Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 1, 219–224

INVESTIGATION OF THE PHASE TRANSFORMATION BEHAVIOUR OF CONSTRAINED SHAPE MEMORY ALLOY WIRES

P. Petalis, N. Makris and G. C. Psarras[*]

Department of Materials Science, School of Natural Sciences, University of Patras, Patras 26504, Greece

Adaptive or smart hybrid composites consisting of a polymer matrix reinforced by aramid fibres and incorporating pre-strained Shape Memory Alloy (SMA) wires are able to tune some of their properties, such as their shape, the natural vibration frequency or the damping coefficient, in response to an external stimulus. The functional properties of these systems are directly related to the reversible martensitic transformation in the SMA elements. In this work the transformational behaviour of both free SMA wires and SMA wires embedded in polymer matrix is investigated by means of DSC. The martensitic transformation of the constrained wires is impeded by the polymer matrix, while the interface integrity plays a crucial role.

Keywords: *adaptive composites, DSC, martensitic transformation, shape memory alloys*

Introduction

Shape Memory Alloys such as the binary NiTi or the ternary NiTiCu exhibit functional properties associated with the Shape Memory Effect (SME). SME is related to a reversible transformation, imposed by the influence of thermomechanical load, between different crystal structures. SMA materials undergo a solid state transformation between a low temperature martensitic phase and a high temperature austenitic or parent phase. The diffusionless phase transformation is governed by four characteristic temperatures M_s/M_f and A_s/A_f denoting the start and finish temperatures of each transformation [1]. During the forward and reverse transformation SMA have the ability to recover their original shape after a cycle, which includes cooling-deforming-heating with the simultaneous generation of mechanical work (Fig. 1).

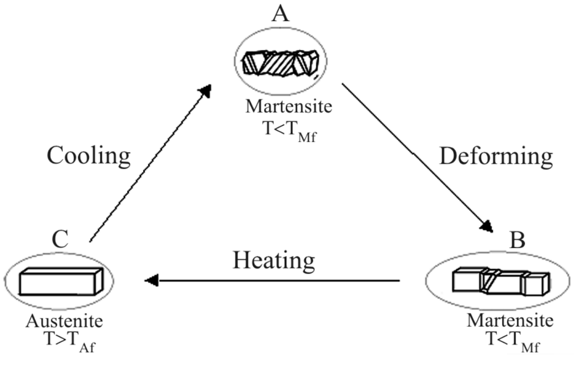

Fig. 1 Schematic representation of the Shape Memory Effect (SME), during heating (B→C) the initial shape and dimensions are totally recovered

Adaptive or smart composites integrate actuating and sensing materials into a structural composite system. Materials of this class are able to vary some of their properties in response to an external stimulus [2]. Polymer composite systems consisting of an epoxy resin reinforced by aramid fibres and incorporating pre-strained SMA wires have the ability to control their own shape and other characteristics such as the natural vibration frequency or the damping coefficient [3–5]. The functional properties of adaptive composites with embedded SMA wires are directly related to the reversible martensitic transformation in the SMA elements. Although considerable attention has been given to the structural, mechanical, functional and long term behaviour of the plain SMA [1, 6–13], little information is available for the behaviour of embedded, in a polymer matrix, SMA elements [4]. The phase transformation behaviour of embedded and free SMA is not expected to be the same, since strain recovery of pre-strained martensitic SMA wires, during heating, should be obstructed by the stiffness of the host matrix, resulting thus in the generation of mechanical stresses inside the hybrid system.

In the present work pre-strained SMA wires are used as passive actuating elements in, autoclave produced, epoxy resin–aramid fibres composite systems. The thermal response of free SMA wires and SMA composites is recorded by means of DSC and is used in order to investigate the transformational behaviour of the constrained SMA wires.

---

[*] Author for correspondence: G.C.Psarras@upatras.gr

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

Ternary NiTiCu(12%) Shape Memory Alloys supplied by Memry Co. (USA) were employed in the present study. The alloys were in the form of thin flexible wires with 150 μm diameter and used without any further surface treatment or modification. Unidirectional prepreg tapes of Kevlar 29 (Du Pont de Nemours) fibres embedded into LTM 217 epoxy resin were supplied by Advanced Composites Group (UK). A specially designed mould [3, 4] was used for the preparation of the hybrid composite systems, under autoclave conditions. The SMA composite laminates were consisted of a layer of pre-strained (3%) SMA wires, placed between equal number of prepreg plies. The employed mould contains a frame suitable for pre-straining the wires and for maintaining the tensile strain, as well as, the alignment of the wires during the composites cure. SMA wires were heated above A_f, in order to remove the influence of any undesirable pre-strain level and then cooled freely to ambient temperature where the alloys are in the martensitic state, before being located into the mould. Detailed description of the materials choice criteria and the preparation procedure can be found elsewhere [3, 4]. The transformation behaviour of free SMA wires and SMA-composites was studied by means of DSC via a Q100 TA Instruments device, under nitrogen atmosphere. Samples were placed in aluminum crucibles and an empty aluminum crucible was serving as reference. For comparison reasons the epoxy resin – Kevlar fibres system was also examined. Composite samples were cut into suitable dimensions by employing a diamond saw and a ceramic scissors. The heating/cooling rate for all the examined specimens was kept constant at 10 K min^{-1}, while temperature was varied between 273 and 393 K. The epoxy resin – aramid fibres system was tested up to 473 K in order to determine the glass transition temperature of the matrix. Aiming to examine the influence of temperature upon the functionality of adaptive systems each composite specimen was subjected to two or three identical thermal cycles successively. Although the employed thermal runs were identical, the modified status of the hybrid composite systems, after the completion of each cycle, impeded the determination of statistical parameters such as variance or standard deviation for the derived quantities.

Results and discussion

In the DSC curve of Fig. 2a, a complete thermal cycle of the ternary NiTiCu(12%) alloy with no pre-strain is presented. On the cooling trace an exotherm peak, associated with the martensitic transformation, is recorded.

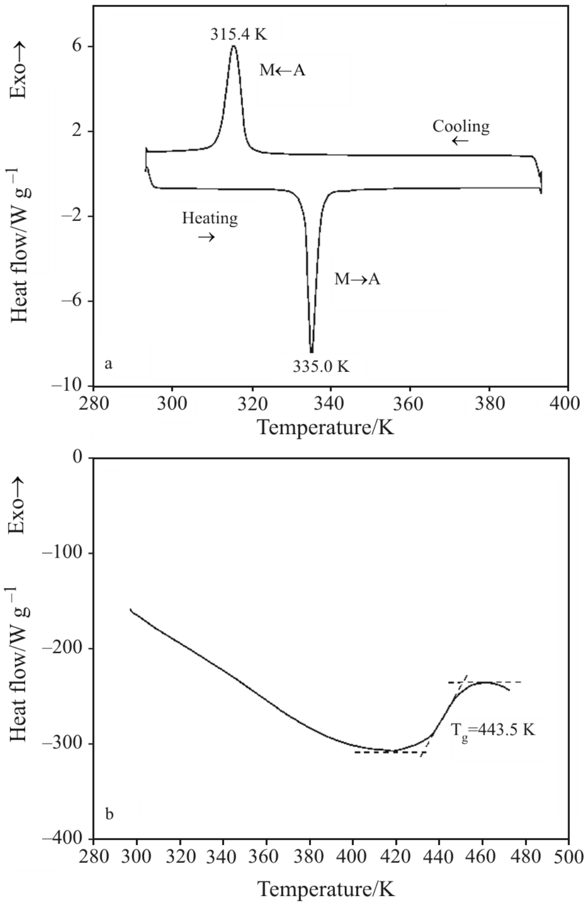

Fig. 2 DSC curves of the a – NiTiCu(12%) alloy in free conditions and b – epoxy resin – Kevlar 29 fibres composite

Table 1 Transformation temperatures and heats of: a – plain NiTiCu(12%) wires with no pre-strain, b – embedded in a polymer matrix, NiTiCu(12%) wire, pre-strained at 3% during the first and c – the second thermal cycle. The subscripts *s*, *p*, *f* correspond to the start, peak and finish temperature of each transformation

	M_s/K	M_p/K	M_f/K	A_s/K	A_p/K	A_f/K	$\Delta H_{M\to A}$/J g^{-1}	$\Delta H_{A\to M}$/J g^{-1}
(a) Plain wires with no pre-strain	319.2	315.4	311.3	332.4	335.0	339.0	13.6	14.2
(b) Embedded wires pre-strained at 3%, 1st cycle	327.8	321.3	313.4	328.2	351.1	360.2	1.3	6.3
(c) Embedded wires pre-strained at 3%, 2nd cycle	327.7	321.6	313.4	329.3	335.8	342.1	6.3	6.3

The endotherm peak at the heating cycle corresponds to the reverse transformation, namely the martensite to austenite or parent phase transformation. The transformation temperatures were determined using a standard line crossing technique, which is well established in the literature [4, 14, 15], while the transformation heats were elaborated by calculating the area between the heat peak curve and the baseline (Table 1). Since the heating/cooling rate during all the conducted thermal runs was kept constant, the occurring variations of the characteristic temperatures are attributed to the deformation of SMA wires [4, 14, 16].

In Fig. 2b the thermal response of the epoxy resin – Kevlar 29 composite system, upon heating, is shown. Analysis of the thermoanalytical curve allows the determination of the glass transition temperature of the polymer matrix, which was found to be very close to 443 K. The employed curing procedure leads to a T_g much higher than A_f, permitting thus the exploitation of the functional properties of the activated SMA wires. In the hybrid composites the activation of the embedded wires is achieved by resistive heating above A_f, while the adaptive behaviour of the systems is based on the resulting stress generation [3, 17] by the constrained SMA wires. On the other hand, a T_g lower than the characteristic temperatures of the reverse transformation should produce an early softening of the polymer matrix, canceling any functional ability of the hybrid system [3, 17].

It is generally accepted [4, 14, 18] that a Shape Memory Alloy in the martensitic phase, free of any mechanical load, is consisted of many variants of Self Accommodating Martensite (SAM). The strain of each SAM variant is compensated by the adjacent variants so that, as the variants extent and shrink the total net strain remains zero [14]. SAM can be reversibly transformed to parent phase (austenite) when heated above A_f. The influence of mechanical strain on an alloy at the martensitic phase, forces the variants to attain a common orientation resulting in the gradual transformation of SAM to Preferentially Oriented Martensite (POM). The existence of POM variants is always accompanied with the occurrence of a non zero net strain on the SMA element. The amount of POM can be expressed as follows:

$$(\mathrm{POMVol\%}) = \frac{\varepsilon_{\mathrm{SMA}}}{\varepsilon_{\max}} \times 100 \qquad (1)$$

where $\varepsilon_{\mathrm{SMA}}$ is the pre-strain level of the deformed wires and $\varepsilon_{\max}$ is the maximum recoverable strain by SME [14]. When $\varepsilon_{\max}=\varepsilon_{\mathrm{SMA}}$, Eq. (1) implies that no SAM variants exhibit in the alloy and thus no endotherm peak, corresponding to the transformation of SAM to austenite, should be recorded in a DSC curve. Straining further the specimen results in entering into the plastic region and the generated strain is no more recoverable by SME. When a pre-strained SMA, free of any mechanical constrain, is heated at a temperature above A_f the entirety of SAM and POM is transformed to austenite and the shape memory strain is recovered (Fig. 1). Cooling an alloy, free of any mechanical constrain, from the austenite phase to a temperature below M_f results in the formation of many variants of SAM, which are settled in such a way so that no change to the external dimensions of the specimen occurs (Fig. 1).

The situation becomes different when the SMA element, pre-strained up to a level equal or lower than the maximum recoverable strain, is heated under constrained conditions. The reverse transformation of SAM proceeds undisturbed, while POM's transformation is impeded, since the SMA element is not able to recover its original shape, resulting in stress generation. In Fig. 3a the first and the second heating cycles

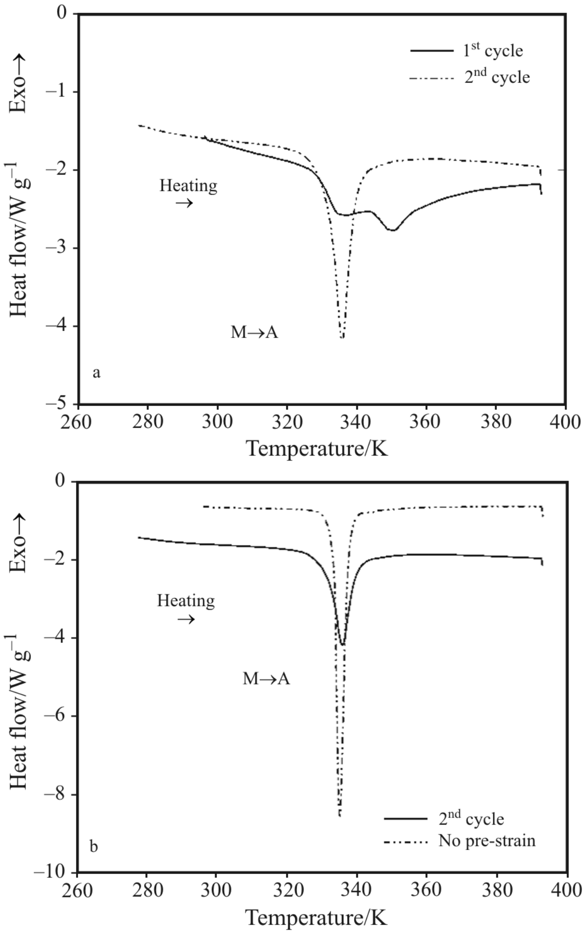

Fig. 3 a – DSC curves of the NiTiCu(12%) – epoxy resin – Kevlar 29 composite during the first and second thermal cycle, b – comparison of the DSC results of the NiTiCu(12%) – epoxy resin – Kevlar 29 composite during the second thermal cycle and the NiTiCu(12%) alloy in free conditions

of a composite system with embedded pre-strained NiTiCu(12%) wires are depicted. The trace of the first cycle attains a complex form due to the presence of overlapping endothermic peaks. Initially, at temperatures lower than A_f, a small endotherm peak associated with the SAM to parent phase transformation is recorded, indicating that the employed pre-strain level (3%) during the preparation of the specimens was lower than ε_{max}.

Heating the pre-strained alloy under constrained conditions up to a temperature equal to A_f, allows only the SAM portion of martensite to be transformed and the magnitude of the recorded peak in a DSC curve is a measure of the existing amount of SAM in the pre-strained alloy prior to heating. The area of the endotherm peak (transformation enthalpy) diminishes with increasing the POM percentage or in other words with the level of pre-strain and it is expected to approach zero when the maximum recoverable strain is applied. In the case of the examined composites the stiffness of the polymer matrix impedes the embedded pre-strained SMA wires to recover their original shape and dimensions. As already stated the transformation of SAM to austenite, during the first heating cycle, becomes evident via the small recorded peak in the vicinity of the characteristic temperatures, while the transformation of POM extends over a wide temperature range and proceeds at a much more lower rate approximately of 0.2 vol%/K [19]. Since the transformation of POM, up to a temperature equal to A_f, is not completed and only a small part of it, is transformed to austenite it is not easy to be detected in a DSC graph as no clear peak is formed and only a shift of the baseline of the heating curve is observed (Fig. 3a). The amount of SAM in the pre-strained SMA wires within the composite specimens can be determined using the following relation:

$$(\text{SAM/Vol\%}) = \frac{\Delta H_{\text{SAM}}}{\Delta H_{\text{ref}}} \times 100 = \\ = 100\% - (\text{POMVol\%}) \tag{2}$$

where ΔH_{SAM} and ΔH_{ref} are the measured transformation heats in the case of pre-strained wires and in the case of wires with zero pre-strain respectively [14]. From Eqs (1) and (2) it follows that the amount of SAM, as well as the measured transformation heat (ΔH_{SAM}) decreases linearly with the employed level of pre-strain (ε_{SMA}) and at a pre-strain level equal to the maximum recoverable strain both quantities reduce to zero. The dependence of the amount of SAM upon pre-strain level and the applicability of Eqs (1) and (2) has been confirmed in previous experimental studies [14, 18]. By employing Eqs (1) and (2) and data listed in Table 1, the amount of SAM and POM in the original hybrid specimen can be estimated at 20.6 and 79.4% respectively, while the maximum recoverable strain appears to be close to 4%. The baseline of the heating curve of the first cycle exhibits an inclination, this is a common characteristic with the epoxy resin – Kevlar 29 system and is attributed to the influence of the polymer matrix. In Fig. 2b and at temperatures below T_g the heating curve displays a negative inclination with temperature.

Heating the composite systems, during the first thermal cycle, at temperatures higher than A_f affects the integrity of the polymer matrix – SMA wires interface. Interface is gradually debonding and the wires are no longer fully constrained. As result from the elimination or disappearance of the constraining conditions, stabilized POM transforms into parent phase forming the second endothermic peak on the DSC curve (Fig. 3a). Consequently, parent phase switches to SAM upon cooling.

During the second heating cycle, the thermal response of the embedded wires significantly differs from the recorded response during the first one, approaching the behaviour of free alloys (zero pre-strain), where shape recovery is not subjected to any restrictions (Figs 3a and b). The endothermic peak, which corresponds to the transformation of SAM to austenite is clearly formed at the characteristic temperature range, while the baseline shift and the recorded broad peak at a certain temperature higher than A_f are not present. Furthermore the inclination of the baseline is now not appearing. These observations are strong indications that the mechanical restriction applied by the polymer matrix preventing the POM variants from transforming, has been removed. As responsible for this behaviour can be considered the degradation of the polymer matrix – SMA wires interface, occurring during the first heating cycle, when the specimens are heated at temperatures close to 353 K. In Fig. 3b the DSC heating curve of free SMA wires with no pre-strain, is compared to the corresponding curve of the second thermal cycle of the composite system incorporating SMA wires with 3% of initial pre-strain level. The similarity of the recorded curves is obvious showing that during the second thermal cycle there are no POM variants, or at least their presence can be considered as negligible, in the SMA wires. The degradation of the interface between SMA wires and polymer matrix permits the transformation of POM to austenite, since the elimination of constraining allows the recovery of the initially applied pre-strain. In some previous work [4, 17] the generated stresses by the embedded SMA wires, were quantified inside the hybrid specimens, at different activation levels, by means of Laser Raman Microscopy (LRM). In these studies it was found that heating the embedded wires at temperatures higher than 353 K has no significant difference upon the magnitude of the generated/transmitted stresses. This is in accordance with the results of the present study, since the degradation of the – wire-matrix – interface integrity does not allow any further stresses to be transmitted.

Aiming to support further our conclusions another hybrid specimen was subjected to successively sets of thermal cycles (heating and cooling), varying the employed maximum heating temperature at each set of cycles (Fig. 4). In Fig. 4a the hybrid specimen is subjected to three complete thermal cycles between 273 and 338 K. Even though 338 K is very close to A_{f}, there is only a small tendency for the formation of an endotherm peak corresponding to the transformation of SAM to austenite. Respectively upon cooling a small exotherm peak is recorded, indicating that the amount of SAM transformed to austenite and via versa is kept at low level. Furthermore it is interesting to note that the successive heating and cooling traces are coinciding. Right afterwards, the same specimen was imposed to a second set of thermal cycles (Fig. 4b). In this case the employed maximum temperature is 353 K, being well above A_{f}. As it can be seen (Fig. 4b), the transformation of SAM and via versa proceeds further, however the absence of a clear peak upon cooling denotes that the initial amount of POM in the specimen remains unaffected. In Fig. 4c the last set of successive thermal cycles is illustrated. Here the maximum employed temperature is 393 K. The heating trace of the first cycle, which is quite different from the next ones, includes the evidences for the transformation to parent phase of both SAM and POM. The last point becomes obvious upon cooling, where the traces of all cycles coincide, forming a clear peak (austenite to martensite transformation). During the second and the third heating cycles only the SAM to austenite peak is recorded making clear the absence of POM variants. Thus, it is reasonable to conclude that the physical restrictions of strain recovery imposed by the polymer matrix stiffness are removed by heating above 353 K, due to the resulting degradation of the wire-matrix interface.

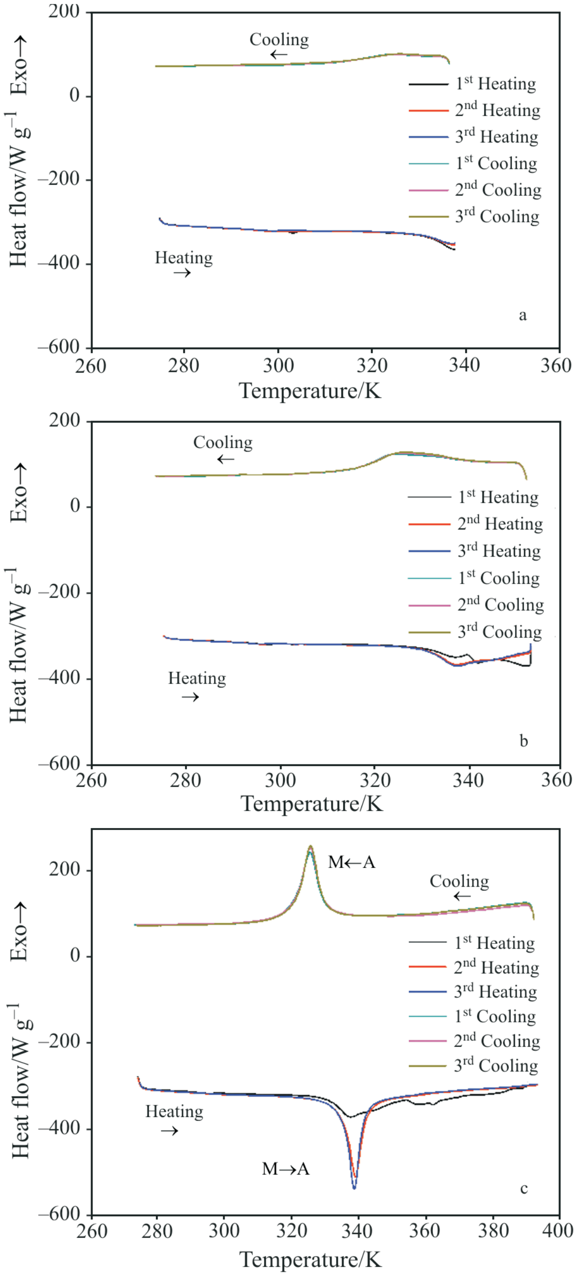

Fig. 4 Successive complete thermal cycles (heating-cooling) of the same hybrid specimen with maximum temperature: a – 338 K, b – 353 K and c – 393 K

Finally, the ability of the examined adaptive systems for internal stress generation and the related functional behaviour is critically affected by the thermal history of the composites and it is possible to define a temperature range where the functional properties should operate undisturbed.

Conclusions

The thermal response of free and embedded in a polymer matrix SMA wires has been studied by means of DSC. The embedded wires are consisted of variants of both Self Accommodating Martensite (SAM) and Preferentially Oriented Martensite (POM) implying that the employed, during the samples preparation procedure, pre-strain level was lower than the maximum recoverable strain. During the first heating cycle only the SAM portion of the constrained wires is transformed to parent phase, at the characteristic range of temperatures. On the other hand the polymer matrix stiffness prevents POM from strain recovery, impeding thus its transformation to austenite. Heating at higher temperature results in degradation of the polymer matrix – SMA wires interface, reducing, as a consequence, the strength of constraining. POM is now able to transform to austenite. The interface failure becomes evident during the second heating cycle, where a clear endothermic peak is formed in the temperature range of transformation. The recorded thermal response of the composite samples resembles to the corresponding of free wires, leading to the conclusion that after the interface degradation, POM transforms to parent phase and then to SAM upon cooling, since the constrain conditions are eliminated and strain recovery is allowable.

Acknowledgements

The authors wish to acknowledge Prof. C. Galiotis (Department of Materials Science, University of Patras, Greece) for kindly providing the examined materials.

References

1 T. W. Duering, K. N. Melton, D. Stöckel and C. M. Wayman, Engineering Aspects of Shape Memory Alloys, Butterworth-Heinemann, London 1990.
2 M. V. Gandhi and B. S. Thompson, Smart Materials and Structures, Chapman & Hall, 1992.
3 G. C. Psarras, J. Parthenios and C. Galiotis, J. Mater. Sci., 36 (2001) 535.
4 J. Schrooten, V. Michaud, J. Parthenios, G. C. Psarras, C. Galiotis, R. Gotthardt, J. A. Månson and J. Van Humbeeck, Mater. Trans. JIM, 43 (2002) 961.
5 V. Michaud, Scripta Materialia, 50 (2004) 249.
6 H. Funakubo, Shape Memory Alloys, University of Tokyo, 1987.
7 V. Torra, A. Isalgue and F. C. Lovey, J. Therm. Anal. Cal., 66 (2001) 7.
8 A. S. Paula, J. P. H. G. Canejo, R. M. S. Martins and F. M. Braz Fernandes, Mater. Sci. Eng. A, 378 (2004) 92.
9 Y. Zheng, L. Cui and J. Schrooten, Appl. Phys. Lett., 84 (2004) 31.
10 Z. G. Wang, X. T. Zu, Y. Q. Fu and L. M. Wang, Thermochim. Acta, 428 (2005) 199.
11 Z. G. Wang and X. T. Zu, Scripta Mater., 53 (2005) 335.
12 Z. G. Wang, X. T. Zu and Y. Huo, Thermochim. Acta, 436 (2005) 153.
13 V. Torra, J. L. Pelegrina, A. Isalgue and F. C. Lovey, J. Therm. Anal. Cal., 81 (2005) 131.
14 K. A. Tsoi, R. Stalmans and J. Schrooten, Acta Materialia, 50 (2002) 3535.
15 E. Abel, H. Luo, M. Pridham and A. Slade, Smart Mater. Struct., 13 (2004) 1110.
16 X. M. He and L. J. Rong, Scripta Mater., 51 (2004) 7.
17 J. Parthenios, G. C. Psarras and C. Galiotis, Composites Part A, 32 (2001) 1735.
18 Y. Zheng, J. Schrooten, L. Cui and J. V. Humbeeck, Acta Mater., 51 (2003) 5467.
19 Y. J. Zheng, J. Schrooten, K. A. Tsoi and R. Stalmans, Mater. Sci. Eng. A, 355 (2002) 157.

DOI: 10.1007/s10973-005-7202-x