

**DETERMINATION OF RESSIDUAL
PSEUDO-CHEMICAL ENERGY AND ENERGY
DISSIPATIVE DURING REVERSIBLE MARTENSITIC
TRANSFORMATION IN $\text{Ni}_{52,2}\text{Mn}_{21,3}\text{Ga}_{26,5}$ ALLOY**

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K e y w o r d s: shape memory alloys, reversible martensitic transformation, Heusler alloys, Ni-Mn-Ga.

A b s t r a c t

In this paper we present results of an analysis of the influence of annealing time on the residual pseudo-chemical energy and dissipative energy $F_{\text{dis}}(z)$ during reversible martensitic transformation. Analysis was performed without equilibrium temperature and basis on the model proposed in the study: (LIKHACHEV 1998).

From designated courses of residual non-chemical and pseudo-chemical dissipative energies come, that carried thermal treatment causes significant changes of them.

Immediately after casting the studied alloy shows continuous increase of the dissipative energy with increasing of martensite fraction. After annealing at the time from 1+0 h, curves $F_{\text{dis}}(z)$ have a curse close to constant function whereas beyond this range show dynamic increasing or decreasing of dissipation energy.

**WYZNACZENIE RESZTKOWEJ ENERGII SPRĘŻYSTEJ ORAZ ENERGII
ROZPRASZANEJ PODCZAS ODWRACALNEJ PRZEMIANY MARTENZYTYCZNEJ
W STOPIE $\text{Ni}_{52,2}\text{Mn}_{21,3}\text{Ga}_{26,5}$**

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Słowa kluczowe: stopy z pamięcią kształtu, odwracalna przemiana martenzytyczna, stopy Heuslera, Ni-Mn-Ga.

A b s t r a c t

W pracy przedstawiono wyniki przeprowadzonej analizy wpływu czasu wygrzewania próbek stopu $\text{Ni}_{52,2}\text{Mn}_{21,3}\text{Ga}_{26,5}$ na resztkową energię sprężystą oraz energię dyssypowaną $F_{\text{dis}}(z)$ podczas odwracalnej przemiany martenzytycznej. Analizę przeprowadzono z pominięciem temperatury równowagi fazowej na podstawie modelu zaproponowanego w pracy LIKHACHEVA (1998).

Z wyznaczonych przebiegów zmian resztkowej energii sprężystej oraz energii rozpraszanej wynika, że przeprowadzona obróbka termiczna powoduje znaczne ich zmiany. W stanie bezpośrednio po wytopie badany stop wykazuje ciągły wzrost energii rozpraszanej wraz ze wzrostem zawartości frakcji martenzytu. Po zastosowaniu wygrzewania w czasach 1+20 h, krzywe $F_{\text{dis}}(z)$ mają przebieg zbliżony do funkcji stałej, natomiast poza nim wykazują dynamiczny wzrost bądź spadek energii dyssypowanej.

Introduction

Ni-Mn-Ga alloys compose intermetallic compound described by general formula X_2YZ . They are among to the so-called Heusler's alloys group. They are characterized by a lot of unique properties such as: structural (e.g. the ability to form modulated super-structures), functional (the ability to reversible martensitic transformation) and magnetic.

Stoichiometric, intermetallic compound with density $\rho = 8.148 \text{ g/cm}^3$ crystallizes at $\approx 1380\text{K}$ temperature, creating at room temperature super-structure, face-centred cubic structure *fcc* ($L2_1$ No 225) and high order degree of atomic packing in crystallographic lattice up to 98% (AYUELA 1999, BISWAS 2006). Unit cell of high temperature (austenite) phase consists of 16 atoms, however, according to literature sources the lattice parameter (a_0) contains in the range of $5,822\div 5,825 \text{ \AA}$ (MARTYNOV 1992, STUHR 1995, VASIL'EV 2003, ZHELUDEV 1995).

Putting the austenitic phase (A) into cooling below characteristic temperature M_s (martensite start) crystal lattice undergoes homogenous deformation to the system of lower symmetry, form low-temperature phase (martensite – *M*). This transformation is reversible by thermal impact. Fundamentals parameters, which characterize each reversible martensitic transformation, are characteristic temperatures: the beginning and end of phase transition (M_s – martensite start, M_f – martensite finish, A_s – austenite start, A_f – austenite finish) and temperature determined thermodynamic equilibrium state (T_0) between occurred phases. Characteristic temperatures can be determined by scanning differential calorimetry (BRECZKO 2005). While, the temperature T_0 describes the experimentally determined by Cornelis and Wayman (CORNELIS 1976) equation (1), which was used among others in the work (KHOVALIO 2004, ROMERO 2003, AHLERS 2003, HUO 1998).

$$T_0 = \frac{M_s + A_f}{2} \quad (1)$$

But as comes from the papers (LIKHACHEV 1997, 1998) their define and value determination is debatable.

The aim of the work

The aim of this study is carrying out the thermodynamic analysis of reversible martensitic transformation occurred in the $\text{Ni}_{52,2}\text{Mn}_{21,3}\text{Ga}_{26,5}$ alloy. The analysis was performed according to the algorithm proposed in study: (LIKHACHEV 1998) which omits temperature of thermodynamic equilibrium (T_0).

The object and methodology of the study

The object of this study were samples of $\text{Ni}_{52,2}\text{Mn}_{21,3}\text{Ga}_{26,5}$ alloy which were undergone homogenizing treatment.

Homogenization process was performed in a tube furnace R09 type in argon atmosphere. The temperature of homogenization was determined by literature study, generally basing on papers: (BESSEGHINI 2001, KHOVAILO 2004). Studies published in the cited papers shows that the thermal treatment of Heusler's alloys affects on the structure, phases volume and lattice parameters.

In order to study the effect of homogenization time on the structure of the $\text{Ni}_{52,2}\text{Mn}_{21,3}\text{Ga}_{26,5}$ alloy were carried out homogenization treatment at 1173K in different annealing time.

During the homogenizing treatment samples were heated and cooled to room temperature in the furnace. In all cases, the heating time (t_1) was 45min, and the annealing time ($t_w = t_2 - t_1$) for individual samples is summarized in Table 1. The whole process ended with slow cooling (in furnace) to room temperature (T_p).

Table 1
Statement of annealing time of individual samples

Sample designation	P0	P1	P2	P3	P4	P5
t_w [h]	after casting	1	5	10	20	60

In order to perform thermodynamic analysis according to described below algorithm, were carried out calorimetric measurements (DSC). Measurement was performed with NETZSCH DSC204 instrument at constant heating/cooling rate of 10 K/min in the range 173÷473 K. As protective gas was used argon (Ar). In the limit temperatures of analyzed range i.e. 173 K and 473 K was used 5 min holding in order to stabilize thermodynamic processes that may occur.

Before measurement, calorimeter was calibrated by finding the melting point of pure indium (*In*).

Kinetics of reversible martensitic transformation proceeded in this alloy, based on the analysis of thermal hysteresis loop trajectory and so called elastic coefficients was reported earlier in paper (BRECZKO 2007).

Thermodynamic parameters describing reversible martensitic transformation

To analyze the kinetics of reversible martensitic transformation was used the algorithm and thermodynamic parameters proposed and widely described in papers (LIKHACHEV 1998). Likhachev, based on the first and second law of thermodynamics, introduces parameters that describe:

- pseudo-chemical (Δu_p) transformation energy,
- residual non-chemical energy (φ) – depended on volume martensite fraction during transformation: $M \rightarrow A$ and $A \rightarrow M$,
- pseudo-chemical equilibrium temperature (T_{0p}).

Parameters mentioned above and dissipative energy (F_{dis}) which is a result of internal friction are described by equations (2)-(5) (LIKHACHEV 1998):

$$\Delta u_p = \Delta s \int_0^1 dz T_{eq}(z) = \Delta s T_{0p} \quad (2)$$

$$\varphi(z) = \Delta s \int_0^z dz (T_{eq}(z) - T_{0p}) \quad (3)$$

$$T_{0p} = \int_0^1 dz T_{eq}(z) \quad (4)$$

$$F_{\text{dis}}(z) = -\frac{1}{2} \Delta s [T_+(z) - T_-(z)] \quad (5)$$

where:

z – martensite volume fraction,

$T_{eq}(z)$ – represents the dissipative thermoelastic equilibrium line described by equation (6) (LIKHACHEV 1998):

$$T_{eq}(z) = \frac{1}{2} [T_+(z) - T_-(z)] \quad (6)$$

where: (+) – means temperature achieved during heating (transformation $M \rightarrow A$), while (–) – means temperature achieved during cooling cycle ($A \rightarrow M$).

According to the mentioned model, the energy balance in each point of reversible martensitic transformation, in heating and cooling cycle is described by the following equation (7) (LIKHACHEV 1998):

$$\Delta s T_{eq}(z) = \Delta u_p + \frac{d\varphi(z)}{dz} \pm F_{dis}(z) \quad (7)$$

Results and discussion

The performed thermodynamic analysis, based on the methodology proposed in paper (LIKHACHEV 1998), allows to better understanding of the impact of heat treatment on the kinetics of reversible martensitic transformation which occurs in $\text{Ni}_{52,2}\text{Mn}_{21,3}\text{Ga}_{26,5}$ alloy.

From plotted courses of residual non-chemical energy and dissipative forces showed in Fig. 1a and Fig. 1b, follow that the thermal treatment causes significant thermal changes in both residual non-chemical potential $\varphi(z)$ and forces F_{dis} dissipative during internal fiction. Transformation $A \rightarrow M$ occurred in $\text{Ni}_{52,2}\text{Mn}_{21,3}\text{Ga}_{26,5}$ alloy after the melt has continuous increase of the dissipative energy with increasing fraction of martensite (Fig. 1b), while after annealing at a time $t=0$ h, curves $F_{dis}(z)$ take the characteristic shape. In the range $z \approx 0,1 \div 0,9$, function $F_{dis}(z)$ becomes similar to a constant, and beyond this range shows dynamic increase or decrease of dissipative energy.

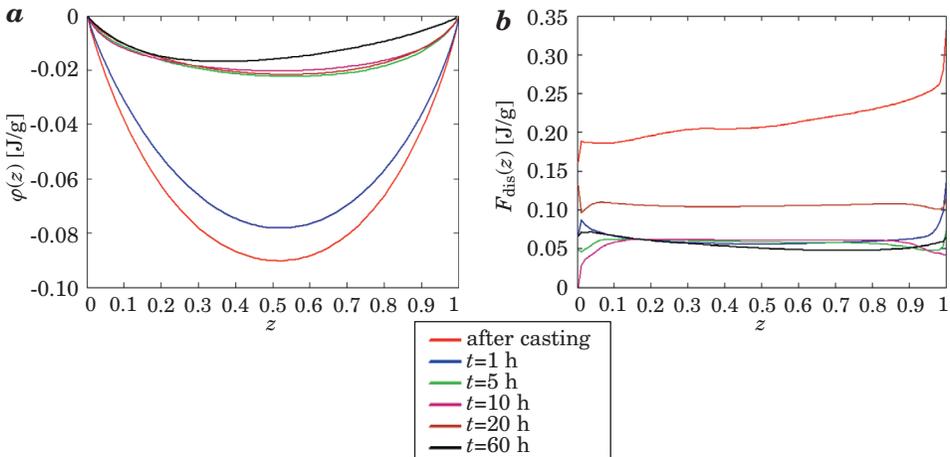


Fig. 1. Changes of: a) residual non-chemical energy, b) dissipative energy

Follows from the residual potential, that it achieves a minimum for the $z(T_{eq} = T_{0p})$, above the minimum its function $\varphi(z)$ is increasing. As it comes clear from Fig. 1a minima $\varphi(z)$ for samples P0-P4 coincide (with some

approximation), while in the plotted curve of function $\varphi(z)$ for P5 sample its minimum has significant shift in the direction of prevailing fraction of austenite. This situation may suggest a formation of different crystallographically martensite, or most likely the increase of the quantity of variants self-accommodation groups of martensite crystallites. In this case the growth of martensite plates is inhibited by a previously established crystallite of low-temperature phase. Detailed results of these calculations are presented in Table 2.

Table 2
Values of pseudo-chemical equilibrium temperature, pseudo-chemical transformation energy and energy dissipative during transformations: $A \rightarrow M$ and $M \rightarrow A$

Marking the sample	The time of warming up [h]	T_{op} [K]	Δu_p [J/g]	$\int_0^1 F_{dis}(z)$ [J/g]
P0	0	278.0	4.985	0.214
P1	1	282.5	5.365	0.062
P2	5	284.0	3.975	0.058
P3	10	284.5	3.983	0.058
P4	20	284.0	4.687	0.105
P5	60	289.0	1.734	0.055

Conclusions

Based on carried out experiment it was found, that applied heat treatment caused changes of residual non-chemical energy and dissipative energy. After applying the 60-hour soaking, the value of dissipative energy in the consequence of internal friction, decreased quadruple. It is probably a result of less extend of defected structure compared to the state after casting. However, function courses $\varphi(z)$ and $F_{dis}(z)$ plotted basing on the quoted model, as well as the distribution of their peaks, represent in the vivid way the kinetics of martensitic transformation.

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