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Influence of Heat Transfer on Determination of Transient Temperatures for $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ Shape Memory Alloy from Dilatometric Data

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Abstract The martensitic phase transformation in a $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ shape memory alloy is an athermal phase transformation that starts practically, immediately after reaching a certain transient temperature. The final temperature is given at each point of the sample by two processes: heat conduction and phase transformation. Both processes take place in tandem. The thermal expansion and calculation of the temperature fields in a dilatometer are used to determine the transient temperatures and to study the transient temperature ranges.

Keywords NiMnGa shape memory alloy · Martensitic phase transformation · Thermal expansion

1 Introduction

The martensitic phase transformation is an athermal phase transformation. In this transformation, the measured transition temperature does not depend on the experimental heating–cooling rates. Many results presented in the literature, however, show that transformation temperatures are dependent on the heating–cooling rates [1,2]. For example, the dilatation characteristics for copper-based shape memory alloys are observed to be dependent on the heating–cooling rates in [3]. DSC results in [4] show an important shift of the transformation peaks as a function of the heating rate.

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Two causes for this effect are presented in the literature: the measurement technique and the changes in the materials connected with the martensitic transformation. A detailed analysis of this problem is found in the work of Fraile-Rodríguez et al. [5]. Martensitic phase transformations in Cu–Al–Ni shape memory alloys studied by DSC exhibit some kinetic effects strongly dependent on the temperature rate. This result is in agreement with internal friction results [6]. However, dynamic measurements of Fraile-Rodríguez et al. show a net dependence on the temperature rate. A solution to this problem is very important for appropriate technological applications.

The thermal dependences of the physical properties of materials, especially of metals, are measured in the atmosphere of inert gases to prevent oxidation. The measuring atmosphere is not always presented in the papers, but Ar is used in most cases. An argon atmosphere as the inert atmosphere was used, for example, in [7,8]. If a certain distance between a thermometer and sample exists, then it is very important to know the type of atmosphere used. The thermal conductivity of this media influences the difference in the temperatures between the thermometer and the sample. Two important questions occur in these cases: (a) Does the temperature difference between the thermometer and the sample depend on the type of the atmosphere in the experimental device? (b) Does the temperature difference between the thermometer and the sample depend on the heating–cooling rate in various atmospheres used?

It is known that the physical parameters such as the specific heat and the thermal expansion of shape memory materials change dramatically with temperature in the transition temperature range. The relation between elucidation of the temperature fields in the instrument and the transition phase temperatures has not yet been systematically investigated. It is important to note that the solution to this problem is very important for optimum use of shape memory materials in practice. The aim of this work is to investigate the dependence of transient phase temperatures of a $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ shape memory alloy on the experimental conditions, where the temperature distribution between the sample and the thermometer is varied. This problem is solved by studying the dilatation characteristics of a given shape memory alloy in the temperature range from room temperature to 380 °C. Analysis of the temperature fields was made using a finite element method (FEM) system COSMOS/M.

2 Experimental Details

The dilatation characteristics of a $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy were studied in the Netzsch 402 C dilatometer. It was measured in argon and helium protected atmospheres. The specimens of the alloy were 6 mm in diameter and 25 mm in length. A polycrystalline ingot of a $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy was prepared by arc melting the pure elements under an argon atmosphere. The samples prepared from the ingot were annealed for 4 days at 850 °C, and they were studied in the pre-deformed state (up to 1 %). The heating–cooling rates were (0.5, 2, 5, and 7) $^\circ C \cdot min^{-1}$. The arrangement of the interior of the dilatometer is shown in Fig. 1. This arrangement was used to define boundary conditions for modeling of the temperature fields in the dilatometer.

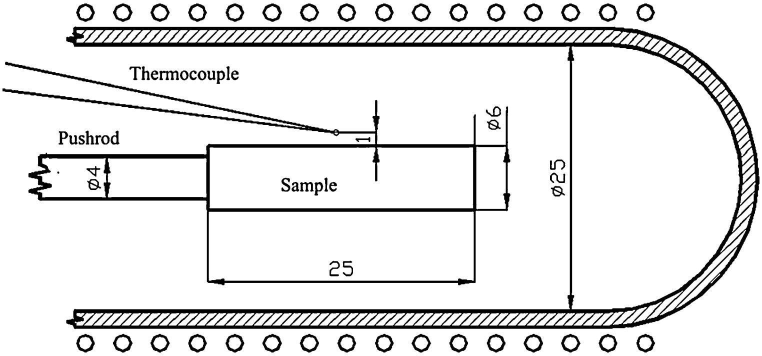


Fig. 1 Schematic diagram of the inner arrangement of the dilatometer

3 Results and Discussion

Figure 2 shows the temperature dependences of CTE (the thermal expansion coefficient) for heating, measured in He (Fig. 2a) and Ar (Fig. 2b). It is necessary to note here that special attention has been paid to accuracy of these measurements. The calibration of the dilatometer was made with a Pt standard sample with the same dimensions as the specimen of the $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy. All measurements were performed at one sample deposition (only the rates of heating–cooling and atmosphere were changed) to ensure that all changes of the CTE are only due to temperature changes. The transformation temperatures, the temperature T_{MP} corresponding to the maximum CTE, and the temperature T_S of the start of the phase transformation, are presented in Table 1. The method of determination of these temperatures is shown in Fig. 2b. Figure 2 and Table 1 clearly show a significant influence of the gas atmosphere and heating rate on T_{MP} and T_S. The influence of the heating rate is more important in Ar than in He. The differences between the transient temperatures are connected with the different thermal conductivities of Ar and He. The thermal conductivity of He gas at a pressure of 1 atm and at room temperature is $0.152\,W \cdot m^{-1} \cdot K^{-1}$, and the thermal conductivity of Ar at the same conditions is $0.0177\,W \cdot m^{-1} \cdot K^{-1}$. The higher thermal conductivity of He secures better heat transfer between the thermocouple and the sample. The dependence of the transformation temperatures on the heating–cooling rates is a consequence of the heat transfer between the sample and its surrounding.

The martensitic phase transformation is an athermal phase transformation. The transformation parameters are only temperature dependent. Any time dependence therefore cannot have a kinetic nature. Kostov et al. [3] studied Cu–Zn–Al shape memory alloys in the Netzsch 402 E dilatometer at different heating rates of (3, 5, 10, 15, and 20) $°C \cdot min^{-1}$ in a nitrogen–hydrogen protective atmosphere. The transformation temperature increases with an increasing heating rate in a range of 40 °C to 80 °C. Results were used for calculation of the activation energy. These authors reported that the time dependence of the transformation temperatures has a kinetic nature. It is a different hypothesis than the one presented in our conclusions because we assume that the influence of the heating–cooling rates on the transformation temperatures is a consequence of the heat transfer in the experimental arrangement. The dependence of

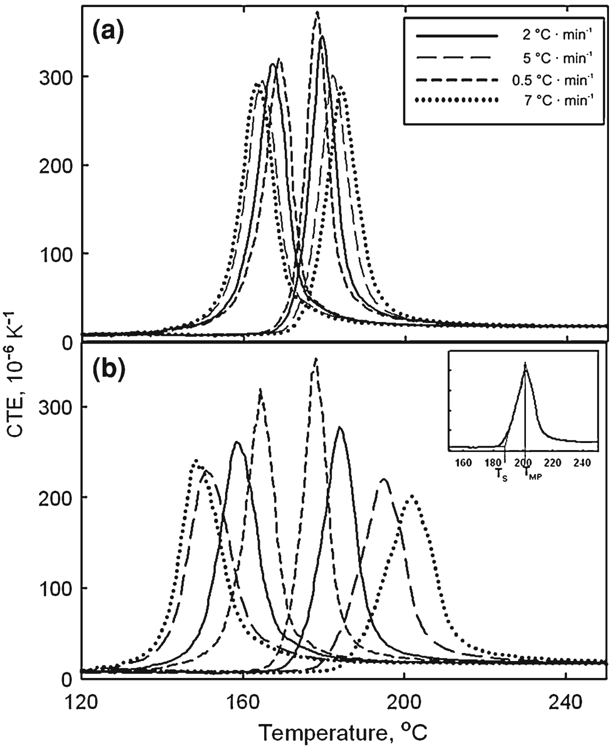


Fig. 2 Temperature dependence of CTE for heating–cooling rates of (0.5, 2, 5, and 7) °C · min^{-1} in (**a**) He and (**b**) Ar; inset in (**b**) shows method of determination of T_S and T_{MP}

Table 1 Dependence of the maximum peak temperature (T_{MP}) and the start temperature (T_S) on the heating rate

Heating rate (°C · min^{-1})	Ar		He	
	T_{MP} (°C)	T_S (°C)	T_{MP} (°C)	T_S (°C)
0.5	177	171	178	171
2	183	174	179	172
5	194	182	182	174
7	201	187	184	176

the transformation temperatures on the heating–cooling rates was studied by DSC in NiTi by Nurven et al. [9]. They found that the transformation temperatures are strongly sensitive to the heating–cooling rate. The transformation temperature increased with increasing heating rate. No analysis of the heat transfer in the experimental device was made in this work as well.

Computational analysis of the heat transfer process corresponding to the CTE measurement arrangement (Fig. 1) has been carried out. We used a one-dimensional (1D) axially symmetric model created in the numerical system Cosmos/M based on the finite element method. The model considers heat transfer from the furnace wall through the

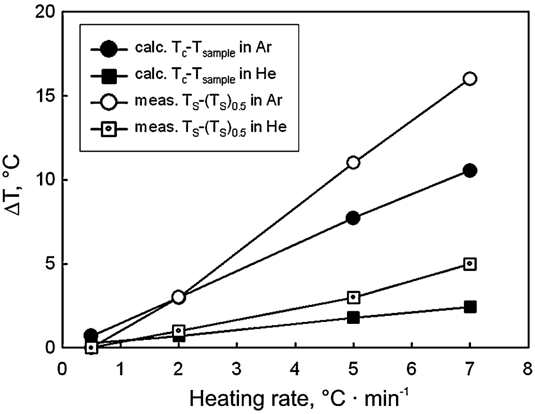


Fig. 3 Dependence of the temperature difference calculated between the surface of the sample and the thermocouple when the temperature of the sample was 164 °C, and the difference of $T_S - (T_S)_{0.5}$ on the heating rate in Ar and He (where T_S is a temperature when the phase transformation starts at a given heating rate and $(T_S)_{0.5}$ is that for the heating rate of 0.5 °C · min^{-1})

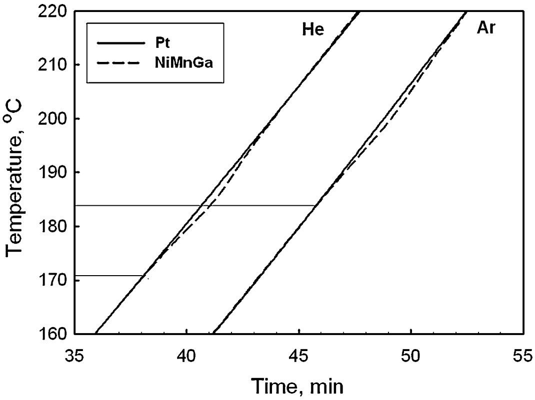
gas into the measured sample. The initial temperature was 80 °C. Considering the boundary conditions, the sample surface is subjected to radiation from the furnace wall at a given temperature. The furnace temperature increased linearly from 80 °C to 380 °C, and the slope was dependent on the heating rate. The emissivity of the sample surface was 0.2. Perfect thermal contact was considered to exist between the furnace wall and the gas and between the gas and the sample surface. Heat conduction throughout the gas was computed using temperature-dependent material properties of the gas. Heat conduction throughout the solid sample was computed with a temperature-dependent thermal conductivity, and the heat capacity was considered to be constant [10–12], without latent heat. The element size was 0.06 mm; the time step was 1 s.

The thermocouple was not simulated as an additional part of the model; its temperature is evaluated as equal to the temperature of the gas at a selected distance from the sample surface. Figure 3 shows the calculated temperature differences between the thermocouple (T_c) and the sample (T_{sample}), $T_c - T_{sample}$, which is dependent on the heating rate. These differences were obtained for $T_{sample} = 164$ °C (this temperature was chosen to be just below the phase transformation temperature). Figure 3 also shows the measured temperature differences $T_S - (T_S)_{0.5}$ dependent on the heating rate (where T_S is a temperature when the phase transformation starts at a given heating rate and $(T_S)_{0.5}$ is that for the heating rate of 0.5 °C · min^{-1}). Temperature differences between the measurement and the model can be influenced by assuming perfect contact between the gas and the sample surface.

It can be seen that both dependences have the same characteristics. The difference increases with increasing heating rate. Hence, we can assume that when the given transient temperature is reached on the sample surface, the temperature of the thermocouple is higher than the surface temperature in all the cases presented here. We can see that all differences in the transformation temperatures of the shape memory alloy in our experiments are due only to changes in the temperature fields in the measuring system (the athermal phase transformation depends only on the temperature).

Figure 4 shows the time dependence of the thermocouple temperature above the Pt sample and the shape memory alloy measured during heating at a rate of 5 °C · min^{-1}.

Fig. 4 Time dependence of the temperature measured by the thermocouple for Pt and $Ni_{53.6}Mn_{27.1}Ga_{19.3}$



The figure clearly reveals the influence of the latent heat on the temperature measured by the thermocouple. We can see a higher influence of the latent heat in the He atmosphere because there is better heat transfer than in the case of Ar. The curves for Pt and $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy start to diverge at about 172 °C in He and above 184 °C in Ar. These temperatures are nearly the same as T_s determined from dilatation results (Table 1). It is evident that the phase transformation starts in the sample in He, as well as in Ar at a certain temperature that is the same for both gases. The observed difference is a consequence of our experimental arrangement in the dilatometer where the temperature is measured above the sample surface. The real temperature of the sample is always lower than the temperature measured by the thermocouple outside the sample. Table 1 shows that the difference between He and Ar is minimum at the lowest heating rate of $0.5\,°C \cdot min^{-1}$.

Figure 4 shows further important information, i.e., duration times of phase transformation. For heating rates of (0.5, 2, 5, and 7) $°C \cdot min^{-1}$ in He, duration times of (40, 10.5, 7, and 4.5) min, respectively, were determined. The higher are the heating rates, the shorter is the duration of phase transformation. The phase transformation starts in the sample when the surface sample temperature reaches the transient temperature. The phase interface then propagates into the sample. The rate of the transient process (u) depends on the thermal conductivity of both phases ($K_{M,} K_A$), the latent heat (H), density (ρ), heating rate, and of course, on time. For a given time, u is given by the following relation:

$$u = \frac{1}{\rho H}\left(K_M\left(\frac{\partial T}{\partial x}\right) - K_A\left(\frac{\partial T}{\partial x}\right)\right) \tag{1}$$

This relation was adapted from the relation that was originally derived for propagation of a melting front in a conduction region [13]. In this relation it was assumed that the density of both phases is the same. The rate propagation of the phase interface u increases/decreases with increasing/decreasing temperature rate during heating–cooling. Distribution of the temperature in the sample during phase transformation is a result of the cooperation of heat conduction and propagation of phase transformation (with the latent heat). The mathematical solution to this very complex problem can be found in [14].

4 Conclusion

(a) The phase transformation of martensite↔austenite is characterized by a single temperature of phase transformation that is identical with the start temperature (similar to the phase transition of ice–water).

(b) This work shows that the transient temperature determined from the dilatation characteristics strongly depends on the experimental arrangement, the sample size, and the method of temperature measurement. We assume that this is a consequence in that the dilatation characteristics are related to the temperature which is measured outside the sample. While the sample temperature decreases/increases due to latent heat, the thermocouple temperature increases from the given heating–cooling rate. The temperatures of the sample and the thermocouple are not the same. This behavior is also confirmed by modeling of the temperature fields during measurement of the dilatation characteristics. The transformation temperature of the athermal phase transformation is a material property, which would be independent on the experimental conditions of its determination.

(c) The time at which the phase transformation takes place in the sample is determined by heat conduction and propagation of the phase transformation across the sample. Both processes take place in tandem, and they depend on the heating–cooling rate.

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