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Influence of anisotropy, the latent heat and the thermal history of alloy on martensitic transformation strain in Ni_3Ta single crystal

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ABSTRACT

Transformation characteristics in the single crystal of Ni_3Ta shape memory alloy were studied by the dilatation measurement in the temperature range of room temperature up to 500 °C. The transformation strains were positive in the direction of the *b*-axes and the *c*-axes and negative in the direction of *a*-axes. The martensitic phase transformation takes place without volume change of the sample. Thermal diffusivity of the single crystal measured in two directions *b*-axes and *a*-axes was higher than that for polycrystalline material.

The latent heat of the martensitic phase transformation influences the temperature distribution inside sample. Absorption (releasing) of the latent heat during heating (cooling) leads to cooling (heating) of the sample in place where the phase transformation takes place. This decrease (increase) of the temperature in the interface between both phases leads to stopping of the phase transformation. This effect is visible on the temperature dependence of the dilatation characteristics. The martensitic phase transformation in Ni_3Ta single crystal took place with hysteresis of 30 °C. This hysteresis changes depending on the thermal history of the sample. Hysteretic behaviour of the Ni_3Ta single crystal was analyzed and compared with behaviour of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy where no hysteresis was found.

1. Introduction

The shape memory effect is based on the phase transformation martensite ↔ austenite. Martensitic transformation is a strain transformation. The lattice strain is a transformation parameter that determines the physical states of an initial phase and a product phase, as well as local intermediate states of the alloy during the phase transformation. The gradual relaxation of the elastic energy during the phase transformation leads then to complex polydomain structure of the martensite. If the neighbouring atoms in an initial phase remain neighbours in a product phase then the phases are coherent [1]. The coherency creates elastic distortions and internal stresses. The increase of internal stresses can result in plastic deformation, which destroys coherency. Plastic deformation may essentially change the course of the phase transformation. The phase transformation takes place in the sample in the temperature gradient. This temperature gradient is determined by the heat flow into the sample, by the thermal conductivities of the both phases and by the latent heat. Heat conduction and the phase transformation take place in cooperation. The thermal properties are determining parameters for the athermal phase transformation. Athermal martensitic phase transformation takes place instantaneously when the transformation temperature is reached. It can be seen that the thermal conductivities of both phases are the determining parameter of the martensitic phase transformation, however, study of this parameter is disregarded.

To find a new high temperature shape memory alloy Firstov, et al. [2] have studied Ni_3Ta shape memory alloy. The binary phase diagram of Ni–Ta is similar to the binary phase diagram of Ni–Ti. The tetragonal-monoclinic phase transformation in Ni_3Ta was found to be of martensitic origin [3]. The thermally induced martensitic phase transformation took place with 50 °C hysteresis. The alloy was also studied after 10% pre-straining in compression at room temperature. This deformation was completely recovered during heating over a wide temperature range. The same results were obtained in our previous work [4]. Recovery process took place in the martensite, in the transformation temperature range and chiefly in the temperature range of the austenite, high above the M → A phase transformation. One-way shape memory effect could not be defined in this alloy. Large hysteresis, 60 °C was found also in our work. Small or no hysteresis is presented in the literature for stoichiometric Ni_2MnGa alloys. For example, no hysteresis we can find in the work of Kreissl et al. [5] as determined by the resistivity measurement. Xu et al. [6] using DSC have found $A_s = 263$ °C and $M_s = 260$ °C for $Ni_{54}Mn_{25}Ga_{21}$ (heating/cooling rate was 10 K/min). Hysteresis depends on the heating/cooling rate [7,8]. The higher

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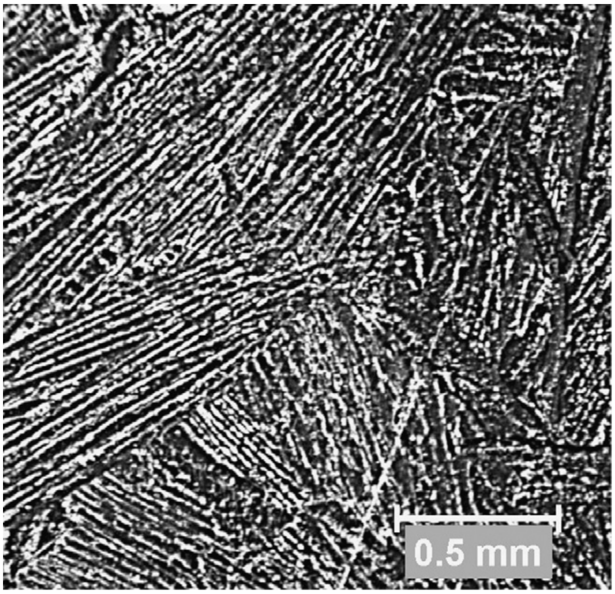

Fig. 1. Microstructure of the Ni_3Ta polycrystalline sample.

heating/cooling rate, the larger is hysteresis. Hysteresis in NiTi shape memory alloy was found from 25 up to 40 °C depending on the heat treatment. The authors assume that the presence of Ni_4Ti_3 precipitates causes phase hardening by stopping the movement of dislocation. Uchil et al. [9] showed that increase of the heat treatment temperature lowers the phase hardening tendency. Study of hysteresis is important not only from viewpoint of basic research but also from practical viewpoint. Different transformation temperatures for forward and reverse phase transformation are probably a consequence of non-thermodynamic factors as dislocations, grain boundaries, precipitation, re-crystallization and so on.

A better understanding of the complex behaviour of shape memory alloys during phase transformation requires experiments on single crystals. The aim of this work is to study the behaviour of the single crystal of Ni_3Ta shape memory alloy during the martensitic phase transformation. The transformation strain will be studied in dependence on the crystal anisotropy and the thermal history of the alloy. The detailed study of the dilatation characteristics in the transformation temperature range will shown influence of the latent heat on these characteristics. Thermal diffusivity and the thermal expansion of Ni_3Ta single crystal will be studied in the temperature range from room temperature up to 500 °C. Influence of the thermal conductivity on the character of the transformation strain will be discussed.

2. Experimental

Polycrystalline samples (PC) of Ni_3Ta alloy were prepared in a water-cooled copper ingot mould under the Ar (6 N) protective atmosphere from high-purity components (Ni – 99.995%, Ta – 99.95%). The microstructure of the polycrystalline sample is shown in Fig. 1. The single crystal (SC) was made in optical floating zone furnace (four mirrors furnace with halogen laps (4×1000 W) model FZ-T-4000-VI-VPM-PC, Crystal Systems Corp., Japan). The final size of the crystal was more than 10 mm in diameter and 40 mm in length. The samples prepared were annealed for 1 h at 1000 °C.

The crystal quality and orientation were checked out by the standard Laue technique in back reflection arrangement using Cu white X-ray radiation at room temperature. X-ray data revealed that the crystal crystallizes in the correct monoclinic crystal structure with $P2_1/m$ space group. Although, one can expect a simple structure for the binary compound the situation is not as simple as it is shown in works [10–13]. The Laue diffractogram of our single crystal is presented in Fig. 2.

The linear thermal expansion of the samples was measured in a helium atmosphere using the Netzsch 402E dilatometer over the range from room temperature to 500 °C. The heating and cooling rates were 2 K/min. The SC sample was in the form of a small cube (size $5 \times 3 \times 3\,\mathrm{mm}^3$) with perpendicular crystallographic axes.

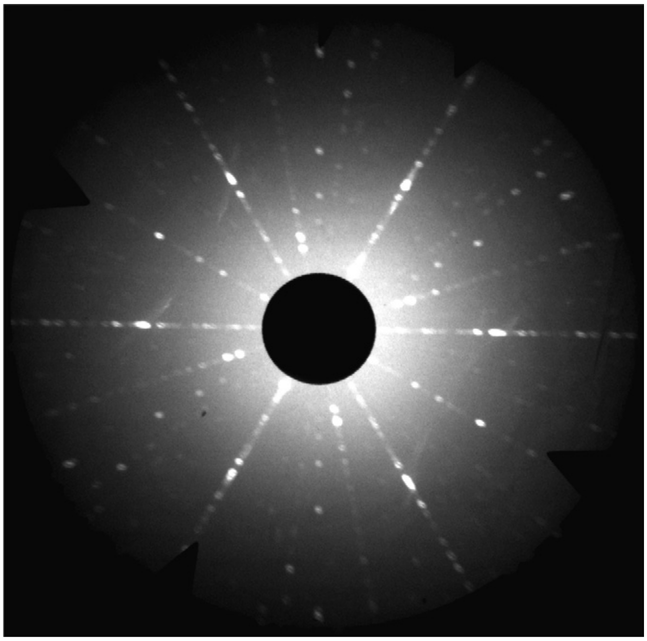

Fig. 2. The Laue pattern of the Ni_3Ta single crystal in the orientation [0 0 1].

The thermal diffusivity was measured by flash method in a helium atmosphere and in the temperature range from room temperature to 500 °C. The front of the sample was irradiated by short pulse energy (1 ms) from a Xe-flash lamp. The time dependence of the temperature rise was measured on the back side of the sample. Samples had a diameter of 16 mm and thickness of about 1.9 mm. The SC sample was measured in direction of *a*-axes and *b*-axes. The thermal diffusivity was obtained from the half time (this is the time when half of the maximum temperature rise is reached on the back side of the sample) and the thickness of the sample. Results were related to the sample temperature before irradiating.

3. Results and discussion

Figs. 3 and 4 reveal anisotropy of the transformation strain. Fig. 3 shows the temperature dependence of the relative elongation and Fig. 4 shows the temperature dependence of the CTE (the coefficient of the thermal expansion). It can be seen that a negative transformation strain is in direction *a*-axis, positive is found in directions *b* and *c*-axes. The sample volume does not change during the phase transformation. The PC samples were prepared by

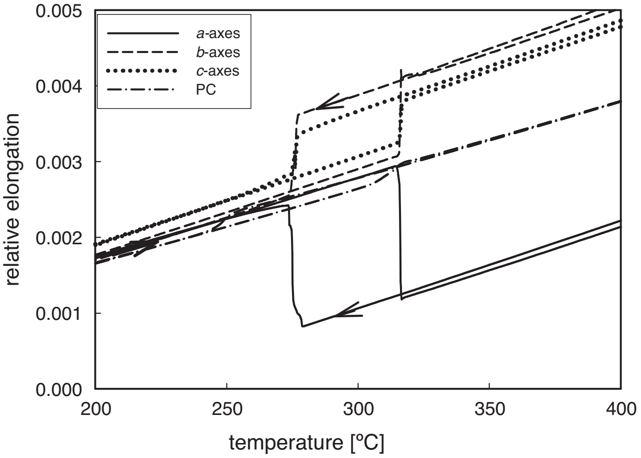

Fig. 3. Temperature dependence of the relative elongation for three directions of the single crystal and for polycrystalline sample (PC).

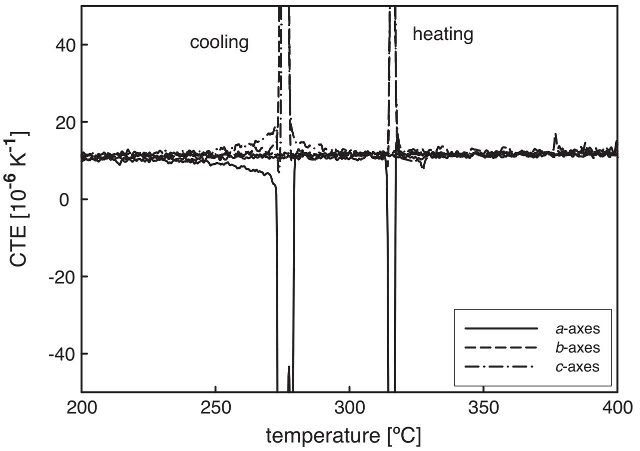

Fig. 4. Temperature dependence of the CTE for the single crystal.

arc melting of stoichiometric amounts of components in a water-cooled copper crucible. They show noticeable texture. Temperature gradient during preparation cooling acts perpendicular on longitudinal axis of the sample. The dilatation measurements are made in the direction of this longitudinal axis. The transformation strain in this direction is a positive. During manufacture cooling the columnar grains occurs in direction of the temperature gradient. It is probable that a negative transformation strain would be found in this direction. The samples with isotropic structures do not show the transformation strain. That is also the case for the samples with equiaxed grains. We have studied the samples with this structure for $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ shape memory alloy. Structures with equiaxed grains were obtained from the central part of the cylinder ingot while the rest of the ingot consisted of columnar grains. These columnar grains were perpendicular to the longitudinal axes of the ingot (in direction of the temperature gradient). The results obtained for both types of structures are described in our previous work [14].

When the sample is heated (or cooled) in the furnace during measurement or during application then the heat propagates from the surface sample into its centre. The highest temperature is reached on the surface. If the surface temperature spans the phase equilibrium temperature $T_{PE,}$ the phase transformation takes place and the phase interface propagates through the sample in the conduction region. The martensitic phase transformation is a first order phase transformation. Gebhart [15] shows scheme of the phase transformation of ice-water (it is also a first order phase transformation) where the melting front at $T = 0\,°C$ propagates into the conduction region when the surface of ice was raised to $T_o > 0\,°C$. The process is sketched in Fig. 5 where T is temperature and t is time. The instantaneous phase interface is at $X(t)$. The interface velocity, $u(t) = dX(t)/dt$, decreases with time, for fixed T_o and T_∞, as conduction resistance between the surface and the phase interface increases. The heat flux, in the liquid at the interface, is $q''_L(X,t)$, into the solid, $q''_S(X,t)$. The latent heat absorption rate, per unit area at the front is ρuH where H is the latent heat and ρ is the density. Here it is assumed that the density of both phases is the same. Since the phase equilibrium temperature is higher than T_∞ in this sample, heat is also conducted away from the moving interface. The energetic balance at the interface is then

$$q''_L(X,t) = \rho u H + q''_S(X,t) \qquad (1)$$

This case is discussed in Carslaw and Jaeger [16] and demonstrated by Lunardini [17].

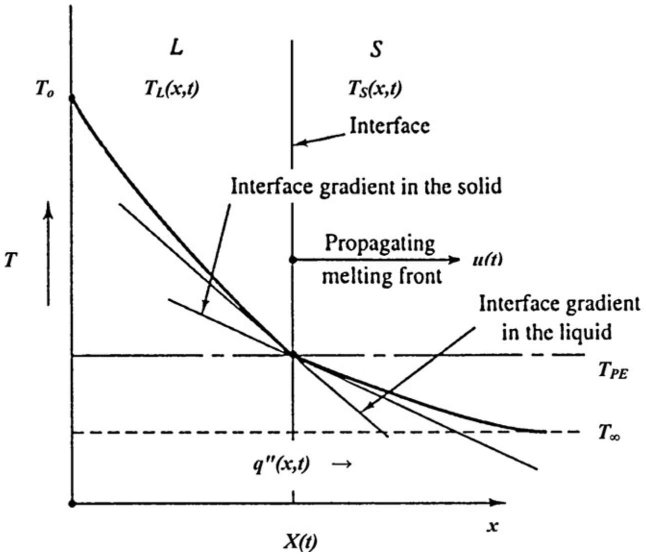

Fig. 5. Phase change fronts in a conduction region [16] ($q''(x, t)$: the heat flux, $u(t)$: the interface velocity, T_{PE}: the phase equilibrium temperature).

Figs. 3 and 4 show that phase transformations in the Ni_3Ta single crystal take place in a narrow temperature range. The rate of the phase interface movement in the SC is evidently higher than that in the PC (Fig. 3). The polycrystalline alloy has a lower transformation temperature for forward phase transformation than that single crystal and has larger hysteresis. The phase transformation temperature is defined as temperature when the phase transformation starts on the sample surface. For the single crystal this temperature was determined to be 313 °C for M → A and 281 °C for A → M. Hysteresis is about 30 °C. When the surface sample temperature reaches the transformation temperature T_{PE} the phase transformation starts and the phase interface propagates into the sample with a constant interface temperature T_{PE}. The temperature distribution in the sample is strongly influenced by the latent heat, as can be seen from Fig. 6 and relation (2). In Fig. 6 the time dependence of the thermocouple temperature for the single crystal during cooling is displayed when the thermocouple is placed right above the sample. The heat transfer between the sample and the thermocouple is given by the heat conduction through He and by radiation. It can be seen that the increase of the thermocouple temperature due to the latent heat is higher than 1 °C. We can assume that the sample temperature changes on the surface or otherwise the inside sample will be higher.

During the phase transformation the temperature changes the interface due to latent heat can be so large that the interface tem-

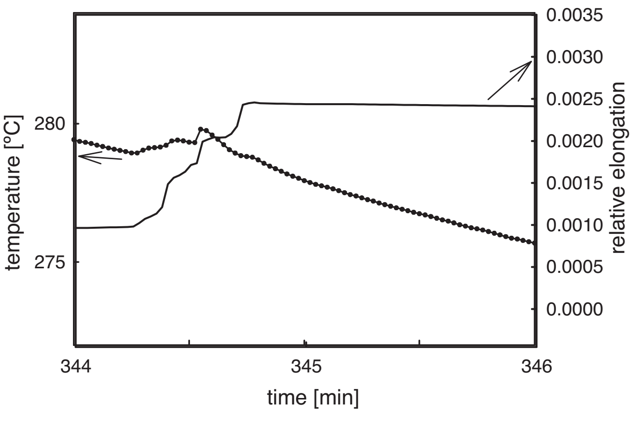

Fig. 6. Time dependence of the thermocouple temperature above the sample and of the relative elongation during the phase transformation A → M.

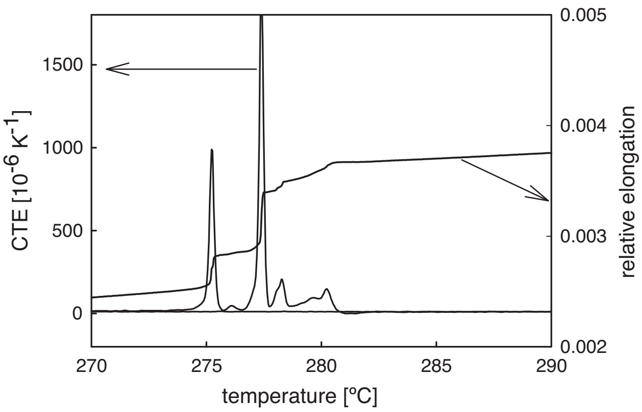

Fig. 7. Temperature dependence of the relative elongation and the CTE for the single crystal (*b*-axes) during cooling.

perature falls below T_{PE} (heating) or increases above T_{PE} (cooling) and the phase transformation stops. It can be seen in Fig. 6 where case of cooling is presented (changes are more perceptible than for heating). When the sample temperature increases above T_{PE} then the phase transformation stops, the relative elongation does not change anymore and the temperature dependence of the relative elongation has a stair character. The temperature dependence of the CTE is shown in Fig. 7 for the sample in direction of *b*-axes. Rate of the phase transformation is determined by the temperature changes inside sample.

No transformation hysteresis was found in $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ shape memory alloy [7,14]. When the phase interface propagates through the sample without hysteresis and its interface temperature decreases below $T_{\mathrm{PE},}$ then the reverse phase transformation immediately takes place (athermal phase transformation) in this alloy. This process is accompanied by releasing (absorption) of the latent heat and it changes the temperature distribution in the sample. Releasing of the latent heat in the transformation temperature range is shown in Fig. 8 for $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy. This result was obtained by utilizing flash method. The result presents the derivation in time dependence of the temperature increase on the back side of the sample after its irradiation on the front side. The sample temperature before irradiation was near below transformation temperature. Only one peak was found at the room temperature or at the temperature above the transformation temperature. The second maximum in this figure is a consequence of the latent heat released inside the sample. This can occur only if no hysteresis exists in the alloy. It was not found in Ni_3Ta alloy where hysteretic behaviour is dominant. A decrease of the temperature below T_{TR} inside the sample, suspension or turning of the phase transformation is the likely cause of the well-known effect of multiple peaks in DTA measurements [18,19]. This effect is explained by the authors of reference [18] as “the transformations proceedings in a discontinuous manner due to microstructural inhomogenities” or by the inhomogeneous storage of elastic energy. We assume that the temperature fluctuations inside the sample are connected with fluctuations of all physical properties in the transformation temperature range.

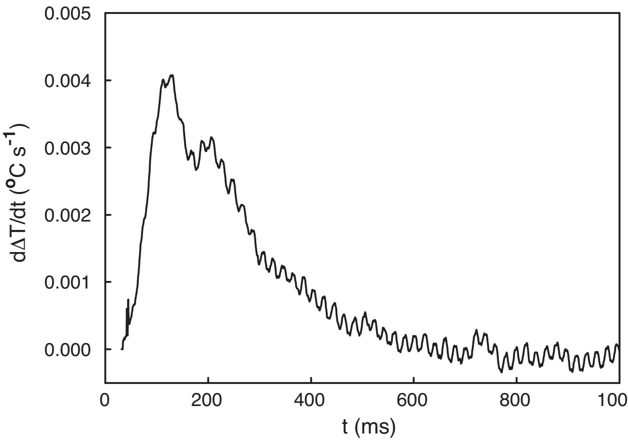

Fig. 8. Time derivation of the temperature increases on the opposite side of the sample after irradiation of its front side for $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy and starting temperature 170 °C.

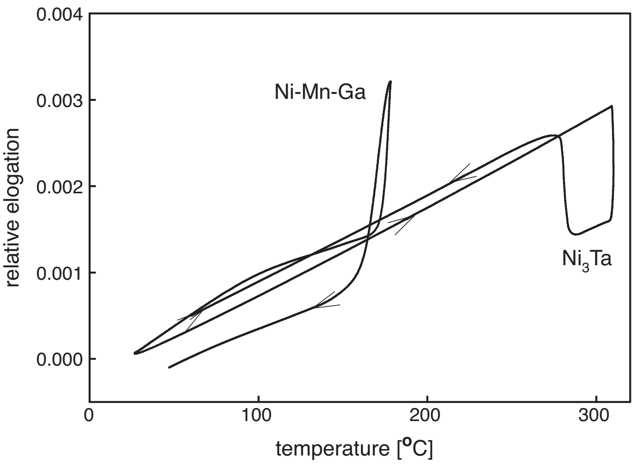

Fig. 9. Temperature dependence of the relative elongation for the PC of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy and the Ni_3Ta single crystal. The maximum cycle temperature was placed in the transformation temperature interval.

Hysteresis plays an important role in those cases where the phase transformation is interrupted. This case can arise during practical applications or in experiments when the maximum thermal cycle temperature is placed in the temperature range where the phase transformation occurs. The temperature dependences of the relative elongation obtained in those experiments are shown in Fig. 9 for the polycrystalline sample of the $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ [20] alloy and the Ni_3Ta single crystal. In the first alloy the reverse phase transformation takes place immediately after interruption (phase transformation takes place without hysteresis). The alloy with hysteresis cannot transform during cooling immediately after interruption because the reverse phase transformation temperature is lower than the forward phase transformation. Up to reaching the reverse phase transformation temperature the sample is composed of two parts: the austenitic peel and the martensitic centre. This composite is stable at temperatures between forward and reverse phase transformation temperatures. The reverse transient temperature has a higher transformation temperature than in the case when whole sample has been transformed as it is shown in Fig. 10 where the dilatation characteristics for the single crystal are displayed for the completed and interrupted phase transformation. Results show that shape memory alloy without hysteresis can be more advantageous for the practical use because it is “more sensitive” to the temperature changes. It reacts practically immediately and reversible on small temperature fluctuations inside sample.

The martensitic phase transformation is thermoelastic phase transformation that is based on a balance of chemical and elastic forces during the course of the forward and reverse transformations. In thermoelastic phase transformations the stored elastic energy can influence M_s, and A_s. Salzbrenner and Cohen [21] studied thermoelastic martensitic phase transformation in the polycrystalline as well as single crystal Cu–14Al–2.5Ni alloy. In the single crystal, hysteresis at about 30 °C was found despite the fact

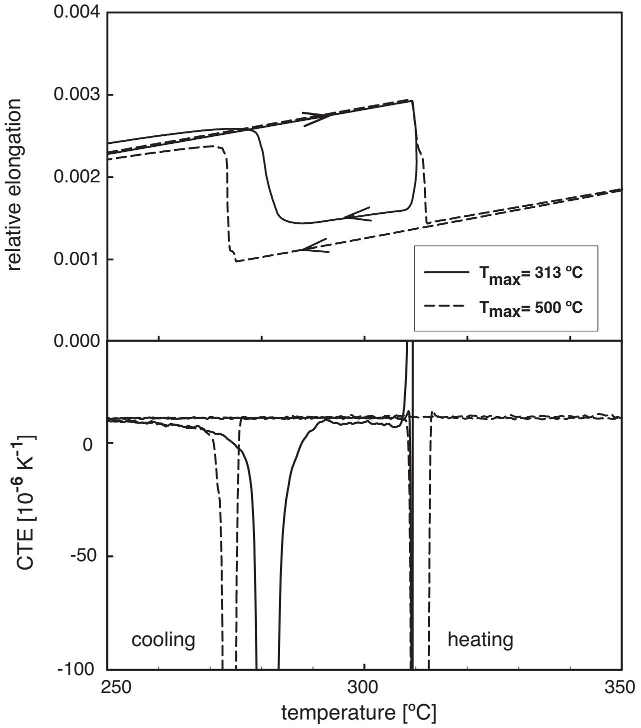

Fig. 10. Temperature dependence of the relative elongation and the CTE for the thermal cycle with the maximum temperature 314 and 500 °C.

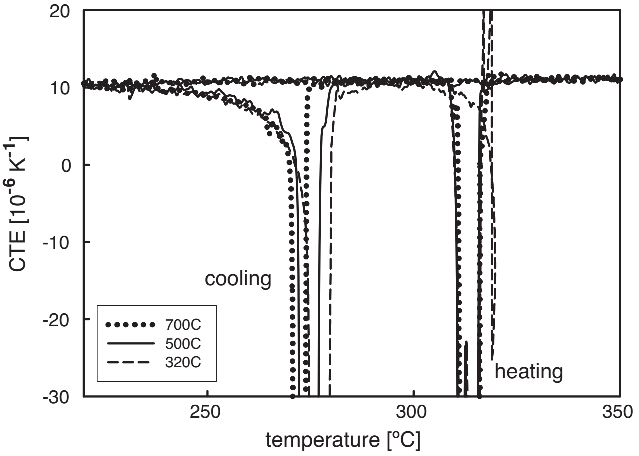

Fig. 11. Temperature dependence of the CTE for the temperature cycles with the maximum temperature 320, 500 and 700 °C.

that no stored elastic energy was involved. The authors assume that the hysteresis is a manifestation of frictional resistance to the interfacial motion. In the single crystal both phase transformations take place practically immediately, while in the polycrystalline samples the transformation takes places in the temperature region at about 30 °C, like in our experiments. The authors assume this difference in the transformation characteristics as a consequence of difference in stored elastic strain energy. The transformation temperatures of the single crystal are higher than that for the polycrystalline samples. It is also the same result as in our work.

Important information concerning hysteresis was obtained in the experiments where the maximum thermal cycle temperature was changed [22]. The transformation temperature for the reverse phase transformation depends on the maximum thermal cycle temperature for the polycrystalline samples as well as for the single crystals. The higher thermal cycle maximum temperature the lower is the transformation temperature for the A → M transition. This is displayed in Fig. 11 for the Ni_3Ta single crystal (*a*-axes). In this figure, the temperature dependence of the CTE is presented. It can be seen that an increase of the maximum thermal cycle temperature with about 200 °C decreases the reverse phase transformation to roughly 10 °C. This effect is substantially higher in the polycrystalline Ni_3Ta alloy.

When the phase transformation takes place in the solid state, a second factor giving rise to hysteresis operates. The martensitic phase transformation in Ni_3Ta single crystal occurs between high-temperature tetragonal phase and low-temperature monoclinic phase. This transformation is connected with the shape changes as is shown in Fig. 3. When the phase boundary propagates through the sample the shape changes cannot occur freely because rigidity of the surrounding matrix, and elastic strains are induced. The total free energy changes by relation [23]:

$$\Delta G = V\Delta G_v + A\gamma + V\Delta G_s \tag{2}$$

where V is volume, A is a area of interface between two phases, γ is interfacial energy per unit area and ΔG_s is a misfit strain energy per unit volume of a new phase. The strain energy and surface energy are positive contributions to the free energy and so tend to oppose the transformation and to increase of hysteresis. The value γ can change in wide range depending on the coherency of the interface. A coherent interface occurs when two crystalline structures go continuously through the interface. When the interface is not perfect it is still possible to maintain coherency by straining one or both phases. Increase of the coherent strain can lead to a semi-coherent interface. When the dislocation strain fields overlap the discrete nature of the dislocations is lost and the interface becomes incoherent. Misfit dislocations in the interface can relax elastically only in thin films when the film thickness is lower than a critical thickness [24]. In solids the lattice around each dislocation is elastically distorted, these strains extend up to the new phase and a dislocation network occurs. Our results presented in Fig. 11 show that a dislocation network exists in the austenite and its architecture is temperature dependent. Reconstruction of the dislocations network due to heat treatment leads to an increase of the third member in Eq. (2). The transformation temperature for the reverse phase transformation decreases and hysteresis increases.

Thermal diffusivity of the single crystal is higher than of the polycrystalline alloy as can be seen in Fig. 12. In this figure, the temperature dependence of the thermal diffusivity is shown in two directions *b*-axes and *a*-axes and for PC sample. There exists anisotropy in the thermal diffusivity as well as in the dilatation

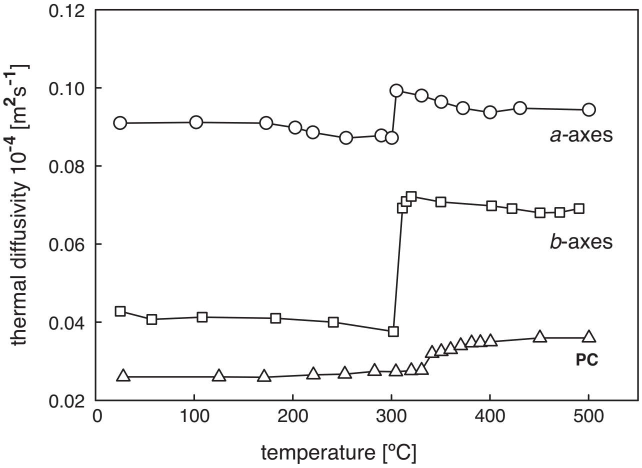

Fig. 12. Temperature dependence of the thermal diffusivity for SC and PC of the Ni_3Ta.

characteristics. Thermal conductivity is given as a product of the thermal diffusivity, specific heat and density. Thermal conductivity is a crucial parameter in the athermal phase transformations as it is perceptible from Eq. (1). The example displayed in Fig. 5 is different from our case where linear heating is used. The latent heat increases (decreases) the sample temperature in the place where the phase interface propagates through the sample. This heat is conducted in the direction of decreasing temperature gradient. In the case of the flash method this heat is conducted to the opposite side of the sample related to the irradiated sample side. The rate of the phase transformation depends on conducting this heat from the interface.

4. Conclusion

The transformation strain for the Ni_3Ta single crystal was negative in direction of *a*-axes and positive in directions of *b*-axes and *c*-axes. During the phase transformation, the samples changed only in shape and not in the volume of the sample.

During the martensitic transformation the phase interface propagates through the sample in the temperature gradient. Both the phase transformation and the heat conduction take place in cooperation. The phase transformation is accompanied by release or absorption of latent heat. The temperature gradients in the sample are strongly influenced by this latent heat. The relative elongation in the transformation temperature range has a step-like character. The rate of the phase transformation in the single crystal is more rapid than in the polycrystalline Ni_3Ta alloy. The martensitic phase transformation in the single crystal shows hysteresis at about 30 °C. This hysteresis depends on the maximum thermal cycle temperature that influences the transformation temperature for A → M transformation.

The thermal diffusivity of the austenite is higher than the martensite. The thermal diffusivity in the direction of the *b*-axes is threefold higher than for in the polycrystalline sample and twofold higher than the thermal diffusivity in the *a*-axes.

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References

[1] A.L. Roitburd, Mater. Sci. Eng. A 273–275 (1999) 1.
[2] G.S. Firstov, Yu.N. Koval, J. Van Humbeec, P. Ochin, Mater. Sci. Eng. A 481–482 (2008) 590.
[3] Yu.N. Koval, G.S. Firstov, Metallofizika I Noveishie Tekhnologii 29 (2007) 815.
[4] A. Rudajevova, Pospisil, J. Mater. Sci. Eng. A 527 (2010) 2900.
[5] M. Kreissl, K.U. Neumann, T. Stephens, K.R.A. Ziebeck, J. Phys.: Condens. Matter. 15 (2003) 3831.
[6] H.B. Xu, Y. Li, C.B. Jiang, Mater. Sci. Eng. A 438–440 (2006) 1065.
[7] A. Rudajevova, Met. Mater. 46 (2008) 71.
[8] K. Nurven, A. Akdogan, W.M. Huang, J. Mater. Process. Technol. 196 (2008) 129.
[9] J. Uchil, K. Ganesh Kumara, K.K. Mahes, Mater. Sci. Eng. A 332 (2002) 28.
[10] T. Saburi, M. Nakamura, S. Nenno, J. Less-Common Met. 41 (1975) 135.
[11] B.C. Giessen, Acta Crystallogr. 17 (1964) 615.
[12] J.T. Zhao, L.M. Gelato, E. Parthé, Acta Crystallogr. C 47 (1991) 479.
[13] Y. Hayashi, P. Delavignette, S. Amelinckx, Phys. Status Solidi 42 (1970) 637.
[14] A. Rudajevova, M. Frost, A. Jager, Mater. Sci. Technol. 23 (2007) 542.
[15] B. Gebhart, Heat Conduction and Mass Diffusion, McGraw-Hill, Inc., New York, 1993.
[16] F.R. Carslaw, J.C. Jaeger, Conduction of Heat in Solids, 2nd ed., Oxford University Press, London, 1959.
[17] V.J. Lunardini, Heat Transfer in Cold Climates, Van Nostrand Reinhold, New York, 1981.
[18] C. Segui, V.A. Chernenko, J. Pons, E. Cesari, V. Khovailo, T. Takagi, Acta Mater. 53 (2005) 111.
[19] C. Segui, V.A. Chernenko, J. Pons, E. Cesari, J. Phys. 112 (2003) 903.
[20] A. Rudajevova, Adv. Mater. Sci. Eng. 2008 (2008) (article ID 659145).
[21] R.J. Salzbrenner, M. Cohen, Acta Metall. 27 (1979) 739.
[22] A. Rudajevova, Int. J. Thermophys. 31 (2010) 378.
[23] R.E. Smallman, R.J. Bishop, Modern Physical Metallurgy and Materials Engineering, Elsevier Science Ltd., 1999, p. 82.
[24] J.W. Matthews, A.E. Blakeslee, J. Cryst. Growth 27 (1974) 118.