Zuzanka Trojanová[1], **Zdeněk Drozd**[2], **Kristián Máthis**[3], **Pavel Lukáč**[4]

Charles University, Faculty Mathematics and Physics, Ke Karlovu 5, CZ - 121 16 Praha 2, Czech Republic

Stanislav Kúdela[5]

Institute of Materials & Machine Mechanics SAS, Račianska 75, SK - 838 12 Bratislava, Slovakia

HARDENING AND SOFTENING IN Mg-Li-Al MATRIX COMPOSITES

Mg-xLi-yAl (x = 4, 8, 12, y = 0, 3, 5) matrix composites reinforced with short δ-alumina (Al$_2$O$_3$) fibres were manufactured by the pressure infiltration process. The fibrous preform was prepared using commercial alumina fibres (Saffil) via water dispersion, sedimentation and drying operations without any binder. The structure of composite materials consisted of short δ-alumina fibres (10% vol.) distributed planar-randomly within Mg-Li-Al matrix (*hcp, hcp+bcc, bcc*). No significant fibre damage resulting from the Mg-Li-Al melt attack was observed. Compression tests of cylindrical composite samples were carried out at temperature between 20÷200°C. The results obtained revealed that the flow stresses of the composites are substantially higher than those of unreinforced alloy. These difference decreases with increasing test temperature. Different contributions to the strength of composites were evaluated. The shear stress at fibre/matrix interface were of greatest importance in this regard, though the contribution resulting from the dislocation density increase was also significant.

Key words: metal matrix composites, magnesium alloys, strain hardening, high temperature properties

UTWARDZANIE I UPLASTYCZNIANIE W KOMPOZYTACH NA OSNOWIE Mg-Li-Al

Przedstawiono wyniki badań kompozytów na osnowie stopów Mg-xLi-yAl o różnym udziale składników stopowych (x = 4, 8, 12; y = 0, 3, 5), umacnianych krótkimi włóknami Al$_2$O$_3$. Udział fazy umacniającej ustalono na poziomie 10% obj. Szczególną uwagę poświęcono charakterystykom mechanicznym odkształcania w próbach ściskania, przeprowadzonych w zakresie temperatur pomiędzy 20 a 200°C. Ujawniono, że naprężenie płynięcia plastycznego w kompozytach było wyższe niż w samym stopie osnowy, przy czym różnice te malały w miarę wzrostu temperatury odkształcania. Omówiono mechanizm przenoszenia obciążenia od osnowy do elementu wzmocnienia przez granice faz, jak również inne mechanizmy wpływające na zmianę gęstości dyslokacji w pobliżu włókna wzmacniającego. Wyniki badań dotyczące wzmocnienia stopu osnowy interpretowano w kontekście typu struktury poszczególnych faz (α-A3, β-A2 oraz α+β).

Słowa kluczowe: kompozyty metalowe, stopy magnezu, umocnienie poprzez zgniot, właściwości wysokotemperaturowe

INTRODUCTION

Light alloys reinforced with short fibres or particles allow adapting more exactly the work piece material properties to requirements. There is an increasing trend in the automotive industry to use these materials for various parts. Advanced properties of metal matrix composites are [1]:

- increased apparent limit of elasticity, stiffness, tensile and fatigue strength,
- improved creep resistance and high temperature properties,
- improved material damping,
- increased wear resistance,
- decreased thermal expansion.

Light Mg-Li alloys are attractive candidates for reinforcement with ceramic fibres or particles. Pure Mg has *hcp* structure; alloying with Li powers density and increases ductility. The Mg-Li phase diagram shows that Li is soluble in *hcp* α-phase up to 4 wt.%, while Mg alloyed with greater than 12 wt.% Li has a *bcc* structure.

Mechanical properties of the *hcp* α phase are worse in comparison with the *bcc* alloys, which are very good machinable and weldable. Disadvantages of Mg-Li alloys with *bcc* structure are a high chemical activity and poor corrosion resistivity. Some compromise would be an alloy with 8 wt.% of Li (a mixture of phases α+β), which might exhibit both improved mechanical properties as well as a good corrosion resistance. To improve the mechanical properties, alloying with other elements can be used. The completion of the binary alloy with additional elements as Cd, Al, Zn, Si leads to the precipitation of a coherent transition θ phase MgLi$_2$X, where X is the third element. The further possibility how to improve the mechanical properties of Mg-Li alloys is to reinforce the alloy with the adding of ceramic fibres.

The present work is focused on the mechanical behaviour of composites where the matrices from

[1,4] Prof. RNDr., DrSc, [2,3] RNDr., PhD, [5] RNDr. DrSc

Mg-Li-Al alloys were reinforced with short alumina (Saffil®) fibres.

EXPERIMENTAL PROCEDURE

Mg-Li-xAl matrix composites were manufactured by the gas pressure infiltration of evacuated fibrous preform with metallic melt in the autoclave. The preform consisting of discontinuous δ-alumina fibres (approx. 10%vol.) was prepared by the ultrasonic stimulated dispersion of commercial SAFFIL® product in a water medium, subsequent sedimentation and drying at 150°C to obtain planar-random fibre distribution. Mean fibre length and fibre diameter after infiltration was ~100 μm and ~3 μm, respectively. The preform was embedded without any binder into evacuated low-carbon steel container (8x8x70 mm) and infiltrated under gas pressure (argon) at 690°C/6 MPa/30 s with molten alloy. No significant fibre damage resulting from the Mg-Li-Al melt attack was observed. The composite samples were not thermally treated.

Compression tests were carried out at temperatures between room temperature and 200°C using an INSTRON testing machine. Cylindrical specimens of 5 mm diameter and 7 mm length were deformed at an initial strain rate of 2.7×10^{-4} s^{-1}. Saffil fibres in specimens exhibited a 2D random orientation with the fibre plane parallel to the specimen axis. Temperature in the furnace was kept with an accuracy of ±1°C.
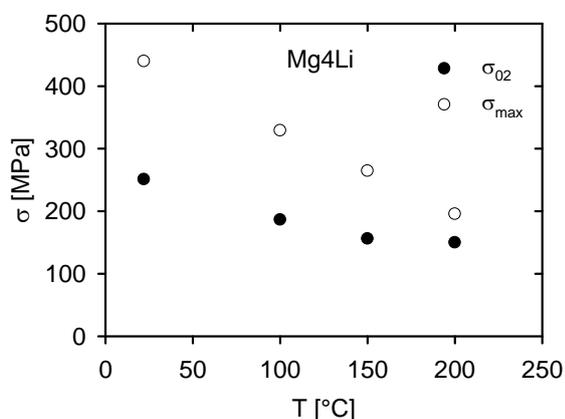

Fig. 1.   Temperature dependence of the yield stress and the maximum stress obtained for Mg-4Li based composite
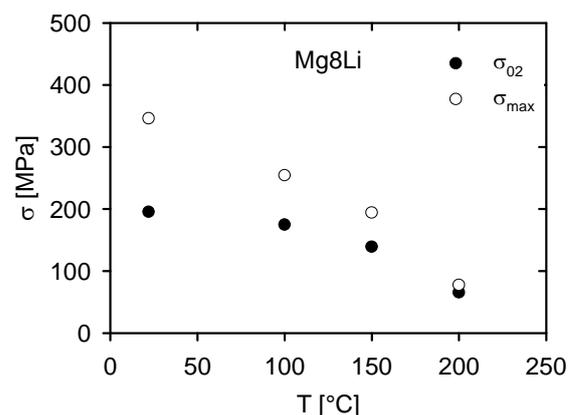

Fig. 2.   Temperature dependence of the yield stress and the maximum stress obtained for Mg-8Li based composite

RESULTS AND DISCUSSION

Temperature dependencies of the yield stress σ_{02} and the maximum stress obtained for composites with the hcp (α) Mg4Li matrix are introduced in Figure 1. Strain hardening (the difference between the yield stress and the maximum stress) is expressive at room temperature and it decreases with increasing temperature. The same dependence measured for (α+β) Mg8Li matrix is introduced in Figure 2. High strain hardening at room temperature decreases with increasing test temperature. The stress-strain curves for composites with (β) Mg12Li matrix deformed at various temperatures are very flat [2]. In contrast to composites with 4 and 8% of Li, where a definite strain hardening was observed, the flow stresses of Mg12Li composites reached their maximum value at the onset of deformation and then they decreased or took on a stationary value. The yield stress as well as the maximum stress Mg12Li matrix is introduced in Figure 3. The obtained stresses are substantially lower in comparison with composites with Mg4Li and Mg8Li matrix. But ductility of these composites was improved [2]. Alloying of Al causes an increase both the flow stress and the ductility of the composites [2]. The influence of Al content on the yield stress of Mg8Li composite is introduced in Figure 4.
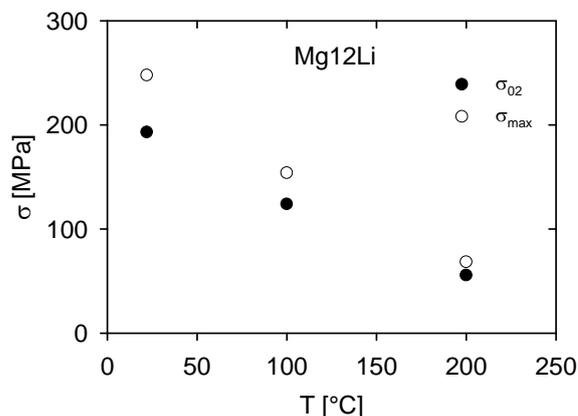
Fig. 3. Temperature dependence of the yield and maximum stress for Mg12Li composite
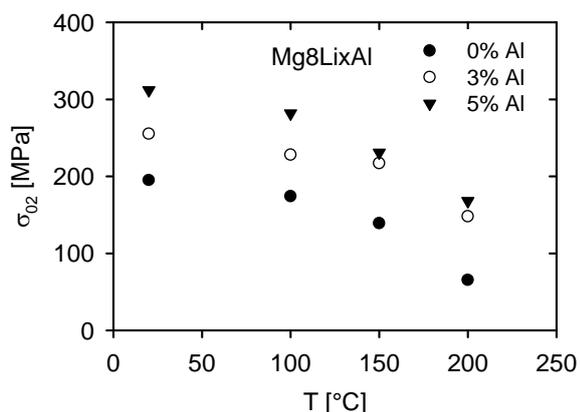
Fig. 4. Influence of the Al content on the yield stress of Mg8Li composite

From the results, it can be seen substantial differences in the deformation behaviour of composites with different structure.

Possible strengthening mechanisms

The temperature dependence of the yield stress of Mg4Li alloy and composite is introduced in Figure 5. It can be seen that addition of the reinforcing phase substantially increases the yield stress. At lower temperatures, the difference is about 200 MPa. Similar effects were found for the yield stress of Mg12Li3Al alloy and composite, which is demonstrated in Figure 6. The differences between the stresses of the matrix and composite decrease with increasing temperature, especially in the case of Mg-12Li alloy. Similar differences between the maximum stress of the alloy and composite were also estimated. The reinforcing phase causes an increase both the yield stress and the maximum stress.
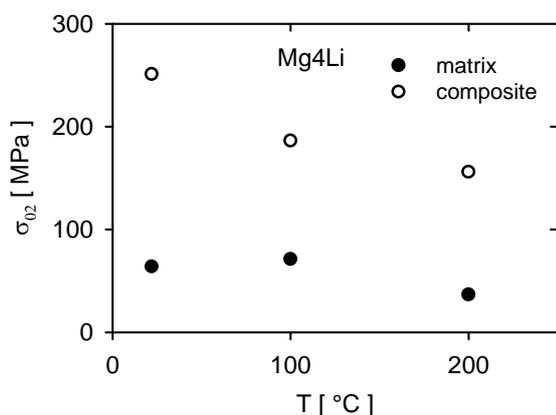
Fig. 5. Temperature dependence of the yield stress of Mg4Li alloy and composite
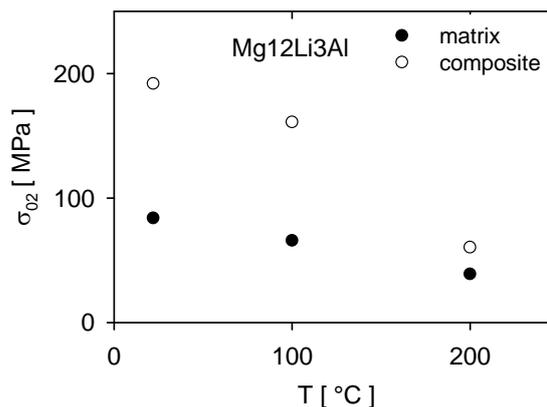
Fig. 6. Temperature dependence of the yield stress of Mg12Li3Al alloy and composite

Several analytical and numerical models have been developed to explain the mechanical properties of composites. In these models, it is assumed that the reinforcement relies mostly on load transfer from the matrix into the mechanically stronger particles or fibres.

Load transfer

The load transfer from matrix to fibre is maintained by the interface. The shear lag theory assumes that the load transfer occurs between a reinforcing particle with high aspect ratio and the matrix via the shear stress at the fibre-matrix interface. According to this mechanism, the fibre can act as a „reinforcement” to carry some of the load. Several authors [3-6] considered the shear lag model. The contribution to the yield stress due to load transfer $\Delta\sigma_{LT}$ can be calculated as [7]

$$\Delta\sigma_{LT} = \sigma_m\left[\frac{(L+t)A}{4L}\right]f + \sigma_m(1-f) \qquad (1)$$

where σ_m is the yield stress in the matrix, L is the fibre size in the direction of the applied stress, t is the fibre size in the perpendicular direction and A is the fibre aspect ratio (L/t). The model is based on the simplifying assumption of uniform matrix deformation and therefore, yields a very simplified expression for stiffness and strength contribution. Except for the stress transfer from the matrix to the fibres, the shear lag model does not account for the contributions from effects, which are associated with the inhomogeneous matrix behaviour, resulting in enhanced dislocation density and residual thermal stresses.

Enhanced dislocation density

It is known that, in many cases, there is a large difference in the coefficients of thermal expansion (CTE) between the matrix and the reinforcement. When the metal matrix composite is cooled from a higher temperature to room temperature, misfit strains occur because of differential thermal contraction at the interface. These

strains induce thermal stresses that may be higher than the yield stress of the matrix. Thermal stresses may be sufficient to generate new dislocations at the interfaces between the matrix and the reinforcements. Therefore, after cooling the composite, the dislocation density in the matrix increases. New dislocations arise directly in the production process as a consequence of the solidification process during preparation of the composite [8]. A higher dislocation density in a composite material invokes a higher level of the internal stress in the composite. The increase in the dislocation density near reinforcement fibres can be calculated as [9]

$$\Delta\rho = \frac{Bf\Delta\alpha\Delta T}{b(1-f)}\frac{1}{t} \qquad (2)$$

where f is the volume fraction of the reinforcement, t is its minimum size, b is the magnitude of the Burgers vector of the newly created dislocations, B is a geometrical constant. We believe that the higher dislocation density arises in composites during the fabrication procedure. The generation of thermally induced dislocations and the related dislocations density gradients increase also the yield stress of the composite according to the well-known relationship

$$\Delta\sigma_{CTE} = \alpha_1\psi\,Gb(\Delta\rho)^{1/2} \qquad (3)$$

where α_1 is a constant, ψ is the Taylor factor and G is the shear modulus. The density of the newly produced dislocations during the preparation process is approximately $\Delta\rho = 1.10^{13}$ m^{-2} and, hence, $\Delta\sigma_{CTE} \approx 36$ MPa. This result is in good agreement with the estimate of Drozd et al. [10], who found, in Mg reinforced with short Saffil fibres, proportionality between the stress on the end of the Hooke's straight line and the fibre volume fraction $\sigma_H \propto (f/1-f)^{1/2}$. Incompatibility between the matrix and particles causes generation of geometrically necessary dislocations during deformation, resulting in an increase of the strain hardening rate.

Orowan strengthening

The yield stress is characterised by the state when the matrix plastic flow is developed. Fibres in the matrix are obstacles for dislocation motion. Therefore, the stress necessary for motion of dislocations in the composite is higher than in the matrix without fibres. We consider a similar mechanism as in the case of strengthening by incoherent particles, i.e. Orowan strengthening. It is caused by the resistance of closely spaced hard fibres to the passing of dislocations. Asides from fibres, dislocations overcome stresses from dislocation pile-ups in the vicinity of the fibres. For strengthening caused by this mechanism, one may use to a first approximation the expression [11]

$$\Delta\sigma_{OR} = \frac{Gb}{\Lambda} + \frac{5}{2\pi}Gf\varepsilon_p \qquad (4)$$

where Λ is the distance between fibres, G is the shear modulus of the matrix and ε_p is plastic deformation. It is widely accepted, however, that Orowan strengthening is not significant for metal matrix composites because the reinforcements are coarse and the interfibre spacing is large. In our case if Λ measures in units of µm, the increase of the yield stress $\Delta\sigma_{OR}$ is only some units of MPa.

Grain size refinement

Discontinuously reinforced composites usually have very fine grains, smaller than their unreinforced matrices [12]. The contribution to the yield stress can then be estimated using the Hall-Petch relation, which relates the yield stress enhancement to grain size d

$$\Delta\sigma_{GS} = Kd^{-1/2} \qquad (5)$$

where K is a constant. Arsenault et al. [8] observed smaller subgrain size in Al composites reinforced by SiC particles. They suggested other contribution to the strengthening due to reduction of dislocation cell size.
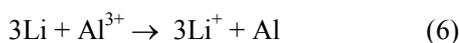
Strain hardening in the matrix

The Li addition is used to increase the ductility of hcp magnesium alloys by activating additional slip planes. Hence, it is obvious that Li addition reduces the c/a axial ratio of Mg and leads to an increase of ductility even at lower temperatures. For Mg4Li with low c/a ratio, the prismatic $\{10\bar{1}0\}\langle11\bar{2}0\rangle$ slip system provides two additional independent slip systems, giving a total of five independent slip systems, which are required for accommodation of the grain boundary continuity during deformation of polycrystals. The primary deformation mechanism, basal slip, is essentially athermal in the temperature range studied [13, 14]. However, the non-basal slip mechanisms involving cross slip of <a> dislocations on prismatic or first-order pyramidal planes [15] and the slip of <c+a> dislocations on second order pyramidal planes [16, 17] are strongly thermally activated. Intensive activity of non-basal slip systems with <c+a> dislocations at higher temperatures provides explanation for the observed decrease of the flow stress. The higher degree of symmetry in Mg12Li-yAl matrix provides a higher ductility of these composites.

Influence of the Al content

The results obtained clearly demonstrate that the strain response of short δ-alumina fibre reinforced Mg-xLi-yAl matrix composites to compressive loading is highly dependent on the crystallographic structure and on the Al content in matrix alloy. In general, the matrix

alloying may result directly to an increased matrix strength and indirectly to an improved fibre/ matrix interfacial bond in comparison with unalloyed matrix composites.

As concluded elsewhere [18], the formation of the interfacial bond in alumina fibre reinforced Mg based composites is strongly promoted with lithium alloying. There are strong driving forces for redox reactions at fibre/melt interfaces during the melt infiltration process producing Li^+ that reacts immediately with adjacent alumina to form metastable spinel-like compound $\delta(Li)$ structurally coherent with $\delta\text{-}Al_2O_3$. Elemental aluminium as a by-product of the redox alumina decomposition is dissolved in Mg-Li-Al matrix causing thus its additional alloying. Schematically:

$$3Li + Al^{3+} \rightarrow 3Li^+ + Al \qquad (6)$$

$$Li^+ + \delta\text{-}Al_2O_3 \rightarrow \delta(Li) \qquad (7)$$

$$Al \rightarrow [Al]_{diss.} \qquad (8)$$

where solid state reaction (7) is essential as to formation of interfacial bond. An increase in aluminium content in Mg-Li-Al matrix is small because the extent of interfacial reactions during processing of composites is strictly controlled. Anyway, the concentration of aluminium is kept too low to influence significantly the lithium activity [19] so that the role of Al alloying in the formation of the interfacial bond is taken for marginal. The solid solution hardening should be restricted predominantly to α-region owing to higher solubility of aluminium in α-phase. Hence, an increased strength level of Mg-Li-Al based composites might be attributed to the matrix strengthening. The age hardening by metastable Li_2MgAl precipitates (~0.2 μm in size) is very effective, nevertheless, this is not the case because it requires thermal treatment that includes the quenching from ~350ºC and subsequent ageing at <150ºC [20]. Aluminium in as-cast Mg-Li-Al matrix might cause either the solid solution strengthening of α-phase or the precipitation hardening by stable Al-Li particles in β-phase. The solid solution hardening should be restricted predominantly to α-region owing to higher solubility of aluminium in α-phase. However, the solid solution hardening results only in a small contribution because the difference between atomic radii of the solute and the solvent is small (<15%), whereby only less than 1 wt.% Al (solution limit) is effective in this respect. Likewise, relatively coarse and rather sporadic Al-Li particles (~2 μm in size) precipitating inside β-region [21] can hardly be considered to be responsible for a remarkable strength increase.

Possible softening mechanisms

Cross slip recovery process

The variation of the flow stresses with increasing temperature may be accounted for by increasing activity of cross slip. The values of the maximum stress could be, therefore, considered as characteristics of the cross slip activity. The maximum stress should then decrease with increasing temperature in similar way as the stress necessary for cross slip, i.e. the temperature dependence may be expressed by the following equation

$$\ln \sigma_{max} = K_0 - K(\gamma, \dot{\varepsilon})\, T \qquad (9)$$

where K_0 is a constant and $K(\gamma, \dot{\varepsilon})$ is a function of the stacking fault energy γ and the strain rate $\dot{\varepsilon}$. This cross slip is more facile in *bcc* (β) structure where the screw dislocation segments are easy mobile at elevated temperatures. The edge components of dislocations remain in the slip plane and they may climb or subsequently form the cell substructure.

Local climb of dislocations

Plastic deformation in a composite begins in the vicinity of fibres where the dislocation density is higher than elsewhere in the matrix. Dislocations cannot pass the fibres without cutting them or leaving loops around the fibres. This athermal passing mechanism is similar to the Orowan mechanism. Dislocation pile-ups at the fibres can act as stress concentrators. Screw dislocation components locally cross slip forming superjogs having a height of about fibre diameter and at higher temperatures edge components are able to climb. Both may then annihilate in neighbouring slip planes. Annihilation of dislocations may also be supported by diffusion of vacancies in the thin layer at the matrix-fibre interface. Shewfelt and Brown [22] assumed that the metal-ceramic boundary is disordered and as such acts as a low energy channel for movement of atoms. The gradient of hydrostatic stress provides a driving force for vacancy transport. If the vacancy concentration far away from the fibre is the equilibrium concentration c_{v0}, the vacancy flow at the interface occurs at the rate

$$J \cong \frac{4\pi D_v}{b k_B T}\left(\tau b \Lambda - \sqrt{2E_L}\right) \qquad (10)$$

where τ is the shear stress acting in the slip plane, E_L is the dislocation line tension and Λ is the spacing between fibre ends. The plastic strain rate in this case is given by

$$\dot{\varepsilon} = (1/\Psi)\,\rho_c b v_c = (1/\Psi)\,\rho_c b \frac{Jb}{d/b} = \frac{8\pi b D_v}{d k_B T}\left(\tau b \Lambda - \sqrt{2}E_L\right)$$

$$(11)$$

where ρ_c is the density of climbing dislocations and d is the climbing distance, which is about fibre diameter.

Local climb of dislocations may reduce the work hardening in the matrix and is very probably an important recovery process. With increasing temperature, the plastic strain rate is also increasing (diffusion constant increases with temperature exponentially). Accordingly, this mechanism influences the deformation behaviour of the composite.

Influence of interface

The dislocation density in the soft matrix can decrease due to the network growth or annihilation of dislocations. Dislocations stopped at the interface cannot disappear unless they are absorbed by the interface. The ease of absorption is dependent on temperature, as it requires diffusion. On the other hand the shear stress imposed to the interface by dislocations may relax by sliding of the interfaces. Internal friction studies of composites showed that the interface sliding is possible under the support of diffusion processes [23]. The interface bonding plays very important role. Weak interface bonding may impair mechanical properties of a composite.

CONCLUSIONS

A series of Mg-Li-Al based composites was prepared by the gas pressure infiltration into a fibrous perform. Matrix alloys of composites exhibit *hcp* (α), *bcc* (β) and mixture ($\alpha+\beta$) structures. Compression tests were carried out in the temperature range from room temperature up to 200°C.

The results show that, for the composites with *hcp* matrix alloy in which cross slip is limited, there is a high strain hardening throughout the whole temperature interval studied. For *bcc* matrix alloys, in which the cross slip is possible, a two stage strain behaviour was observed in which there is a sudden lowering of the strain hardening capacity, the transition being attributed to the onset of cross slip. The most important strengthening mechanisms are the load transfer and enhanced dislocation density. The cross slip and subsequent annihilation of dislocations very probably cause softening. Local climb of dislocations in the vicinity of fibres supported by interface diffusion is probably important recovery mechanism.

Acknowledgements

REFERENCES

[1] Weinert K., Lange M., Schoer M., Magnesium Alloys and their Applications, ed. K.U. Kainer, DGM, Willey-VCH, Frankfurt 2000, 412.
[2] Trojanová Z., Drozd Z., Lukáč P., Kúdela S., Key Engn. Mater. 2003, 419-422, 817.
[3] Fukuda H., Chou T.W., J. Compos. Mater. 1981, 15, 79.
[4] Nardone V.C., Prewo K.M., Scripta Metall. 1986, 20, 43.
[5] Clyne T.W., Mater. Sci. Eng. 1989, A122, 183.

[6] Taya M., Arsenault R.J., Scripta Metall. 1986, 20, 349.

[7] Aikin Jr. R.M., Christodoulou L., Scripta Metal. Mater. 1991, 25, 9.

[8] Arsenault R.J., Wang L., Feng C.R., Acta Metall. Mater. 1991, 39, 47.

[9] Arsenault R.J., Shi N., Mater. Sci. Eng. 1986, 81, 151.

[10] Drozd Z., Trojanová Z., Pahutová M., WDS'97, Faculty Mathematics and Physics, Charles University, Praha 1997, Part I, 153.

[11] Lilholt H., Mater. Sci. Eng. 1991, A 135, 161.

[12] Miller W.S., Humphreys F.J., Scripta Metall. Mater. 1991, 25, 33.

[13] Shelly W.F., Nash R.R., Trans. AIME 1960, 218, 149.

[14] Lukáč P., Phys. Stat. Sol. 1992, (a) 131, 377.

[15] Piehler H.R., Backhofen W.A., Metall. Trans. 1971, 2, 249.

[16] Obara T., Yoshinaga H., Morozumi S., Acta Metall. 1973, 21, 885.

[17] Ando S., Tonda H., Materials Trans., JIM 2000, 41, 1188.

[18] Kúdela S., Rennenkamp R., Baunack S., Gergely V., Oswald S., Wetzing K., Microchimica Acta 1997, 127, 243.

[19] Moser Z., Agarwal R., Sommer F., Predel B., Z. Metallkunde 1991, 82, 317.

[20] Schemme K., Entwicklung superleichter Magnesium Werkstoffe, Reihe 5, Nr. 293, VDI-Verlag, Düsseldorf 1993.

[21] Kim D.H., Han Y.S., Lee H.I., Cantor B., Scripta Met. Mater. 1991, 31, 819.

[22] Shewfelt R.S.W., Brown L.M., Phil. Mag. 1977, 35, 945.

[23] Trojanová Z., Ferkel H., Lukáč P., Riehemann W., Phys. Stat. Sol. (a) 2002, 193, 205.

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Stanisław Wierzbiński