

ON THE HEAT OF TRANSFORMATION IN NITI SHAPE MEMORY ALLOYS UNDER LOAD

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Abstract. *The thermomechanical behavior of the Shape Memory Alloys (SMAs) has been intensively investigated in the last years. On the other hand the caloric behavior of them has received less attention and therefore there are some important open questions about this subject. One of them concerns the heat of transformation of the SMAs under load. In standard caloric measurements the specimen is usually in a state free of stress. In all applications however the material is always subjected to certain loads. The aim of the present work is to investigate the influence of the load on the heat of transformation in SMAs. To reach this goal by means of a standard calorimeter a special specimen holder had to be constructed, which allowed the fixation of a pre-strain during the calorimetric measurements. The pre-strain was prescribed by means of a tension machine specially developed to work with small dimension specimens. The heat of transformation of Ni50.2Ti (wt %) shape memory specimens under constant pre-strain were measured. The obtained results show that the heat increases with the pre-strain, as far as the elastic range of deformation of the austenitic phase upon heating is not exceeded. Out of this range a decrease of the heat of transformation with increasing pre-strain was observed. It is experimentally observed that under constant strain the phase transformation occurs under load, and one could conclude that the higher the load, the larger the heat of transformation within the elastic range of the austenite. On the other hand, the higher the load, the smaller the heat of transformation out of this range.*

Keywords. *Shape Memory Alloys, heat of transformation*

1. Introduction

As far as the thermomechanical behaviour of the Shape Memory Alloys is concerned it is usual to analyse three types of diagrams: the Load-Deformation diagram (L-D diagram) under different constant temperatures, Figure 1a, the Deformation-Temperature diagram (D-T diagram) under different constant loads, Figure 1b, and the Load-Temperature diagram (L-T diagram) under different constant deformations, Figure 1c.

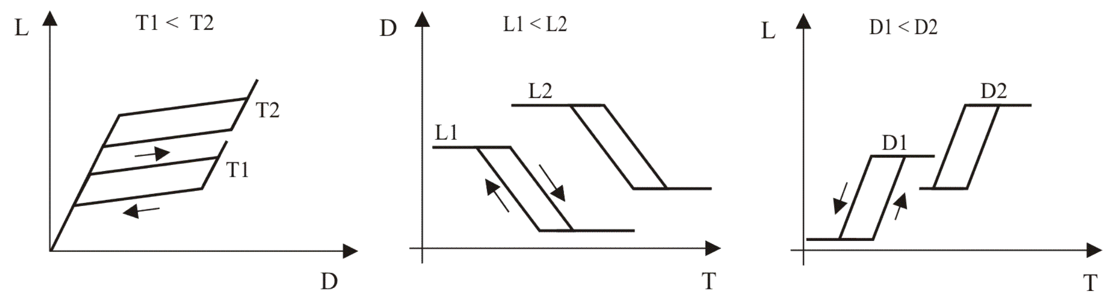

Figure 1. a) L-D diagram. b) D-T diagram. c) L-T diagram – Schematic.

In the present work a very important observation about the L-T diagram under different loads, Figure 3c, is that the higher the prescribed strain, the higher the load under which the transformation takes place (Da Silva, 2000; Glasauer, 1996). This is very important to understand the experiments and results presented in this work.

As one can see in the curves presented in Figure 3 the behaviour of SMAs is always characterized by a hysteresis loop, which has been intensively investigated. Xu (1992) investigated the size of the hysteresis, the temperature dependence of the hysteresis area, and the behaviour inside the hysteresis loop within the elastic range of Cu81.8Al14Ni (wt %) and Cu26Zn6.2Al (wt %) single crystal. According to his work the size of the hysteresis depends not much on the temperature, as far as the phases undergo complete phase transformation in both directions, austenite to martensite and vice-versa. Glasauer (1996) investigated the quasiplastic behaviour under both tension and compression, and the transition from quasiplastic to pseudoelastic behaviour of Cu75Zn18Al (wt %). According to his observations this alloy could show, at the same temperature, quasiplastic or pseudoelastic behaviour, depending on the direction of the temperature change, it means, if the test temperature was reached from one higher (after heating) or from one lower temperature level (after a cooling process). The reason for such behaviour has been not completely understood yet.

These two cited works should only point out the major interest of a great number of works that have been carried out about the thermomechanical behaviour of SMA in the last years. On the other hand the caloric behaviour of these alloys has received less attention. Because of that there are some important open questions about it. One of these questions concerns the load influence on the heat of transformation in these alloys, since in their applications they usually work under certain loads, and not free of stress as in the standard caloric measurements.

By heating a shape memory alloy up to a critical temperature A_s (Austenite start temperature) a phase transformation from martensite to austenite starts, and at A_f (Austenite finish temperature) the transformation is finished.

During this transformation a certain amount of heat is added to the sample (endothermic reaction). By cooling the material up to another critical temperature M_s (Martensite start temperature) a reverse phase transformation from austenite to martensite starts. Reaching the critical temperature M_f (Martensite finish temperature) the martensitic transformation is over. During this transformation the heat added to the sample during the heating is now liberated (exothermic reaction). This heat absolved during heating and set free during cooling is called heat of transformation.

In standard measurements of heat of transformation the sample is usually in a free stress state. In most applications however the shape memory component works under certain loads. In this context the knowledge about the load influence on the heat of transformation may be of great importance for the development of models based in thermodynamics theories.

There are only few reports related to this question (Planes et al, 1981; Sade et al, 1989; Wollants, et al, 1983). From none of these works one can have a clear idea about the load influence on the heat of transformation in SMAs. In addition, in all these works one investigates single crystal alloys. If the obtained results apply also to polycrystalline alloys was not investigated yet.

The aim of the present work is to investigate the load influence on the heat of transformation of a NiTi polycrystalline shape memory alloy by means of a standard calorimeter. To reach this goal a special specimen holder had to be developed. The calorimetric measurements were performed in Ni50.2Ti (wt %) based shape memory alloy. The results were analysed making use of others thermomechanical experiments and some assumptions of the Achenbach-Muller model (1986).

2. Experimental setup and measurement description

A Differential Scanning Calorimeter from Perkin Elmer (DSC7) was used to measure the heat of transformation. Due to the relative small dimensions of the calorimeter furnace (9.0mm diameter and 7.0mm depth) a special specimen holder had to be developed under these restrictions to set the specimen under load. In practice it meant to set the specimen under constant strain. This was possible by means of the developed specimen holder that is shown in Figure 2. It consists of a two-parts block of Aluminium. The upper part (1) has four holes without thread and the bottom part (2) four holes with thread. The pre-strained specimen is placed between the two parts (1) and (2) and these are fixed together by means of four bolts (3). Before this the specimen were pre-strained by means of a tension machine developed in the Institute of Thermodynamics at the University of Berlin. This machine was developed specially to work with small dimension specimens (Glasauer, 1996). The analysed alloy was a Ni50.2Ti (wt %) wire of 0.29mm diameter.

The calibration of the calorimeter was performed following the standard procedure, but using two identical empty specimen holders, instead of the standard capsule. After that the calorimetric measurements were performed following the standard procedure. The specimens were heated and cooled in the range from 10 to 120°C at 1°C/min.

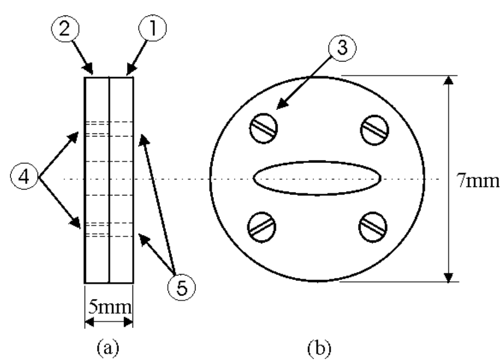

Figure 2. Specimen holder.

3. Results and discussion

In this section some experimental results obtained by the author in this work will be presented. The Figures 3 and 4 show the measured transformation temperatures *As* and *Ms* under three different pre-strains. One may observe that the temperatures of transformation undergo an increase with increasing constant pre-strains.

In order to understand this result showed in Figures 3 and 4 one can analyse some Load-Deformation experiments at different prescribed test temperatures as shown in Figure 5 for Ni50Ti48Cu (wt %) at 25°C, 65°C and 100°C. One can see that the higher the test temperature, the higher the load necessary to induce the transformations. Another experiment that helps one to understand the shifts of the transformation temperatures is the Deformation-Temperature curve under different constant prescribed loads. The Figure 6 shows such curves for Ni50.2Ti (wt %) under 4N and 12N. One can see that the higher the prescribed load, the higher the transformation temperatures. These two observations concerning Load-Deformation and Deformation-Temperature curves agree qualitatively with the observed changes in the measured transformation temperatures obtained by means of the calorimetric measurements presented in Figures 3 and 4.

As one can observe from experimental Deformation-Temperature diagrams (under constant loads), the bigger the prescribed deformation, the higher the load under which the phase transformation takes place, see the schematic curves in Figure 1c. From this observation one can conclude from the Figures 3 and 4 that the bigger the load, the higher the transformation temperatures.

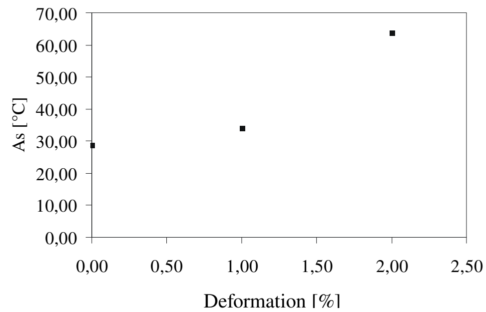

Figure 3. A_s under different prescribed constant strains (under load) in Ni50.2Ti (wt %).

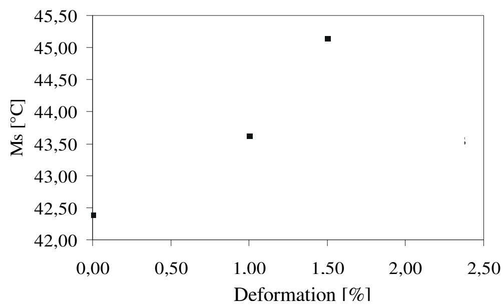

Figure 4. M_s for different prescribed constant strains (under load) in Ni50.2Ti (wt %).

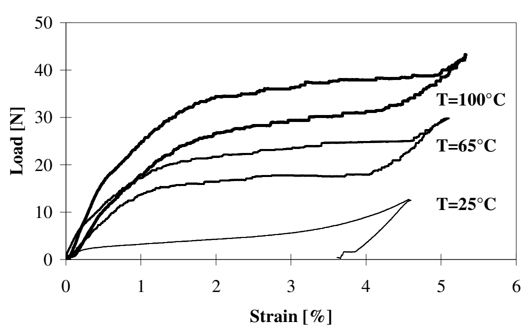

Figure 5. Load-Deformation curves for Ni50Ti48Cu (wt %) unde different prescribed temperatures (Da Silva, 2000).

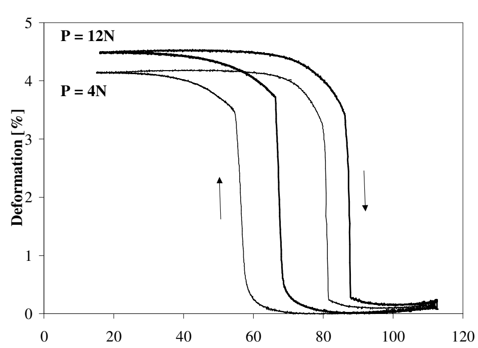

Figure 6. Deformation-Temperature curves for Ni51Ti (wt %) under different prescribed loads (Da Silva, 2000).

The Figure 7 shows the experimental results obtained by the author for the heat of transformation under different pre-strains. One sees that the heat of transformation shows an initial increase and than a decrease with increasing pre-strain, or equivalently, with increasing load.

To understand this result one may consider here the model for Shape Memory Alloys proposed by Achenbach and Muller (1986). This model takes into account three possible phases, being two variants of martensite and denoted by M_+ and $M\_$. The other one is the austenite and denoted by A. The two variants of martensite are thermodynamically stable below *Ms*. It means that when the material is cooled below *Ms* in a state free of stress, these two variants of martensite nucleate and grow statistically at the same proportion. In these conditions the specimen will have 50% of martensite M_+ and 50% martensite $M\_$. This assumption is based on the self-accommodation nature of the martensitic phase transformation (Delaey, 1974). The austenite A is thermodynamically stable above *As*. It means that when the material is heated above *As* in a state free of stress, the austenite phase A will be the only one stable phase. The martensite may be also mechanically induced (Delaey, 1974). Below *Ms* the self-accommodated martensite variants may be reoriented and above *As* the austenite phase may be transformed into martensite by means of a load (Delaey, 1974). The model proposed by Achenbach and Muller (1986) assumes that under tensile loads the formation of variant M_+ is favoured. On the other hand, under compressive loads the formation of $M\_$ is favoured. When the specimen receives a tensile load below *Ms* the martensite variant $M\_$ starts to reorient into M_+. This transition proceeds as long as the load is high enough. After the unloading a quasiplastic strain remains.

Based on these considerations let us analyse the results presented in Figure 7. Consider the Load-Deformation curves at different constant prescribed temperatures shown in Figure 8. First of all consider the strain range from 1.0% to 3.6%. In state free of stress and strain ($P = 0$ and $D = 0$) at $T = 25^oC$ there are statistically 50% of M_+ and 50% of $M\_$. The points A, B, C, D and E represent five quasiplastic pre-strains corresponding to 0.5%, 1.0%, 2.0%, 3.0% and 3.6% respectively. The fractions of M_+ and $M\_$ given in Figure 8 are assumed considering the Achenbach and Muller model (1986) as described above.

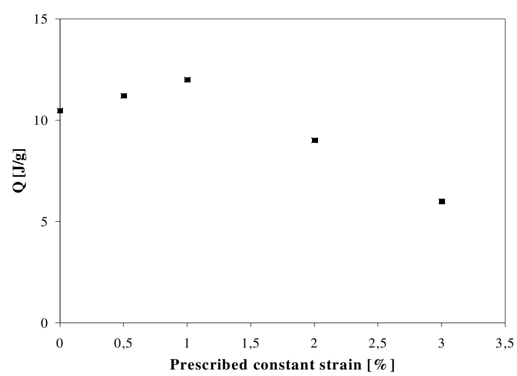

Figure 7. Heat of transformation under prescribed strains (under load) in Ni50.2Ti (wt %) – Upon heating.

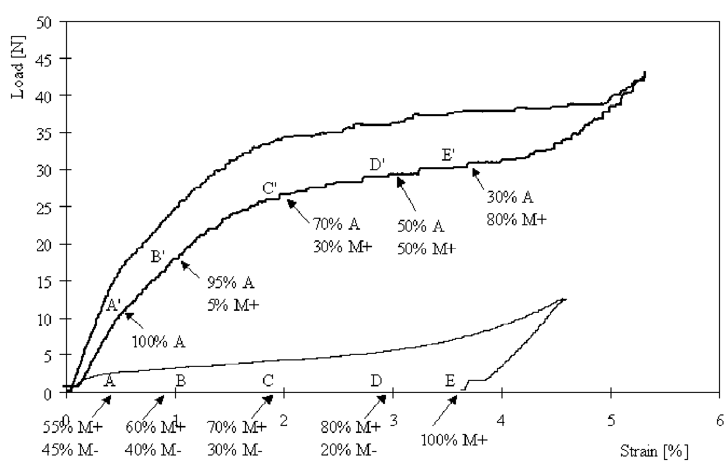

Figure 8. Graphic interpretation of the calorimetric results – Ni50%Ti48%Cu (wt %) - (Da Silva, 2000).

At $T = 100^oC$ in a state free of stress and deformation ($P = 0$ and $D = 0$) only the austenitic phase is present. Under high enough load the austenite transforms to stress induced martensite. The points A', B', C', D' and E' represent the states for the prescribed constant pre-strains (prescribed at $T = 25^oC$) after the heating from 25°C to 100°C. In these states the phases A and M_+ can coexist if the strain during the heating is held constant. For these states the fractions of austenite and martensite are also approximated values. The variant $M\_$ transforms completely to austenite during the heating, independently of the prescribed deformation, so there is no variant $M\_$ at points A', B', C', D' and E'. On the other hand not all M_+ variant transforms to austenite. Due to the load under which it is, part of it transforms direct to the stress-induced martensite M_+ at 100^{o}C. In this situation the martensite M_+ at 25^{o}C contributes less or maybe nothing to the heat of transformation, because they are already in martensitic state. Due to the fact that the fraction of martensite M_+ at 25^{o}C increase with increasing prescribed pre-strain, its contribution to the heat of transformation decreases with increasing load. This explains why the heat of transformation decreases with increasing load.

If the prescribed strain at 25^{o}C falls in the elastic range of the pseudoelastic curve at 100^{o}C, approximately until 1.0%, this analysis is not valid. In this range all martensite transforms to austenite upon heating. So the higher the pre-strain in this range, the higher the load under which the transformation takes place, and the higher the heat needed to induce the transformations. This explains the initial increase of the heat of transformation with increasing load.

4. Concluding remarks

The heat of transformation under load on Ni50.2Ti (wt %) shape memory alloy was measured by means of a special specimen holder, which allowed the fixation of a constant strain by calorimetric measurements. The pre-strains were previously prescribed to the specimens by means of a tension machine. The results showed that the temperatures of transformation increase with increasing load for all prescribed strains. The heat of transformation also increases with the load as far as the elastic range of the austenitic phase (upon heating) is not exceeded. Out of this range a decrease of the heat of transformation with increasing load was observed. Analysing other curves such as Load-Deformation for different temperatures and Deformation-Temperature for different loads and applying some assumptions of the Achenbach-Muller model one could understand the reasons for this behaviour.

5. References

Da Silva, E. P., 2000, “Zur Kalorimetrie von Gedächtnislegierungen und zur ihrer Anwendung als elektrisch aktivierten Aktuatoren“,PhD. Theses, Technische Universitäte Berlin, Germany.

Delaey, L., Krishnan, R. V., Tas, H., 1974, “Thermoplasticity, pseudoelasticity and the memory effects associated with martensitic transformations – Part 1: Structural and microstructural changes associated with martensitic transformations“, Journal fo Materials Science, 9, 1521-1535.

Glasauer, F. U., 1996, “Gächtnislegierungen – Experimentelle Untersuchungen und Aufbau einer Wärmekraft-maschine“, PhD. Theses, Technische Universitäte Berlin, Germany.

Planes, A., Macqueron, J. L., Morin, M., Guenin, G., 1981, “Study of martensitic transformation of Cu-Zn-Al alloy by coupled enthalpy and acoustic emission measurements“, Phys. Status Solidi, 66, 717-724.

Sade, M., Cesari, E., Hornbogen, E., 1989, “Calorimetry of Cu-Zn-Al single crystal during pseudoelastic transformation“, J. Mat. Sci Letters, 8, 191-193.

Xu, X., 1992, “Experimentelle und theoretische Untersuchung des Hystereseverhalten in Formgedächtnis-legierungen“, PhD. Theses, Technische Universität Berlin, Germany.

Wollants, P., De Bonte, M., Ross, R. J., 1983, “The stres-dependence of the latent heat of transformation in beta-CuZnAl single crystal“, Z. Metallkunde, Band 74, Heft 3(2), 127-131.