Int J Thermophys (2010) 31:378–387
DOI 10.1007/s10765-010-0713-0

Study of the Thermal Properties of a Ni_3Ta Shape Memory Alloy

A. Rudajevova

Received: 27 October 2009 / Accepted: 31 January 2010 /

Abstract Dilatation characteristics, thermal diffusivity, and thermal conductivity of a Ni_3Ta shape memory alloy were studied over the temperature range from room temperature up to 950 °C. The Ni_3Ta alloy was investigated in both polycrystalline and single crystal forms. The shape memory effect was positive for the polycrystalline samples and negative for the single crystal. While the transformation temperature of the M (martensite) → A (austenite) phase transformation was the same for both types of alloys and all measurements, the transformation temperature for the reverse phase transformation A → M was dependent on the maximum cycle temperature. Higher maximum temperatures of the thermal cycle yielded lower transformation temperatures for the A → M transformation. The thermal diffusivity and thermal conductivity of the austenite were higher than those of the martensite. No latent heat was found for the phase transformations.

Keywords Ni_3Ta shape memory alloy · Thermal conductivity · Thermal diffusivity · Thermal expansion

1 Introduction

The best known and most used shape memory alloy (NiTi) has transformation temperatures above room temperature. There are many applications where high-temperature shape memory alloys (HTSMA) are in demand. However, the use of shape memory alloys with high temperatures of transformation is complicated by physical processes occurring at these high temperatures, such as, for example, recrystallization, recovery,

---

A. Rudajevova (✉)
Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Charles University,
Ke Karlovu 5, 121 16, Praha 2, Czech Republic
e-mail: rud@mag.mff.cuni.cz

precipitation, etc. Studies on the high-temperature thermal properties of these potential alloy material candidates of HTSMA are therefore a necessary condition of their use in practice.

The shape memory effect is based on the phase transformation martensite ↔ austenite. It is known that this type of phase transformation takes place practically immediately [1]. However, all literature presenting, for example, DSC results [2,3] or dilatation results [4,5], shows that the phase transformation takes place in a given finite time. The martensitic phase transformation is mostly athermal phase transformation that depends only on the temperature. During heating of a sample, a temperature gradient always occurs in the material. The phase boundary propagates in the direction of the temperature gradient by a finite rate because the heat conduction and phase transformation propagate together. The energy balance at the interface between both phases is [6]

$$-\lambda_{\mathrm{A}}\left(\frac{\partial T}{\partial x}\right)_{\mathrm{A}} = u\rho H - \lambda_{\mathrm{M}}\left(\frac{\partial T}{\partial x}\right)_{\mathrm{M}} \tag{1}$$

where $-\lambda_{\mathrm{A}}\left(\frac{\partial T}{\partial x}\right)_{\mathrm{A}}$ is heat flux into the austenite at the interface, $u\rho H$ is the latent heat absorption rate and the last term, $-\lambda_{\mathrm{M}}\left(\frac{\partial T}{\partial x}\right)_{\mathrm{M}}$, is the heat conducted away from the moving interface into the martensite. The term u is the interface velocity, ρ is the density (it is assumed that the densities in both phases are the same), and H is the latent heat per unit mass. The interface velocity u and temperature are time-dependent. The total time of phase transformation duration is therefore determined also by the size and shape of the shape memory material. Often presented values A_{f} and M_{f} (final temperatures of the phase transformation) are therefore not material properties. The thermal conductivity is a very important parameter because it determines the temperature gradient in the sample. The thermal conductivity in the sample is complicated by the latent heat that is released or consumed during the phase transformation. The thermal conduction and the phase transformation take place in coordination. The thermal conductivity of the martensite in shape memory alloys is lower than that of the austenite, as was found for NiMnGa alloys [7,8].

The martensitic transformation is a strain-induced transformation. The lattice strain is a transformation parameter that determines the physical states of an initial phase and a product phase, as well as the local intermediate states of the alloy during the phase transformation. Most of the alloys in the martensitic state show anisotropy of dilatation characteristics (textured polycrystals or single crystals). In the textured samples, the same martensitic variants dominate in a certain direction. In these materials, there is a drop in the temperature dependence of the relative elongation in the phase transformation temperature range. Dilatation characteristics of Ni_3Ta were studied by Firstov et al. [9]. The forward and reverse martensitic transformations are characterized by sharp step changes. These changes are consequences of the phase transformation when the martensite preferential orientations transform into ones of the austenite, and they occur once more during the reverse phase transformation. The preferential orientation could not be removed by homogenization annealing. DSC results are also presented, however, the transformation temperature A_{s} differs from that obtained by dilatometry by about 25 °C. The aim of this work is experimental determination of the thermal diffusivity, thermal conductivity, and the dilatation characteristics of Ni_3T shape memory alloys over the temperature range from room temperature to 950 °C. Analysis of the determined thermal properties will be focused on the influence of thermal history on the transformation temperatures.

2 Experimental Details

The polycrystalline samples of Ni_3Ta were prepared by arc melting stoichiometric amounts of components in a water-cooled copper crucible under an Ar (6N)-protective atmosphere. Samples were re-melted three times to ensure good homogeneity. The microstructure of the polycrystalline sample is shown in Fig. 1. This figure shows the microstructure in the plane perpendicular to the longitudinal sample axis where the columnar grains are perceptible. A single crystal of Ni_3Ta was prepared in a four mirror optical furnace using a polycrystalline rod obtained by arc-melting. The rod was melted under the Ar-protective atmosphere and slowly moved at a speed of (8 to 10) $mm \cdot h^{-1}$ through the hot zone of focused light. Orientation of the single crystal was studied by the powder diffractometer MEREDIT. It was found that the crystal has monoclinic structure at room temperature. The plane parallel to the growth direction was the (201) plane, and the plane perpendicular to the growth plane was the (040) plane (P. Beran, J. Vejpravova-Peltierova, unpublished results).

The linear thermal expansion of the samples was measured in a helium atmosphere using a Netzsch 402E dilatometer over the range of room temperature to 950 °C. The heating and cooling rate was $2\,K \cdot min^{-1}$. The samples were 6 mm in diameter and 20 mm in length. The longitudinal sample axis was perpendicular to the columnar grains in the polycrystalline sample.

Samples for the thermal-diffusivity measurements had a diameter of 16 mm and a thickness of 2 mm. The measurements of thermal diffusivity were performed over the temperature range from room temperature to 500 °C in a helium atmosphere using

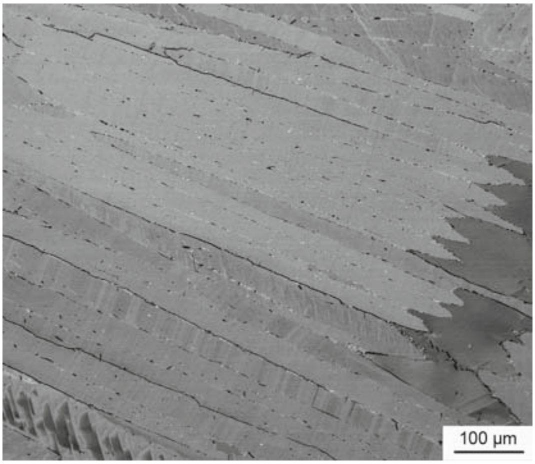

Fig. 1 Microstructure of the polycrystalline Ni_3Ta alloy

the flash method described elsewhere [10]. The accuracy of the measurement was checked by measuring the thermal diffusivity of an Inconel sample (Inconel is a standard material for the measurement of thermal diffusivity and thermal conductivity). The difference between the measured and tabulated values [11] is about ±3 %.

The temperature dependence of the density was calculated from the density measured at 20 °C by weighing the sample in rectified and dried toluene and from respective values of thermal expansion data. The thermal conductivity was calculated using the thermal diffusivity, the specific heat, and the density. The specific heat was determined by calculation using the Neumann–Kopp rule.

3 Results

Dilatation characteristics of the polycrystalline Ni_3Ta sample and the single crystal of Ni_3Ta are presented in Fig. 2. It can be seen that the transformation strain of the polycrystalline sample is positive, in contrast to the single crystalline sample of this alloy where the transformation strain is negative. There are large differences between starting temperatures A_s and M_s in both shown cases. This difference is about 55 °C, and it is not constant but rather depends on the maximum temperature of the thermal cycle. This dependence is shown for the polycrystalline sample in Fig. 3 and for the

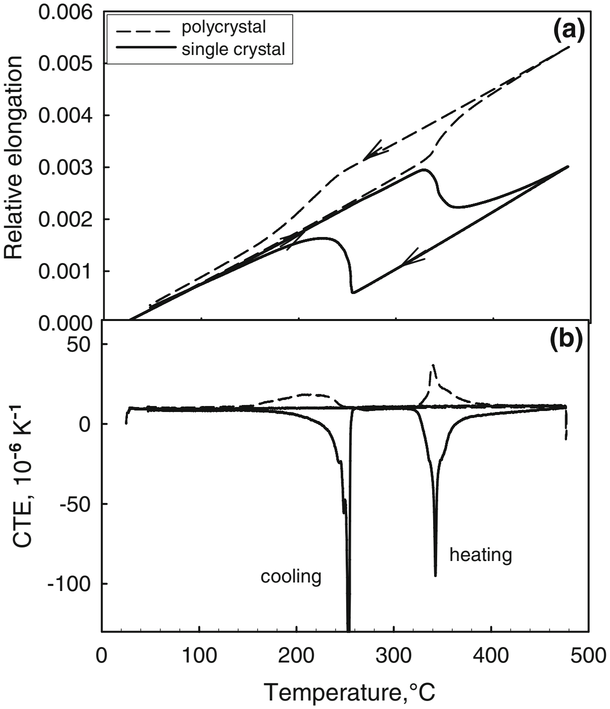

Fig. 2 Dilatation characteristics of polycrystalline and single crystalline Ni_3Ta alloy (heating/cooling rate of $2\,K \cdot min^{-1}$)

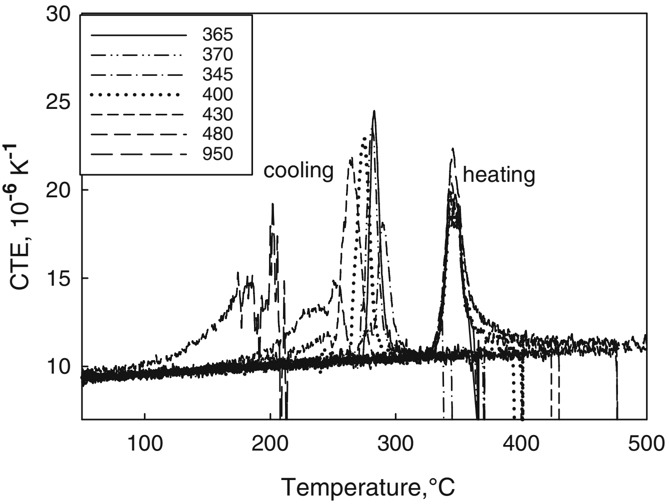

Fig. 3 Temperature dependence of the CTE for polycrystalline alloy (heating/cooling rate of $2\,\mathrm{K \cdot min^{-1}}$)

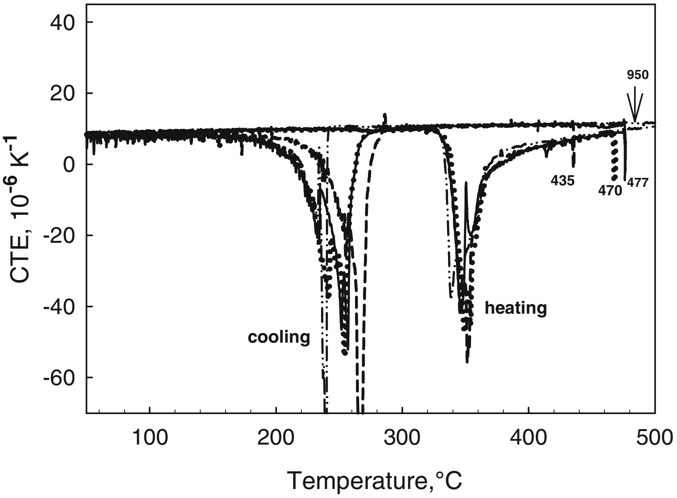

Fig. 4 Temperature dependence of the CTE for single crystal alloy (heating/cooling rate of $2\,\mathrm{K \cdot min^{-1}}$)

single crystal in Fig. 4. Higher maximum temperatures of the thermal cycle yield lower M_s values. The effect is more distinguishable for the polycrystalline sample. Dependence of the starting temperature of the A → M phase transformation on the maximum temperature of the thermal cycle is shown in Fig. 5. This figure also shows the results obtained with samples pre-deformed up to 1 % in runs where no permanent length change already occurred. The starting temperature for the M → A phase transformation was always the same.

Figure 6 shows the temperature dependence of the thermal diffusivity for the Ni_3Ta sample. It can be seen that the thermal diffusivity of the austenite is higher than that of

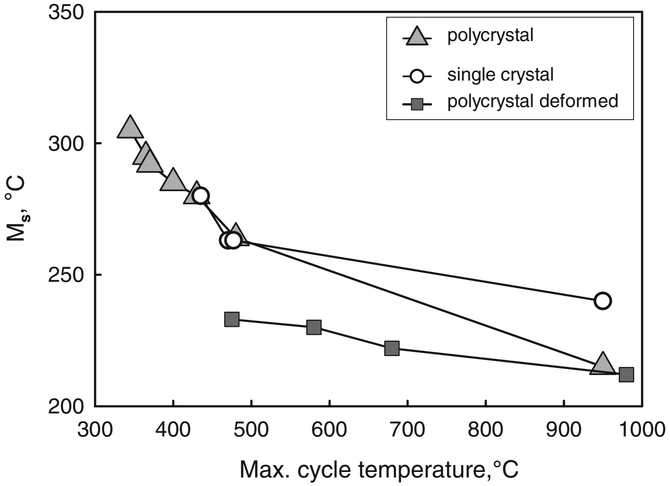

Fig. 5 Dependence of the initial temperature (M_S) of phase transformation A → M on the maximum temperature of the thermal cycle

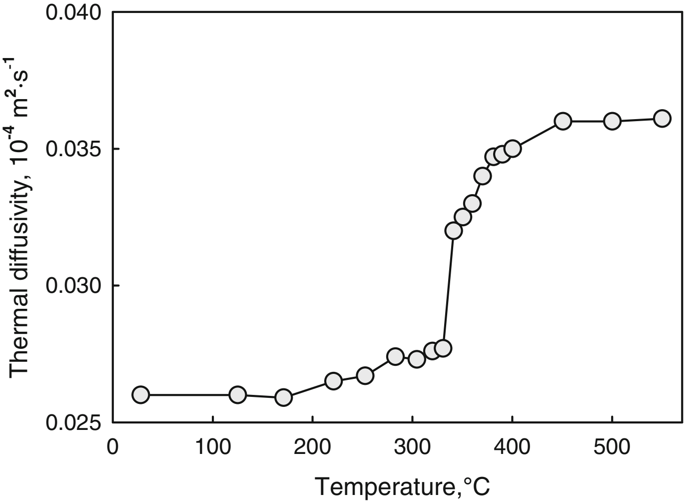

Fig. 6 Temperature dependence of the thermal diffusivity

the martensite. The temperature dependence of the thermal conductivity determined as a product of the thermal diffusivity, the specific heat, and the density is shown in Fig. 7.

4 Discussion

Figure 2 shows different transformation strains for the polycrystalline sample and the single crystal. It has been shown in our previous studies that polycrystalline

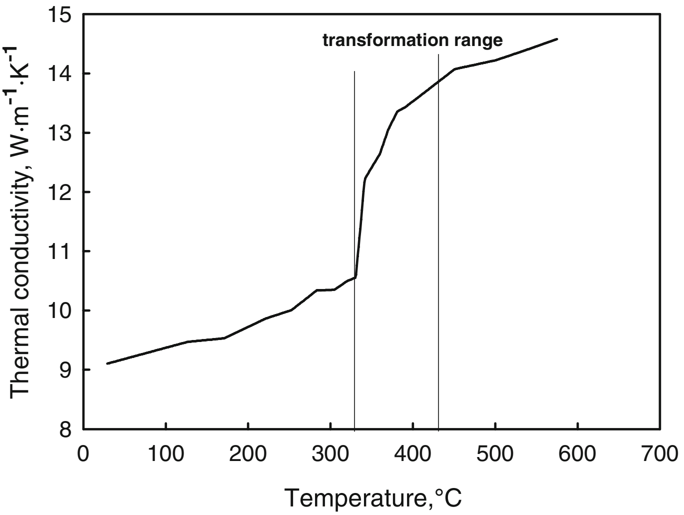

Fig. 7 Temperature dependence of the thermal conductivity

samples have mostly textured structures. This is a consequence of the manner of cooling during preparation. Ni_3Ta polycrystalline samples were prepared so that the temperature gradient during cooling was perpendicular to the longitudinal sample axis. This manner of cooling makes long grains perpendicular to the sample axis. Preferential crystal orientations and preferential martensitic orientations are natural consequences of this preparation. Dilatation characteristics measured in the direction of the longitudinal sample axis show the transformation strains. Transformation deformation means the relative elongation in the transformation temperature range. This also includes the relative elongation due to lattice vibrations, but this contribution is small. We could not measure perpendicular to the longitudinal sample axes, where, however, we assume negative transformation strain. Positive transformation strain was found in a Ni–Mn–Ga alloy with the columnar grains perpendicular to the sample axes [12]. This alloy was prepared by a different method than the Ni_3Ta alloy. The samples were cut from the center and peripheral parts of the cylinder ingot (diameter of 40 mm and length of 100 mm) parallel to the ingot axes. While samples from the peripheral parts of ingots (columnar grains) had positive transformation strain, the samples from the center of the ingot (equiaxed grains) were nearly without transformation strain. When the ingot had a quadratic shape, only columnar grains were found in the ingot. Strong anisotropy of the textured samples is also perceptible in this case. During preparation of the single crystal of the Ni_3Ta sample, the temperature gradient had a direction parallel to the sample axes. It can be seen that the direction of the temperature gradient in the sample during its preparation is a determining factor for the formation of preferential orientations and therefore for the size, direction, and shape of the transformation strain. The influence of texture on the shape memory effect has been studied predominantly in NiTi shape memory alloys [13,14]. Casting of this alloy is often followed by hot working (rolling for strips or drawing for wires), where preferential crystal orientations are always found.

Our previous studies of the Ni_3Ta alloy have shown the need to study the dilatation characteristics in thermal cycles with various maximum cycle temperatures. It was found that the temperature M_s and the shape of the CTE peak during cooling depends on the maximum temperature of the thermal cycle, so the thermal history determines the character of the reverse phase transformation. The results are shown in Figs. 3, 4, and 5. The CTE of the austenite is the same for all the thermal cycles. This means that, in the austenite, some processes take place that are not connected with volume or length changes in the sample. These processes are thermally activated.

If the sample is placed in the furnace, the phase transformation always propagates from the surface to the center of the sample. In the temperature range of the phase transformation, the hetero-phase state of the sample exists. If a coherent interface occurs between the parent and new phases, then no change in the number of or no movement of dislocations is assumed. This occurs when the strain associated with the new phase formation is not very large. If coherence becomes energetically unfavorable, an interphase dislocation network develops and a non-coherent interphase boundary occurs. A detailed characterization of the non-coherent boundary is presented in [15]. If we assume a non-coherent boundary in our Ni_3Ta alloy, the dislocation network exists in the martensitic phase. When the reverse phase transformation M → A occurs in Ni_3Ta, then these dislocations are not relaxed and they stay in the austenite. For this assumption there is evidence from our previous work [16], where a compression pre-deformed Ni_3Ta alloy was heated. Relaxation of dislocations takes place predominantly in the austenite. The same results were found in the work of Firstov [9]. The amount of relaxed strain was strongly dependent on the temperature. Relaxation of the compression strain in the Ni–Mn–Ga alloy [17] took place only in the temperature range of the martensite and during the phase transformation.

The influence of annealing the austenite on the transformation temperature A → M is evidently due to reconstruction of the dislocation network in this phase. Higher annealing temperatures yield larger changes in the architecture of the dislocations and lower transformation temperatures for the reverse transformation. The boundary between martensitic domains also exists in the single crystal. Therefore, the dislocation network is also presumed in this type of sample. The effect is smaller because there is a lower density of the boundaries.

Equation 1 shows that the latent heat is an important characteristic influencing the temperature of the sample in the transformation range during the first-order phase transformations. We have studied the thermal properties of the $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy [7], and we have found that the latent heat significantly lowers the sample temperature when the phase transformation takes place. Temperature decreases of 50 % were measured by the flash method. No such decrease was found in Ni_3Ta. The latent heat of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ has influenced the temperature of the measuring thermocouple in the dilatation measurement. No similar effect was found in Ni_3Ta. The martensitic phase transformation in Ni_3Ta looks like a second-order phase transformation (without latent heat).

The temperature dependence of the thermal diffusivity is revealed in Fig. 6. The thermal diffusivity of the austenite is at about 40 % higher than that of the martensite. An increase in the thermal diffusivity occurs at 327 °C. The start of the phase transformation M → A, as identified by dilatometry, is 325°C. The thermal diffusivity has the same character of temperature dependence as the thermal conductivity (Fig. 7). There is no peak in the transformation temperature range common for this type of temperature dependence when the measured specific heat is used for calculation of the thermal conductivity. The peak in the temperature dependence of the thermal conductivity as a consequential peak of the specific heat has no physical meaning, since the general heat conduction equation was derived and solved with the condition that no phase transformations occur in the material (thermophysical properties as the thermal diffusivity, thermal conductivity, specific heat, and density are not a function of the temperature). This condition is not evidently fulfilled in the transformation temperature range. The thermal conductivity of the austenite is always higher than that of the martensite. There are two processes by which heat is conducted in solids. Heat (energy) can be transferred by coupling between lattice vibrations or by electronic movement and collisions with atoms. The mean free path that determines the thermal conductivity of both processes is evidently higher in the austenite than in the martensite. The chief cause of the low thermal conductivity of the martensite is apparently the large amount of boundaries between martensitic domains that lower the mean free path.

5 Conclusions

The thermal properties of the polycrystalline and single crystal Ni_3Ta alloy were measured over the temperature range from room temperature up to 950 °C. Study of the dilatation characteristics shows that strains in the transformation temperature range increased in the polycrystalline alloy and decreased in the single crystalline alloy. The initial temperature of the phase transformation $M \rightarrow A$ was the same for both types of the alloy, and it was independent of the thermal history of the sample. The initial temperature for the reverse phase transformation, however, depended on the maximum temperature of the thermal cycle. Higher maximum cycle temperatures yielded lower transformation temperatures. It is assumed that this effect may occur as a consequence of a non-coherent inter-phase boundary during the phase transformation $A \rightarrow M$ when a stable network of dislocations occurs in the martensite. When the reverse phase transformation $M \rightarrow A$ occurs in Ni_3Ta, these dislocations are not relaxed and they stay in the austenite. Their architecture changes during the heating of the austenite, and by this manner the reverse phase transformation is influenced. This process is reversible.

The results obtained by the flash method show that the martensitic phase transformation occurs without latent heat. The thermal diffusivity and thermal conductivity of the austenite are higher than those of the martensite. The mean free path for electrons and phonons is lower in the martensite due to boundaries between martensitic planes.

Acknowledgments This work is a part of the research program MSM 0021620834 that is financed by the Ministry of Education of the Czech Republic. The author wishes to thank R. Sýkora for collaboration on this work.

References

1. A.L. Roitburd, Mater. Sci. Eng. A **273–275**, 1 (1999)
2. K. Nurveren, A. Akdogan, W.M. Huang, J. Mater. Process. Technol. **196**, 129 (2008)

3. Y. Zheng, J. Li, L. Cui, Mater. Sci. Eng. A **438–440**, 567 (2006)
4. A.I. Kostov, Ž.D. Živkovič, Term. Acta **291**, 51 (1997)
5. Y. Sutou, T. Omori, J.J. Wang, R. Kainuma, K. Ishida, Mater. Sci. Eng. A **378**, 278 (2004)
6. B. Gebhart, *Heat Conduction and Mass Diffusion* (McGraw-Hill, Inc., New York, 1993)
7. A. Rudajevová, Int. J. Therm. Sci. **47**, 1245 (2008)
8. Y.K. Kuo, K.M. Sivakumar, H.C. Chen, Phys. Rev. B **72**, 054116 (2005)
9. G.S. Firstov, Yu.N. Koval, J. Van Humbeec, P. Ochin, Mater. Sci. Eng. A **481–482**, 590 (2008)
10. A. Rudajevová, Silikaty **33**, 61 (1989)
11. J. Blumm, A. Lindemann, B. Niedrig, in *17th European Conference on Thermophysical Properties*, Bratislava, Slovak Republic (2005)
12. A. Rudajevova, M. Frost, A. Jager, Mater. Sci. Technol. **23**, 542 (2007)
13. H. Inoue, N. Miwa, N. Inakazu, Acta Mater. **44**, 4825 (1996)
14. Y.C. Shu, K. Bhattacharya, Acta Mater. **46**, 5457 (1998)
15. A.L. Roitburd, Martensitic Transformation as a Typical Phase Transformation in Solids, in *Solid State Physics*, ed. by H. Enrenreich, F. Seitz, D. Turnbull, vol. 33 (Academic Press, New York, 1978), p. 317
16. A. Rudajevova, J. Pospíšil, Mater. Sci. Eng. A (2010, in press)
17. M. Frost, A. Rudajevova, Int. J. Mater. Res. **100**, 898 (2009)