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PROPERTIES OF MAGNESIUM BASED COMPOSITES

Mg-based composites were manufactured by various processing techniques. The reinforcement was in the form of short fibres or particles. The microstructure developed influences properties of composites. Physical and mechanical properties of Mg based composites were investigated in the temperature range from 293 to 673 K. The thermal expansions and thermal conductivity were measured. Strength and deformation behaviour were studied. The volume fraction, shape and composition of the reinforcement significantly influence the properties of a composite. The interface between the matrix and the reinforcement has a great deal of importance in determining the properties of the composite.

Key words: Mg composite, thermal and mechanical properties

WŁAŚCIWOŚCI KOMPOZYTÓW NA OSNOWIE MAGNEZU

Przedstawiono wyniki badań właściwości fizycznych i mechanicznych kompozytów magnezowych. Materiały na osnowie magnezu i jego stopów AZ91 oraz QE22 wytworzono różnymi metodami. Fazę umacniającą stanowiły krótkie włókna δ - Al_2O_3 oraz cząstki ceramiczne SiC. Badania rozszerzalności cieplnej, przewodności cieplnej oraz właściwości wytrzymałościowe kompozytów, jak i stopów osnowy przeprowadzono w zakresie temperatur od 293 do 673 K. Określono jednoznaczny wpływ udziału objętościowego, kształtu oraz składu chemicznego fazy umacniającej na właściwości kompozytów. Uwzględniono również znaczący wpływ granic rozdziału pomiędzy osnową i fazą umacniającą w kształtowaniu właściwości materiałów kompozytowych.

Słowa kluczowe: kompozyty magnezowe, właściwości cieplne i mechaniczne

INTRODUCTION

There is an increasing interest in the automobile industry for light metal matrix composites (MMC). Magnesium alloys as the lightest alloys may be used as a structural metal because they have high specific strength and specific elastic modulus. On the other hand, Mg alloys exhibit poor plastic formability due to their hexagonal close packed structure. Reinforcement of an alloy leads to an increase in strength. Grain refinement leads also to a higher strength and higher ductility of the alloys.

Thermal residual stresses are formed in MMCs due to differences in the coefficients of thermal expansion between the matrix and the reinforcement. The matrix/reinforcement interface is significant in determining mechanical properties. In general, composite properties strongly depend on the properties of the composite components.

The aim of this paper is to show the influence of temperature on the strength and thermal properties of some Mg based composites.

EXPERIMENTAL PROCEDURE

The investigated materials were Mg and its alloys reinforced with δ - Al_2O_3 short fibres (Saffil[®] with a mean diameter of 3 μm and a mean length about 87 μm) prepared by squeeze casting technology. The preforms consisting of Al_2O_3 short fibres showing a planar isotropic distribution and a binder system (containing Al_2O_3 and starch) were preheated to a temperature higher than the melt temperature of magnesium (to about 1000°C) and then inserted into preheated die (290 to 360°C). The pressure for forcing the melt into the die with the preform was applied in two steps (50 MPa for 10 s and 130 MPa for 60 s). The second step closes pores and shrinkage cavities. During this short time of contact between the liquid metal and the fibres, only a slight reaction between the fibres and the matrix can occur.

QE22 (Mg-2% Ag-2% rare earths) alloys reinforced with SiC particles were fabricated by mixing and milling of matrix powder and particles with subsequent hot extrusion of the milled products. The Mg_2Si products were formed around the SiC particles in the SiCp/QE22 composites.

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The mechanical properties of the materials were assessed through tensile tests at temperatures between 20 and 300°C. The specimens with a gauge length of 25 mm and a diameter of 4 mm were deformed in an Instron testing machine at a constant initial strain rate of $8 \times 10^{-5} \text{ s}^{-1}$.

The linear thermal expansion of the as-cast specimens was measured in argon atmosphere using the Netzsch 402E dilatometer between 20 and 370°C at heating and cooling rates of 5 K/min. Specimens with a mean length of 50 mm and a mean diameter of 6 mm were used. The thermal expansion curves for composites were measured with three thermal (heating and cooling) cycles (runs). All materials were studied in the as-cast state. The volume concentration of the Saffil fibres was determined from the density measurements. The fibre planes were parallel to the specimen axis.

RESULTS AND DISCUSSION

Thermal properties

The relative elongation and the coefficient of thermal expansion (CTE) of composites depend on the composition of matrix, volume fraction of reinforcement, temperature and the thermal cycle used. In 9Al₂O₃/Mg composite the irreversible reduction of the specimen length occurs after the first thermal cycle. On the other hand, no change of the specimen length is observed in the second and following thermal cycles (the third cycle had the same course as the second one). From the temperature dependences of the CTE measured in both runs it follows a perfect agreement between the cooling branches, while different variations of the CTE with temperature are observed during heating stages of the cycles. The values of the CTE measured during heating in the second cycle are higher than those measured in the first cycle. It is important to note that the values of the CTE measured during heating decrease with increasing temperature if the test temperature is above about 250°C. The values of the CTE (for heating and cooling) are between $18 \times 10^{-6} \text{ K}^{-1}$ and $24 \times 10^{-6} \text{ K}^{-1}$.

Baker [1, 2] determined that at temperatures between 0 and 550°C, the coefficient of linear thermal expansion α of polycrystalline magnesium can be expressed as

$$\alpha = (25.0 + 0.0188t) \times 10^{-6} \text{ K}^{-1} \quad (1)$$

where t is the value of the temperature in °C. The mean CTE for pure Mg in the temperature range from 20 to 400°C is $29 \times 10^{-6} \text{ K}^{-1}$. It is obvious that the values of the CTE of Mg are higher than those for the 9Al₂O₃/Mg composite. The value of CTE for pure Mg at room temperature is $25.2 \times 10^{-6} \text{ K}^{-1}$.

The temperature dependences of the relative elongation and of the CTE for 30Al₂O₃/Mg composite were estimated both in the temperature range from 20 to 375°C and at temperatures ranging from room temperature to 150°C. The irreversible change of the specimen length occurs after the first cycle. The irreversible reduction of the 30Al₂O₃/Mg composite is higher than that of the 9Al₂O₃/Mg composite. The CTE during heating in the first cycle is slowly decreasing with increasing temperature from the value of about $18 \times 10^{-6} \text{ K}^{-1}$ to about $12.4 \times 10^{-6} \text{ K}^{-1}$ whereas the CTE during heating in the second cycle is constant below 250°C and above this temperature the CTE decreases with increasing temperature. The values of the CTE in the second cycle are higher than in the first one. The temperature variations of the CTE during cooling stages are the same. The CTE values increase with increasing temperature. The range of values is 16 to $21 \times 10^{-6} \text{ K}^{-1}$.

The irreversible reduction of the specimen length of 30Al₂O₃/Mg composite estimated between 20 and 150°C after the first cycle is much lower than that obtained after the thermal cycle between 20 and 375°C. The values of the CTE in cooling stages are the same for both cycles and they ranging from 16.4 to $20 \times 10^{-6} \text{ K}^{-1}$. It is interesting to note that the CTE during heating decreases slowly during the first cycle, whereas it exhibits a very small increase with increasing temperature in the second cycle.

The length reductions of the composite specimens after the first cycle of measurements are given in Table 1.

TABLE 1. Residual changes of specimen length

Composite	T_{max} , °C	Res. ΔL , μm
Mg-9% Saffil	370	-9
Mg-30% Saffil	370	-27
Mg-30% Saffil	150	-9

The curves of relative elongation and the CTE versus temperature for Mg composites depend on the volume fraction of fibres, on heating and cooling stages, on the maximum temperature of the thermal cycle, and the thermal cycle number [3]. It means that the thermal expansion behaviour is dependent on the thermal history.

The measured thermal linear expansion curves show similar characteristics. After a complete heating and cooling first cycle, the composites exhibit residual strain. The value of the residual strain increases with increasing Al₂O₃ fibre volume fraction. The residual strain in the 30Al₂O₃/Mg composite increases also with the maximum temperature of the thermal cycle. Similar behaviour was observed by Chmelík et al. [4] who measured the

influence of thermal cycling on the relative elongation of Mg-based composites.

The thermal behaviour may be caused by thermal stresses arising in the matrix due to the difference in the CTE values between the reinforcement and the matrix, close to the matrix-fibre interface may be calculated in the simple approximation [5-7] as

$$\sigma_{TS} = E_f E_M f \Delta\alpha \Delta T / [E_f + E_M (1 - f)] \quad (2)$$

where E_f and E_M are Young's modulus of the fibres and the matrix, respectively, f is the volume fraction of fibres and $\Delta\alpha \Delta T$ is the thermal strain. With increasing temperature, if the specimen is heated, the internal thermal stresses at the interface may achieve the yield stress of magnesium at a certain temperature, and plastic flow can occur to relieve the stress. Above this temperature the CTE should decrease, which is observed. Once the composite had undergone plastic deformation during heating cycle, the produced thermal stress during cooling cannot cause deformation of the matrix back to its original size. Thus, residual strains arise after a complete heating and cooling first cycle, which is observed experimentally. The value of the thermal stress in the composite with a higher volume fraction of fibres is higher than that in the composite with lower volume fraction of fibres. Thus, the residual strains in the composite with the higher volume fraction of fibres should be higher, which is observed. The influence of the weak interfacial bonding between reinforcements and matrix on the thermal hysteresis behaviour cannot be excluded. Relaxation of the thermal stresses after the first thermal cycle influences the thermal hysteresis in the second and following complete heating and cooling cycles. The residual strains should be smaller or no residual strain should be observed, which is in agreement with experimental results.

A decrease in the CTE with increasing temperature starting at a certain temperature indicates that plastic deformation occurred when the thermal stresses exceed the yield stress of the matrix. A gradually decrease in the CTE for the 30Al₂O₃/Mg composite could be caused by small plastic deformation due to creep; the minimum creep rate increases with increasing temperature. The time at which the specimen is hold at a certain temperature of measurements is very short and the minimum creep rate at temperatures below 150°C is very slow. It means that the plastic deformation induced is very low, so that its influence on reduction of the CTE at temperatures below 150°C is insignificant.

Rudajevová and Lukáč [8] have reported that the thermal strain characteristics of magnesium alloy ZC63 (Mg-6% Zn-3% Cu-0.5% Mn) reinforced with 25 vol.% Saffil fibres are the same as for Mg-9 vol.% Saffil. But the irreversible contraction was twice as much as that for

the Mg composite. This may be a consequence of the twofold volume fraction of Saffil fibres.

The thermal strain characteristics for two phase Mg8Li (Mg-8wt.% Li) alloy reinforced with 12 vol.% Saffil is of a complex nature. The first thermal cycle led to irreversible extension. The Mg8Li composite has the lowest maximum value of the thermal strain even if there is the maximum difference in the CTE both components (CTE for Mg8Li alloy is $30 \times 10^{-6} \text{ K}^{-1}$ [9], for Saffil fibres $7.6 \times 10^{-6} \text{ K}^{-1}$ [10]). The difference in the thermal conductivities of the matrix and the reinforcement is, however, the lowest in the composites studied here (thermal conductivity of the Mg8Li alloy is 52 W/mK [9]). These results show that the thermal conductivities of both components have a large influence on the thermal strain developed in the composites.

Thermal conductivity

The main variables that should effect the thermal conductivity of a composite are the temperature level, the chemical composition and the volume fraction and the arrangement of the various phases present in the material. The temperature variation of the thermal conductivity of specimens of AZ91 (Mg-9% Al-0.7% Zn-0.13% Mn) alloy reinforced with 22.6 vol.% short Saffil[®] fibres is listed in Table 2 [11]. Table 2 presents also the thermal conductivity of unreinforced AZ91 alloy. The thermal conductivity is given in W/mK.

TABLE 2. Thermal conductivity of AZ91 alloy and AZ91 MMC

	50°C	100°C	150°C	200°C	250°C	300°C
AZ91	55.6	60.5	64.7	68.0	71.4	72.8
AZ91MMC	35.5	38.7	40.7	43.9	43.2	46.4

The thermal conductivity of the AZ91 composite increases with increasing temperature. The values of the thermal conductivity of the AZ91 composite at all temperatures are, as expected, lower than those of unreinforced AZ91 alloy.

The thermal conductivity values at selected temperatures for QE22 alloy reinforced with 10, 15 and 25 vol.% SiC particles are given in Table 3 [12].

TABLE 3. Thermal conductivity of SiCp/QE22 composites

	50°C	100°C	150°C	200°C	250°C	300°C
10SiC	112.8	116.0	119.2	119.9	120.4	121.1
15SiC	110.1	113.2	113.8	113.9	113.8	114.4
25SiC	106.6	107.8	107.8	106.6	105.5	104.5

The thermal conductivity of the QE22 composite is lower than that of unreinforced alloy and it decreases with increasing volume fraction of particles.

The thermal conductivity of a composite is a complex function of the thermal conductivity of the matrix, thermal conductivity of particles (fibres) and their radius, and also the thermal conductance of the interface.

Deformation behaviour

The temperature dependence of the yield stress of both monolithic AZ91 alloy and reinforced with 20 vol.% Saffil fibres (the fibres planes parallel and perpendicular to the specimen axis) is given in Figure 1. The maximum stress for the same specimens as a function of temperature is given in Figure 2.

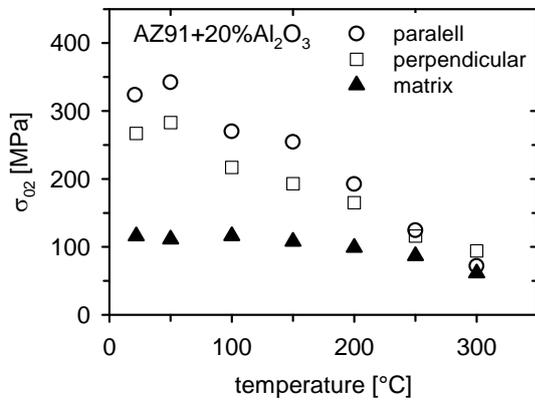


Fig. 1. Temperature behaviour of the yield stress obtained for two orientations of the fibres plane and the matrix alloy

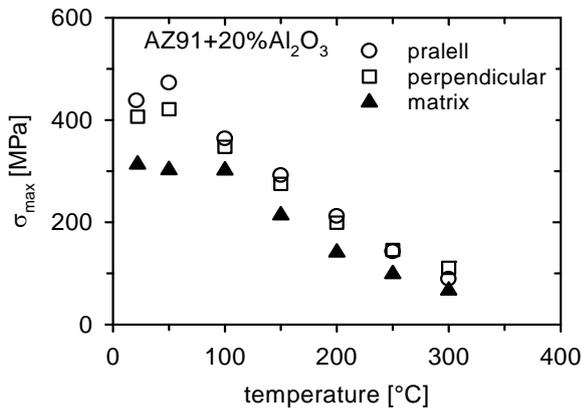


Fig. 2. Temperature behaviour of the maximum stress obtained for two orientations of the fibres plane and the matrix alloy

The yield stress and the maximum stress decrease very rapidly with increasing temperature. At about 300°C the values of the yield stress for the composite are the same as for the monolithic alloy (matrix). On the other hand, the values of the maximum stress for composite are close to those for the unreinforced alloy. This may indicate that fibres influence the yield and that dislocation motion is more important for strain hardening. The difference

between the maximum stress and yield stress decreases with increasing temperature. This indicates a softening process at higher temperatures.

Yield stress

It is clear that the yield stress of the AZ91 composite is higher than that of monolithic alloy. The same conclusion is valid for other Mg based MMCs. The load transfer was found to be the most important. The load transfer from matrix to fibre is maintained by the interface. According to the shear lag theory the load transfer occurs between a high aspect ratio reinforcement and the matrix by means of shear stress at the fibre-matrix interface. In this mechanism the fibre can act as a “reinforcement” to carry some of the load. A contribution to the yield stress due to load transfer $\Delta\sigma_{LT}$ is given, according to shear lag model [13], as

$$\Delta\sigma_{LT} = \sigma_m \left[\frac{(L+t)A}{4L} \right] f + \sigma_m(1-f) \quad (3)$$

where σ_m is the yield stress of the matrix, L is the fibre size in the applied stress direction, t is the fibre size in the perpendicular direction and A is the fibre aspect ratio (L/t). The strengthening component $\Delta\sigma_{LT}$, arising from the load transfer from matrix to fibres, has a value of 186 MPa in the case when all fibres are aligned in the specimen axis. In our case only fibres plane was oriented into the applied stress direction and the difference between the yield stresses of the composite and the alloy is about 210 MPa. Calculating the strength increase of 2D randomly oriented short fibres one becomes $\Delta\sigma_{LT} = 118$ MPa.

The thermal stresses generated at the matrix-reinforcement interface may relax and new dislocations are formed at interfaces; plastic zones result [14]. The density of the newly formed dislocations, $\Delta\rho$, is given as [5]

$$\Delta\rho = \frac{Bf\Delta\alpha\Delta T}{b(1-f)t} \quad (4)$$

where t is the minimum size of the reinforcing phase, b is the magnitude of the Burgers vector of dislocations and B is a geometrical constant depending on the reinforcement shape. A contribution to the yield stress due to the increase in the dislocation density may be expressed as [15]

$$\sigma_{CTE} = \alpha_1 \psi G b \left(\frac{Bf\Delta\alpha\Delta T}{(1-f)bt} \right)^{\frac{1}{2}} \quad (5)$$

where α_1 is a constant and ψ is the Taylor factor. The density of the newly dislocations formed during preparation process is approximately $\Delta\rho = 1 \times 10^{13} \text{ m}^{-2}$ (if

$B = 10$, $\Delta\alpha = 20 \times 10^{-6} \text{ K}^{-1}$). The stress contribution at room temperature $\Delta\sigma_{CTE}$ is about 35 MPa, if using (5) and taking $\alpha_1 = 0.5$.

As other mechanisms contributing to the yield stress one should consider the generation of geometrically necessary dislocations [16]. The corresponding stress increase is about 10 MPa. The discontinuously reinforced composites have very fine grains; smaller than their unreinforced matrices [15]. The contribution to the yield stress due to this effect can then be estimated using the Hall-Petch relation. The value obtained when all the contributions due to the presence of fibres are added to the yield stress of the matrix is very close to the yield stress of the composite observed experimentally.

Strain hardening

Temperature affects the shape of the stress-strain curves of AZ91 composites. The strain hardening rapidly decreases with temperature. The lower ductility of composites can be attributed to void nucleation at the matrix-fibre interfaces. The fibres in AZ91 alloy crept at 423 and 473 K are interconnected by the massive

β -phase ($\text{Mg}_{17}\text{Al}_{12}$) "bridges". Thicker zones of MgO particles were observed in contact with fibres [17]. The main obstacles for glide of dislocations are solute atoms, precipitates, grain boundaries, fibres and dislocations. The motion of dislocations in the non-basal slip systems should be assumed. The interaction between basal and non-basal dislocations may result to new obstacles or annihilation depending on the dislocation reaction. Dislocation pile-ups at fibres and grain boundaries can act as stress concentrators. Then screw dislocation components may locally cross slip and after the cross slip annihilation of dislocations may occur. With increase in the test temperature, double cross slip is easier leading to a decrease in the strain hardening rate and to an increase in the elongation to fracture, which is in agreement with experimental results. At higher temperatures the coarsening of precipitates may occur during the test. This leads to a reduction to the stress for the dislocation motion. Edge dislocation segments are able to climb (locally) at higher temperatures and then be annihilated.

The residual change of the specimen length observed after the first cycle of the thermal expansion measurements is due to acting of the thermal stress. With increasing temperature the internal stress can achieve the yield stress of the matrix and plastic deformation occurs in the composite during the temperature cycling without any applied stress. The radius of the plastic zone, R_{PZ} , formed at fibres can be expressed as

$$R_{PZ} = R_f(B_1\Delta\alpha\Delta TE_M/\sigma_y)^{1/2} \quad (6)$$

where R_f is the radius of fibres, B_1 is a constant and σ_y is the matrix yield tensile stress [18].

The thermal stresses influence also the behaviour of the AZ91 composites during thermal cycling [19]. The acoustic emission (AE) count rate and the specimen elongation of AZ91 reinforced with 22 vol.% Saffil were measured during a temperature cycle with different upper temperatures. The occurrence of AE and the change of the specimen length depend on the upper temperature T_u . There is no residual strain up to temperature of 200°C. From 220 to 280°C a residual elongation is observed and for T_u greater than 280°C, there is a significant residual contraction that increases with increasing T_u . When T_u reaches 320°C, the total AE count increases by several orders. QE22 alloy reinforced with 20 vol.% Saffil behaves in a similar manner to the AZ91 composite. The transition from residual elongation to residual contraction in QE22 MMC occurs at 360°C [20]. Different values of the transition temperature are to expect because the values of the yield stress of matrix depend on the composition. Chmelik et al. [20] have reported that there is a minimum upper temperature of cycling necessary for appearance of acoustic emission. It is about 150, 320 and 360°C in composites with matrix Mg, AZ91 and QE22, respectively. The volume fraction of fibres was practically the same. The occurrence of AE indicates changes in the microstructure of the matrix and the dislocation motion under action of thermal stresses without external stresses. In the above mentioned cases the occurrence of AE is not connected with any damage in the specimen. More than 1000 thermal cycles are needed to produce any measurable damage in AZ91 composite [20].

Very recently, Trojanová et al. [22] estimated changes in the microstructure of ZE41 composite using internal friction measurements after thermal cycling. A residual contraction was observed if upper temperatures were higher than 280°C.

CONCLUSION

The coefficients of thermal expansion of composites are lower than those of Mg. The thermal conductivity of the AZ91 and QE22 composites is lower than in the monolithic AZ91 and QE22 alloy, respectively. The newly produced dislocations at interfaces due to the relaxation of thermal stresses contribute to the thermal resistance in the vicinity of interfaces and therefore contribute to a decrease in the thermal conductivity.

The difference in the thermal expansion coefficients between the matrix and the fibres in Mg- Al_2O_3 composites results in thermal stresses. After thermal cycling the thermal stresses may relax by the generation and motion of dislocation resulting in residual compressive strains. The residual changes in the specimen length is larger for

a higher volume fraction of fibres and lower for a cycle with lower upper temperature of the cycle. It was documented by the thermal expansion measurements and by in situ monitored acoustic emission.

The largest difference between the yield stress values of the composite and the monolithic alloy is at room temperature. The difference decreases with increasing temperature. At about 250°C the yield stress values are practically the same for the composite and the alloy. The strain hardening rate decreases with increasing temperature. At higher temperatures (523÷573 K), a steady state flow is attained after small strains. The yield stress and deformation behaviour of the composites are also influenced by the thermal stresses.

From the thermal expansion behaviour and acoustic emission measurements it can be concluded that changes in the microstructure of Mg based composites occur after processing and during thermal cycling. The irreversible changes of the specimen length observed after the first thermal cycle indicate the dislocation motion due to the thermal stresses relaxation. Above a certain temperature a reduction (contraction) of the composite specimen length occurs.

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REFERENCES

- [1] Baker H., Physical Properties of Magnesium and Magnesium Alloys, The Dow Chemical Company, Midland 1967.
- [2] Magnesium and Magnesium Alloys, ASM Specialty Handbook, ASM International, Materials Park 1999.
- [3] Lukáč P., Rudajevová A., Kovové Mater. 2003, 41, 281.
- [4] Chmelík F., Trojanová Z., Kiehn J., Lukáč P., Kainer K.U., Mater. Sci. Eng. 1997, A234-235, 774.
- [5] Arsenault J.R., Shi N., Mater. Sci. Eng. 1986, 81, 151.
- [6] Chawla K.K., Materials Science and Technology. Vol. 13, eds. R.W. Cahn, P. Haasen, E.J. Kramer, VCH Weinheim 1993.
- [7] Urreta S.E., Schaller R., Careno-Morelli E., Gabella E.J., Physique IV, 1996, C8-774.
- [8] Rudajevová A., Lukáč P., Acta Mater. 2003, 51, 5579.
- [9] Rudajevová A., Kúdela S., Staněk M., Lukáč P., Mater. Sci. Techn. 2003, 19, 1079.
- [10] Chang S., Lin S., Flemings M.C., Metal. Mater. Trans. 2000, 31A, 291.
- [11] Rudajevová A., Kiehn J., Kainer K.U., Mordike B.L., Lukáč P., Scripta Mater. 1999, 40, 57.
- [12] Rudajevová A., Lukáč P., Phys. Stat. Sol. (a) 1999, 175, 547.
- [13] Aikin Jr R.M., Christodoulou L., Scripta Metall. Mater. 1991, 25, 9.
- [14] Arsenault J.R., Fisher R., Scripta Metall. 1983, 17, 67.
- [15] Clyne T., Whithers P.J., An Introduction to Metal Composites, Cambridge Press, Cambridge 1993.
- [16] Luster J.W., Thumann M., Baumann R., Mater. Sci. Techn. 1993, 9, 853.
- [17] Sklenička V., Pahutová M., Kuchařová K., Svoboda M., Langdon T.G., Key Eng. Mater. 2000, 171-174, 593.
- [18] Dunand D.C., Mortensen A., Acta Metall. Mater. 1991, 39, 127.
- [19] Chmelík F., Kiehn J., Lukáč P., Kainer K.U., Mordike B.L., Scripta Mater. 1998, 38, 81.
- [20] Chmelík F., Moll F., Kiehn J., Lukáč P., Mordike B.L., Kainer K.U., Adv. Eng. Mater. 2000, 2, 600.
- [21] Kiehn J., Köhler C., Kainer K.U., Key Eng. Mater. 1994, 97-98, 37.
- [22] Trojanová Z., Lukáč P., Chmelík F., Riehemann W., J. Alloys Comp. 2003, 355, 113.

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