+10^{-3} \text{ K}^{-1}$. This effect is illustrated in figure 3 for Mg-Al and Mg-Nd alloys. In the latter case α can be seen to vary markedly with the heat treatment (ageing) temperature and this variation is shown in figure 4 for alloys of varying neodymium concentration.

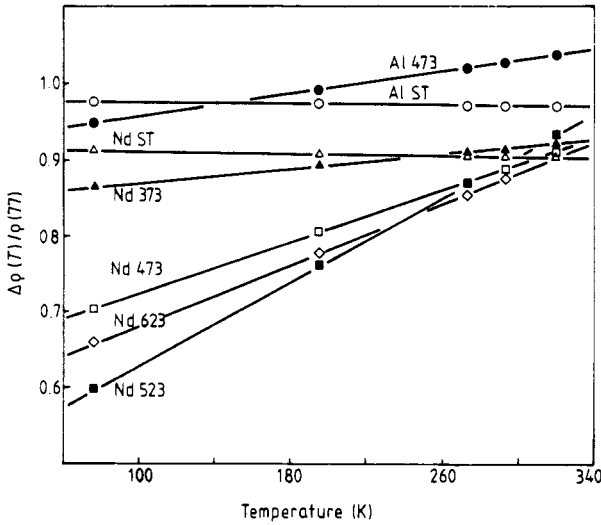


Figure 3. Variation of impurity resistivity quotient after precipitating the solute out of solid solution. Data for Mg-8% Al and Mg-0.5% Nd. Mg-Al, solution treated (○), aged at 473 K (●). Mg-Nd, solution treated (△), aged at 373 (▲), 473 (□), 523 (■) and 623 K (◇).

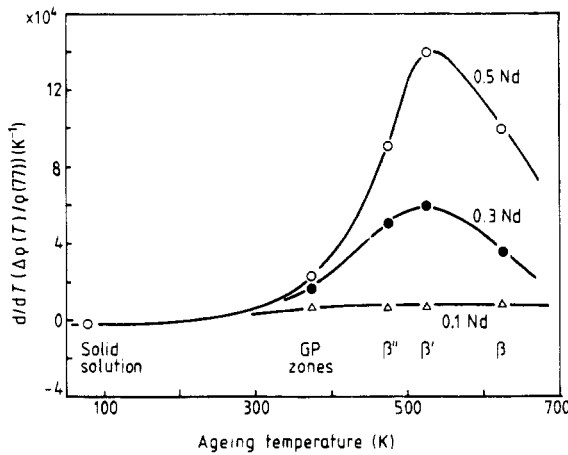


Figure 4. Temperature dependence of $\Delta\rho(T)/\rho(77)$ for various Mg-Nd alloys after ageing at different temperatures to produce the precipitates indicated on the diagram. (○) 0.5% Nd, (●) 0.3% Nd, (△) 0.1% Nd.

4. Discussion

4.1. Concentration dependence of resistivity (solid solution alloys)

Values of the quantity $\Delta\rho(77)/c$ are summarised in table 2. These were obtained from the gradient of the curves in figure 1 where alloys of variable composition were studied, or else from single composition results. The values obtained for the alloys

Table 2. Values of the parameter $\Delta\rho(77)/c$ for various solutes dissolved in magnesium.

Solute	Atomic number	Valency	$\Delta V/V_{\text{Mg}}^\dagger$ (%)	$\Delta\rho(77)/c^\ddagger$
Ag	47	1	-26.6	7.1
Zn	30	2	-34.4	8.1
Al	13	3	-28.5	22.2
Nd	60	3	+47.1	115.0
Sn	50	4	+19.0	84.8
Pb	82	4	+30.6	65.8
Th	90	4	+41.5	67.0

[†]Atomic volume relative to magnesium.

[‡]Resistivity at 77 K per atomic per cent of solute.

containing Ag and Al (7.1 and 22.2 nΩ m per at%) compare favourably with the previous work of Salkovitz *et al* (1957), who obtained values of 7.5 and 20 nΩ m per at% solute respectively. For the cases of the alloys containing Sn and Pb, the present results are somewhat higher than those of Salkovitz *et al* (1957) who obtained gradients of 52 nΩ m per at% solute for both alloys. However, no details are given in their paper of the metallurgical state of the specimens and it is quite possible that in the present work the solution treatment and quenching procedure has resulted in more concentrated super-saturated solid solutions than were obtained by these workers. This is almost certainly the explanation of the difference in $\Delta\rho(77)/c$ obtained for Mg-Nd alloys in the present work (115 nΩ m per at%) and that obtained previously by Das and Gerritsen (1962) (14.7 nΩ m per at%) and by Bijvoet *et al* (1963) (95 nΩ m per at%): these workers respectively annealed, and hot rolled, their specimens rather than solution treating them prior to measuring the resistivity.

Traditionally, the electrical resistivity of pure metals has been studied employing samples which have been carefully annealed before measuring the resistivity: the annealing process reduces to a minimum both lattice strains and the population of structural defects allowing the intrinsic resistivity to be studied. In the case of alloys, contributions are made to the residual resistivity by the structural defects as with pure metals, and by solute atoms. In precipitation hardening systems such as the present magnesium alloys, it is not possible to study in isolation the contribution due to solute atoms, as, in addition to reducing strain effects, annealing would also result in the formation of two-phase structures, usually with an accompanying decrease in the electrical resistivity. Only by solution treatment and quenching can a random distribution of solute atoms be attained (or approached), and the abnormal population of structural defects produced by quenching must be tolerated. However, the greater part of this contribution is removed naturally since in magnesium at room temperature quenched-in vacancies anneal out in about 30 minutes; the contribution to residual resistivity of solute atoms then far outweighs that due to dislocations (Kelly and Nicholson 1963). The present alloys have been examined in the solution treated (as-quenched) condition employing thin film electron microscopy and selected area electron diffraction. In all cases the structure was typical of a single-phase homogeneous alloy, and no precipitated second-phase particles were detected.

The linear increase in the impurity resistivity increment with solute concentration indicates that Nordheim's concentration rule ($\Delta\rho \propto c$ for small c) is obeyed for alloys of magnesium with Zn, Pb, Th and Nd. The values of $\Delta\rho/c$ suggest that both the

valencies and atomic sizes of the solute atoms affect the magnitude of this parameter. Although no clear correlation can be made, it is apparent from table 2 that $\Delta\rho/c$ is small for solute atoms smaller than the magnesium atom, and increases rapidly for atoms larger than magnesium, reaching a maximum at neodymium for alloys in the present study.

4.2. Temperature dependence of resistivity (solid solution alloys)

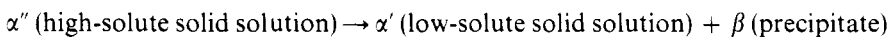
In the solution treated (single-phase) condition only dilute Mg–Th alloys obeyed Matthiessen's rule, the remainder exhibited varying degrees of deviation from the rule. The alloys containing Zn, Pb, Sn, Nd and Al all showed a temperature variation of DMR that was negative (i.e. negative α) and this is in general agreement with previous results for magnesium alloys (Bass 1972). However the concentrated alloys of Mg–Th and Mg–Ag showed a positive value of α which, apart from previous results on Mg–Li, is unusual for magnesium alloys at temperatures above 77 K.

The question arises as to whether the alloys in the solution treated condition are really homogeneous random solid solutions (Massalski 1965). For example it is known that in concentrated alloys of Mg–Ag Guinier–Preston zones can form at low temperatures (Nagashima 1959), and a low-temperature precipitation or ordering reaction occurs in Mg–Th (Noble and Crook 1970). Alloys of Mg–Pb and Mg–Sn are also known to undergo short-range ordering at low temperatures (Henes and Gerold 1962). Segregates may therefore be forming in the as-quenched alloys and these may modify the electrical resistivity behaviour from that of an ideal random solid solution.

To test this possibility, further investigations were carried out on the Mg–Pb and Mg–Sn alloys. X-ray diffraction studies on Mg–Pb and Mg–Sn alloys have shown that short-range order exists immediately after the quench but that this can be removed by cold work. In the alloys containing Pb and Sn used in the present work, cold rolling to 5% reduction in thickness produced a linear resistivity–temperature relationship the slope of which was the same as that observed in the as-quenched specimens indicating that in these alloys at least, the observations are an accurate description of the properties of true random solid solutions. In the remaining alloys, careful electron microscope and selected area diffraction studies of the quenched specimens has shown that the quenched specimens were single-phase structures, but it is still possible that very small clusters of solute atoms exist which are not detectable by either technique because of resolution limitations.

4.3. Temperature dependence of resistivity (aged alloys)

In all the alloy systems studied, heating (ageing) the alloy to produce a low volume fraction of precipitate particles caused the DMR to increase and its temperature dependence to change sign. In the Mg–8% Al alloy aged at 473 K these second-phase particles are the compound $Mg_{17}Al_{12}$, and in Mg–0.5% Nd aged at 623 K the particles are of $Mg_{12}Nd$. The precipitation reaction may be represented as:



and the increase in DMR caused by precipitation may therefore be due to either modifications to $\rho_i(T)$ as the α' solid solution develops or it may be due to the presence of the precipitate itself. One way of testing which process is the important one is to change the nature of the precipitate and determine the effect on DMR.

The nature of the precipitate may easily be changed in the Mg–Nd system where a range of non-equilibrium precipitates can be produced by varying the ageing temperature of alloys containing more than 0.3% Nd (Pike and Noble 1973). Needle-shaped fully coherent Guinier–Preston zones are formed at temperatures around 373 K, plate-shaped fully coherent ordered DO_{19} -type precipitates (β'') are produced at 473 K, partially coherent plate-shaped precipitates (β') are formed at 523 K and the non-coherent equilibrium phase $\beta(\text{Mg}_{12}\text{Nd})$ is produced at ageing temperatures greater than 573 K.

The effect of producing these different types of precipitate is shown in figures 3 and 4 where it can be deduced that changing the form of the precipitate changes the magnitude of the DMR. It is therefore likely that the increase in DMR observed when the quenched alloys are aged is being caused by the presence of a precipitate and not by changes in the α' solid solution.

The data in figure 4 also show that the largest values of DMR are produced when the β' precipitate is present in the alloy. The question therefore arises as to why this particular phase (β') should cause the DMR to rise considerably over the solution treated value and the value obtained for alloys containing zones, β'' or β . Several possibilities exist for the anomalous effect of the β' precipitate. Firstly, additional electron scattering may arise from coherency strain fields that exist around the β' precipitates. However, the Guinier–Preston zones and β'' phases also possess extensive strain fields and yet their effect on DMR is much less than β' . A second possible explanation could be based on the observations in the Al–Mn system where it is found that the dependence of DMR on the ageing temperature has a similar form to that observed in the present magnesium alloys (Kovács-Csetényi *et al* 1971). These authors tentatively attribute the dependence to the magnetic properties of the precipitates which reach some critical value during ageing. The magnetic properties of the Mg–Nd compounds that precipitate during ageing of the alloys in the present investigation are not known, but since large increases in DMR occur in other magnesium alloys after ageing, including the non-transition metal system Mg–Al, such an explanation appears unlikely. Finally it is possible that large amounts of electron scattering may be taking place because of the nature (structure) of the β' precipitate. That such an effect can be produced by a relatively small volume fraction of precipitate has been demonstrated by Thompson and Noble (1973) working with aluminium-based alloys containing Cu and Li.

These results on the effect of precipitation on the magnitude of DMR demonstrate in a striking manner how important it is to know the exact metallurgical state of an alloy when studying its electrical resistivity characteristics. Previous studies on DMR have dealt with the effect of such variables as the concentration, size and valency of solute and solvent atoms, and particularly the temperature range of study. The present work has shown that the effect of the form and distribution of solute atoms on DMR must also be considered before a satisfactory unifying view of DMR can be formulated.

5. Conclusions

The concentration dependence of resistivity of a large variety of binary magnesium alloys has been determined after water quenching to retain all the solute in solid solution. Alloys containing additions of Zn, Pb, Th and Nd were observed to obey Nordheim's rule.

Solid solution alloys based on dilute Mg–Th followed Matthiessen's rule but alloys based on Mg–Zn, Mg–Pb, Mg–Sn and Mg–Nd exhibited DMR, the temperature dependence of which was negative ($\alpha \sim -10^{-4} \text{ K}^{-1}$).

Solid solution alloys based on concentrated Mg–Th and Mg–Ag showed a DMR with a positive temperature dependence.

Heat treatment of alloys to cause precipitation resulted in an increase in DMR and a change in the sign of the temperature dependence from negative to positive ($\alpha \sim +10^{-3} \text{ K}^{-1}$).

The extent of the DMR is dependent on the nature of the precipitate present in the alloy. In Mg–Nd alloys the DMR is at a maximum when particles of the partially-coherent phase β' are present. Lower values of DMR were recorded when the heat treatment produced Guinier–Preston zones or the equilibrium Mg_{12}Nd precipitate.

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