The influence of interfacial chemical reactions on the residual and thermal strain in reinforced magnesium alloys

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Abstract

The residual and thermal strains strongly influence the dilatation characteristics of fibre composites. The dilatation characteristics of two fibre composites, AX41-12 vol.% Saffil fibres and AX41-12 vol.% C fibres, were investigated in the temperature range of 20–380 °C. Three fibre orientations were studied; angles between the axis sample and the preferential plane of the fibre distribution were 0°, 45° and 90°. The thermal strains showed strong anisotropy. The smallest influence of the residual and thermal strain on the dilatation characteristics was found in C-45 composites. The thermal strain in CC composites (reinforced by C-fibres) is three times higher than in CS composites (reinforced by Saffil fibres). It is assumed that this is a consequence of the chemical reaction between the matrix and reinforcement in the AX41-C fibre interface. The reaction products strongly influence the matrix properties at the interface, and therefore, micro-plastic deformation in this part of the matrix. This micro-plastic deformation then influences macroscopic physical properties such as thermal expansion. The products of the chemical reactions at the interface of the CC composite also influence the character of the temperature dependence of the residual strain.

Key words: metal matrix composites, fibres, thermal expansion

1. Introduction

Metal matrix composites (MMCs) have gained increasing interest in automotive and aeronautical applications, where it is important to develop materials with a high strength, high creep resistance, light weight and low or controlled coefficients of thermal expansion (CTE). The effectiveness of composite reinforcements is significantly influenced by the properties of the transition regions between composite components. Interfacial regions in metal matrix composites are important in controlling the mechanical and thermal properties of these materials. It has been shown that the deformation behaviour of magnesium alloys and composites depends on grain size [1, 2], and deformation behaviour influences the thermal expansion behaviour [3].

Metal matrix composites reinforced with short ceramic fibres are typical systems of phases with different coefficients of thermal expansion. Because of these differences, local strains, and with them connected stresses, occur inside the materials. The strains and resulting stresses have important consequences for many material properties. In principle, two types of these strains can be distinguished. First, residual strain depends on the thermal and mechanical history of the material, and as a rule, can be simply removed by heating. Second, the thermal strain depends on the attributes of the system in any state, and can be assigned exclusively to differences in the CTE of phases. In our previous work we have investigated the influence of the interface on the residual and thermal strain in Mg-9 vol.% Saffil fibres as well as in Mg-Li alloys reinforced with 9 vol.% Saffil fibres [4–7]. The temperature dependences of the thermal strain in Mg composites had a different character than that in the

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Mg-Li composites because chemical reactions between Li and Saffil (Al_2O_3) occur at the interfaces in the Mg-Li composites, while no reactions occur in Mg composites [7]. The better adhesion of Mg-Li alloys to Al_2O_3 fibres in comparison with the system Mg-Al_2O_3 is due to the different ability of the Li^+ and Mg^+ ions to enter into the vacant cation interstitial positions in the Al_2O_3 lattice during infiltration of the Saffil preform by the Mg-Li alloy at high temperatures. It is assumed that while the interface between pure Mg and Al_2O_3 is a single area, the interface between the Mg-Li alloy matrix and Al_2O_3 reinforcement is a transition oxide layer composed of the Al_2O_3 and Li_2O oxides.

Over the last decade, many heat resistant Mg-Al--Ca alloys have been developed and investigated [8–13]. The alloys, in some cases containing small (microalloying) additions of strontium, exhibit an improvement in high temperature mechanical properties and excellent creep resistance [8]. The type of precipitates in Mg-Al-Ca alloys depends on the Ca/Al mass ratio [9]. When this ratio is higher than about 0.8, the presence of both Mg_2Ca and Al_2Ca are observed. When the ratio is below 0.8, only Al_2Ca can be detected. Both precipitates are formed along the grain boundaries. The Al_2Ca compound, which is stable at high temperatures, suppresses the formation of the β-$Mg_{17}Al_{12}$ phase, and the formation of a $(Mg,Al)_2Ca$ phase is also observed. The ternary phase has a hexagonal structure with a coherent interface between the phase and both primary α-Mg grains and the eutectic magnesium. The $(Mg,Al)_2Ca$ phases are situated at grain boundaries [11]; they can be effective pinning for grain boundary sliding. It should be mentioned that the ternary $(Mg,Al)_2Ca$ phase has a relatively high melting point of 715 ℃ in comparison with the Mg_2Ca phase, which has a melting point of 445 ℃. A series of Mg-Al-Ca alloys is suitable for elevated temperature applications [13]. These alloys are potential candidates for the preparation of MMCs.

The aim of this work is to determine the dilatation characteristics of two composites with the same matrix based on the AX41 alloy. In the first composite, the AX41 matrix is reinforced with 12 vol.% Saffil fibres, and in the second composite, the same matrix is reinforced by 12 vol.% carbon fibres. The temperature dependences of the dilatation characteristics will be studied from room temperature to 380 ℃; the measured data will be analysed and the possible influence of the different interfaces on the dilatation characteristics will be discussed.

2. Experimental details

The materials for the present study were magnesium composites based on AX41 (Mg-4Al-1Ca in mass %) alloy, which was reinforced with 12 vol.% Saffil fibres and 12 vol.% Sigrafil C-fibres. The composites were supplied by the Centre of Advanced Materials, Clausthal, and were prepared by squeeze casting. The molten alloy (700 ℃) was inserted into a preheated die (350 ℃) with pre-formed Saffil or C-fibres. Two--stage application of pressure was used (40 MPa for 15 s followed by a pressure of 70 MPa for 90 s). The ingot dimensions were 100 × 100 × 30 mm^3.

Short fibres in the composite held their original arrangement existing in the preform; they were planar randomly arranged, i.e., axes of fibres lay randomly in parallel planes. The length of the fibres measured in the composites after squeeze casting was on the order of tens of μm, and their diameter (thickness) was approximately 3 μm. Particles of secondary phases, namely $CaAl_2$, were randomly distributed throughout the structure. From the composite part of the ingot, parallelepipeds were cut at three angles (0, 45 and 90°) to the preferential plane xy of the fibre distribution. Cylindrical specimens with a diameter of 6 mm and length of 25 or 20 mm were prepared for dilatation measurements. The composite samples with the Saffil fibres are hereafter called CS-0, CS-45 and CS-90, and with the C-fibres, CC-0, CC-45 and CC-90.

The linear thermal expansion of the composite specimens was measured in a helium atmosphere using a Netzsch 402 C dilatometer from room temperature to 380 ℃ at heating and cooling rates of 2 ℃ min^{-1}. The thermal expansion curves for composites were measured during three consequent heating and cooling cycles. The first cycle was performed in the as-cast state.

3. Results

Figure 1 shows the temperature dependences of the relative elongation for CS-0, CS-45 and CS-90 and CC-0, CC-45 and CC-90 composites obtained in the second thermal cycle. The main difference between the two types of composites is a higher hysteresis in CC composites; this results from the higher influence of anisotropy in the CC composites. The temperature dependences of the CTE for heating and cooling are shown in Figs. 2 and 3. Both figures also show the temperature dependence of the relative elongation calculated from the rule of mixtures for AX41-12 vol.% Saffil fibres.

The strains in the composite are additive, therefore we can use the following relation for estimation of the measured thermal strains:

$$\left(\frac{\Delta l}{l_o}\right)_{\mathrm{meas}} = \frac{\Delta l}{l_o} + \left(\frac{\Delta l}{l_o}\right)_{\mathrm{i}}, \qquad (1)$$

where $\frac{\Delta l}{l_o}$ is the relative elongation caused by the lat-

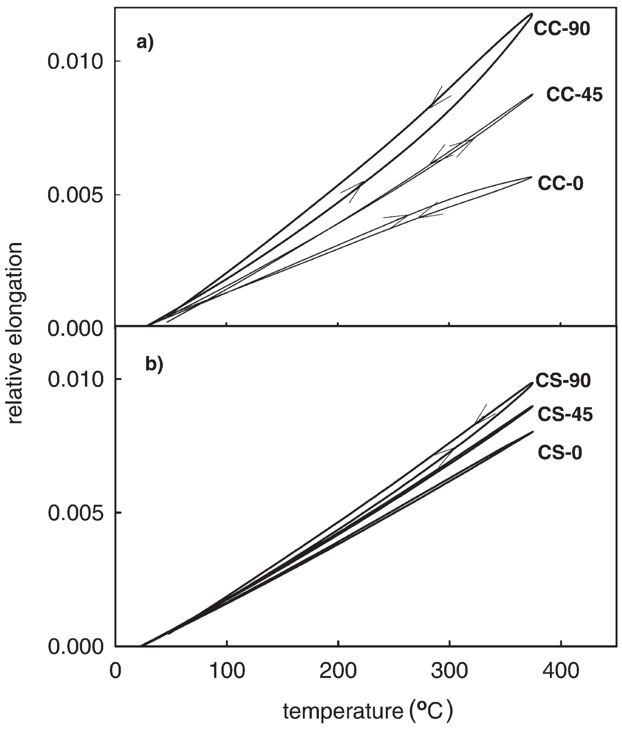

Fig. 1. Temperature dependence of the relative elongation for a) CC composites and b) CS composites.

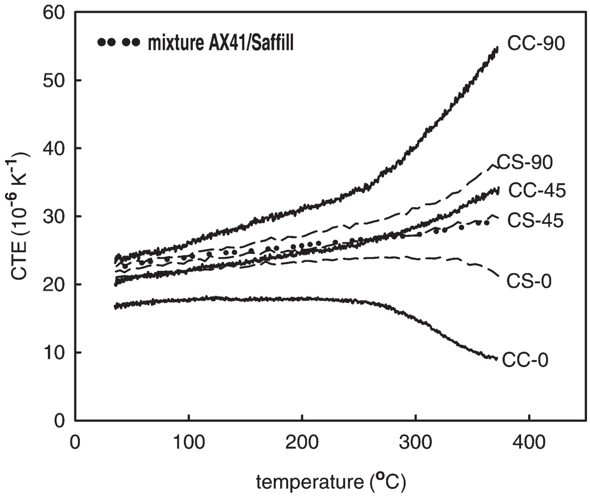

Fig. 2. Temperature dependence of the CTE of CS composites under heating.

tice thermal vibrations and $\left(\frac{\Delta l}{l_o}\right)_i$ are further strains in the material (thermal, residual strain). The term $\frac{\Delta l}{l_o}$ can be determined by the rule of mixtures, and this increases with increasing temperature. The temperature variations of the thermal strain for the CS and CC composites are presented in Fig. 4. The values

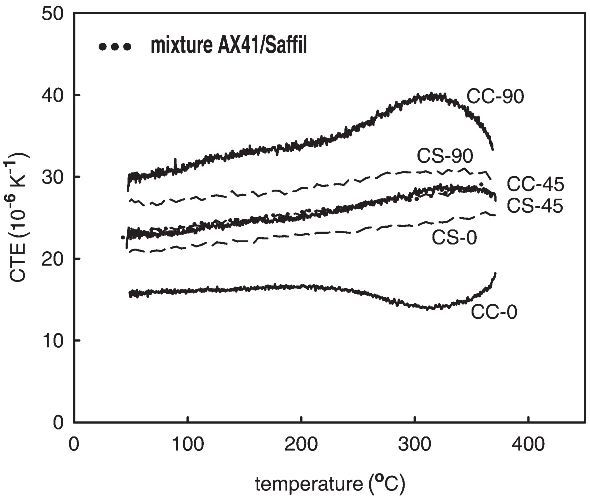

Fig. 3. Temperature dependence of the CTE of CC composites under cooling.

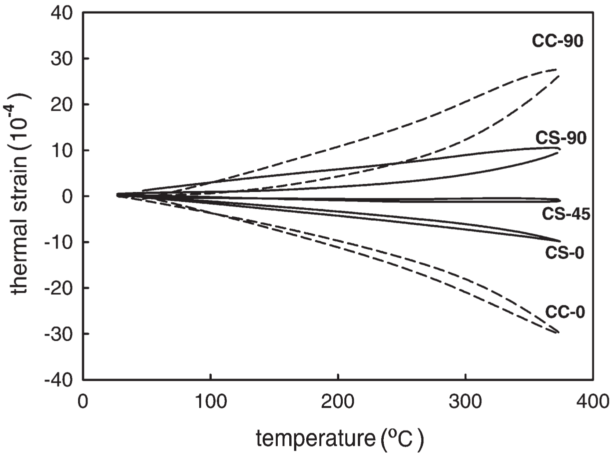

Fig. 4. Temperature dependence of the thermal strain of CS and CC composites.

for the relative elongation for Saffil were obtained from [13], and for C-fibres from [14]. The relative elongation of C-fibres in the direction parallel to the fibre axis is different from that in the perpendicular direction. The CTE has a value of $2 \times 10^{-6}\,\mathrm{K}^{-1}$ and $7 \times 10^{-6}\,\mathrm{K}^{-1}$ in the directions parallel and perpendicular to the fibre axis, respectively.

Figure 5 shows the temperature variations of the thermal strains for composites based on Mg-xLi alloys (x = 4, 8 and 12) reinforced with 9 vol.% Saffil fibres. It can be seen that the thermal strain increases with the Li-content of the matrix.

The dilatation characteristics are also influenced by the residual strain. This type of strain was found only in the as-prepared composites. A release of the residual strain is connected with the permanent change

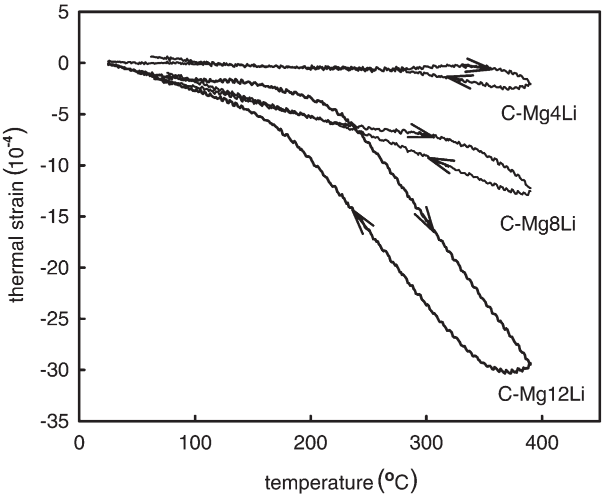

Fig. 5. Temperature dependence of the thermal strain of Mg-Li composites (C means composite).

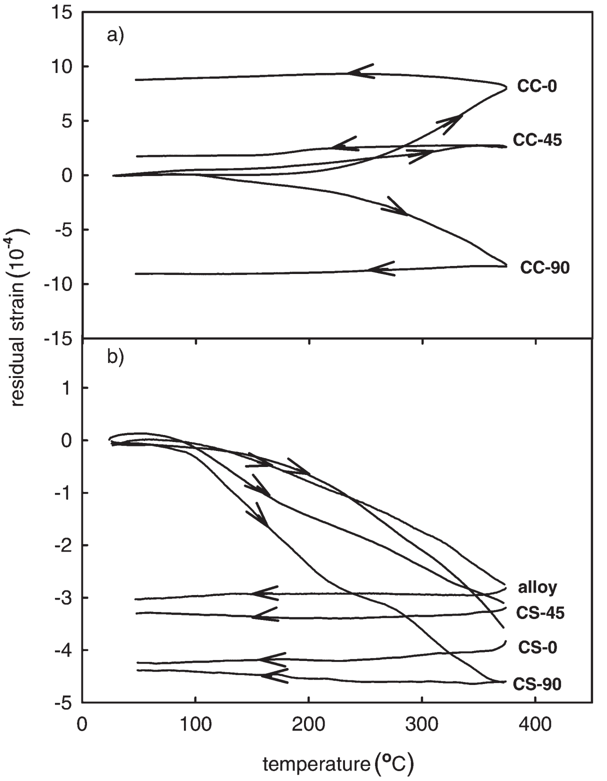

Fig. 6. Temperature dependence of the residual strain of CC (a) and CS (b) composites.

of the sample length, and these changes only occur during heating. The temperature dependence of the residual strain was obtained from Eq. (1) by subtracting the relative elongation obtained in the first and second thermal cycles. The results are presented in Fig. 6. The residual strain has a different character for the two composites. No anisotropy was found for the CS composites. All CS composites as well as the alloy had practically the same amount of permanent reduction after the first thermal cycle of the as-prepared material. The as-prepared samples of CC composites with the C-fibres perpendicular to the sample axis shortened after the first thermal cycle, and this shortening was twice as high as for the CS composites. Unlike the CS-0 composite, however, CC-0 composites elongated after the first thermal cycle, and a similar behaviour was also found for the same orientation of the Saffil fibres in the Mg8Li composite.

4. Discussion

The study of the dilatation characteristics of MMCs shows that the value and shape of the temperature dependences of the relative elongation and the CTE are strongly influenced by the thermal stresses in the composite. The thermal stresses may be sufficient to generate new dislocations at the interfaces between the matrix and the reinforcement. These dislocations are initially formed during cooling during the manufacture of the composite. At room temperature, the total dislocation density in the matrix is higher than in an unreinforced alloy. An increase in the dislocation density $\Delta\rho$ near reinforcement fibres may be calculated as [15]

$$\Delta\rho = \frac{B\, f\, \Delta\alpha\, \Delta T}{b\,(1-f)\,t}, \tag{2}$$

where B is a geometric constant, b is the magnitude of the Burgers vector of dislocations, f is the fibre volume fraction, t is the fibre diameter, $\Delta\alpha$ is the difference in the CTE and ΔT is the temperature change. The newly created dislocations are in the matrix near the interfaces – plastic zones are formed. The character of the plastic zones containing the newly formed dislocations and the density of the dislocations, except $\Delta\alpha$, can also be influenced by chemical reactions between the matrix and the reinforcement.

From Fig. 1, which shows the temperature dependence of the relative elongation of the CS and CC composites, there is an obvious difference between the C-90 and C-0 composites. The relative elongation of the C-45 composites lies between the values of the C-90 and C-0 composites, and it is nearly the same as when the rule of mixtures was used for the calculation of the dilatation characteristics. The differences can be also seen from Figs. 2 and 3, in which the temperature dependences of the CTE are shown for heating and cooling. The temperature dependences of the dilatation characteristics have a linear section and a curved section. This curvature (above

250 °C) is connected with the decrease in the CTE for the C-0 composites and an increase in the CTE for the C-90 composites. The dilatation characteristics of these composites are determined not only by the phonon mechanism but also by further deformations. If the CTE increases as in the case of C-90 composites, then this deformation is positive and the sample length increased during heating; the sample was in compression deformation in a direction parallel to the axis of the sample before heating. On the other hand, when the temperature dependence of the CTE is curved to lower values of the CTE, the sample is in tensile deformation in a direction parallel to the axis of the sample. The sample length is reduced during heating when tensile deformation is released. In our previous work [16], the CTE of the pre-deformed composites were investigated in compression as well as in tension. It was shown that the dilatation characteristics increase/decrease when the composite is pre-deformed in compression/tension. The cause of the curvature of the temperature dependences of the dilatation characteristics is the thermal strain that exists as consequence of the differences of the CTE of both composite components. This thermal strain exists in the composite at room temperature; it decreases during heating and increases during cooling, and it cannot be removed from composite.

The temperature dependences of the thermal strains for both composites calculated by Eq. (1) are shown in Fig. 4. It can be seen that the thermal strains in the CC-90 and CC-0 composites are at least three times higher than those in the CS-90 and CS-0 composites. This large difference cannot be elucidated by the difference between the $\Delta\alpha$ values of the two composites ($\Delta\alpha_{\text{Saffil-Cparallel}} \sim 5 \times 10^{-6}\,\text{K}^{-1}$, $\Delta\alpha_{\text{Saffil-Cperp.}} \sim 0$).

In general, it is assumed that Mg does not react with Al_2O_3 [7], and the system C-Mg is treated as a chemically non-reactive one [17]. The two binary magnesium carbides MgC_2 and Mg_2C_3 are endothermic compounds, which start to decompose at about 500 °C and 650 °C, respectively. The formation of both carbides seems to be very unlikely at the temperatures of MMC processing (700–800 °C). The consequence of the absence of carbides in the interface would be a very weak bonding between the matrix and reinforcement. The bonding is improved by the alloying of Mg with further elements. The AX41, the matrix in both the CS and CC composites, contains aluminium atoms. The aluminium atoms form with carbon the stable binary carbides Al_4C_2 [18], as well as the ternary carbides Al_2MgC_2 [19] and $Al_4Mg_2C_3$ [20]. The presence of these carbides is also assumed at the interfaces between the AX41 matrix and the C-fibres in the CC composites. The occurrence of these carbides is probably connected with a change in the composition of the matrix near the interfaces. Two new layers are formed between the matrix and the C-fibres: the carbide layer on the C-fibre and a new layer in the alloy matrix where the concentration of Al is lower than in other places in the matrix, and the concentration of defects is higher than in the matrix. It is assumed that in this range the first plastic thermal strain occurs during manufacturing cooling at high temperatures, and this plastic strain is considerably larger than in the monolithic alloy (when no chemical reaction occurs).

The influence of the newly created dislocations $\Delta\rho$ on the thermal stresses and the connected thermal strains was investigated in our previous works [4–6], where the reinforcement in three different MgLi based composites was the same with 9 % Saffil fibres. The CTE of matrix was controlled by change of the Li content. The CTE of Mg-Li alloys increases with increasing Li content: the CTE of Mg4Li alloy is $26 \times 10^{-6}\,\text{K}^{-1}$, Mg8Li is $30 \times 10^{-6}\,\text{K}^{-1}$ and Mg12Li is $37 \times 10^{-6}\,\text{K}^{-1}$. The values $\Delta\alpha$ and $\Delta\rho$ in Eq. (2) therefore increase with increasing Li content in the matrix. Thermal strain increases with increasing Li content in the matrix, as shown in Fig. 5. As mentioned in the introduction, a chemical reaction occurs between Saffil fibres and free Li atoms from the matrix. As in the previous case, even here we must assume that due to the chemical reaction between Li and Al_2O_3, the matrix near the interface is depleted of Li. In this system, very complex interfaces exist between the matrix and fibres. This interface may lower the difference in the CTE between the matrix and reinforcement. It is assumed that two effects influence the thermal strain in these composites: the difference in the CTE and the chemical products in the interface.

The chemical products in the interfaces between the matrix and the reinforcement also influence the residual strain. After the first thermal cycle, a permanent shortening of the sample length was observed in the case of the AX41 alloy reinforced with Saffil fibres (also in Mg, and in ZC63 alloy reinforced with the Saffil and further fibre composites). The shortening of CS-0 and CS-90 composite samples after the first thermal cycle means that the tension in the matrix in the as-prepared composite is in all directions (Fig. 6b). This is probably a consequence of the volume change during solidification in the manufacturing process. In CC composites, when chemical reactions can take place in the interface, the values of the length change after the thermal cycle are twice as high as those in the case of the Saffil composite. A further difference between the two composites is an elongation of the CC-0 composite (Fig. 6a). Similar results were obtained for Mg8Li and Mg12Li alloys reinforced with 9 vol.% Saffil fibres. This anisotropy in the residual strain cannot be explained by the present results, nevertheless, this effect once more confirms the strong influence of the interface on the macroscopic physical properties of the composites.

5. Conclusions

The thermal strain influences the dilatation characteristics of the AX41-12 vol.% Saffil fibre and AX41-12 vol.% C-fibre composites. This effect is at least three times higher in AX41-12 vol.% C-fibre composites than in the AX41-12 vol.% Saffil fibre composites. We assume that the different behaviour of the composites is caused by the chemical reactions occurring in the interface between the matrix and the C-fibres during infiltration of the reinforcement by the alloy. The chemical reaction products in the interface change the physical properties of the matrix near the interface where plastic deformation occurs as a result of the difference in the CTEs of the composite components. A strong anisotropy of the thermal strain is observed in both composites. If the fibres are parallel with or perpendicular to the sample axis, then the thermal strain lowers or increases the dilatation characteristics, respectively. If the angle between the sample axis and the fibres is 45°, then the influence of the thermal strain on the dilatation characteristics is minimal. The chemical products in the interfaces between C-fibres and AX41 alloy also influence the residual strains in the as-prepared composites. The residual strains in AX41-12 vol.% C-fibre composites are higher than in AX41-12 vol.% Saffil fibre composites.

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