

Rapidly solidified bulk shape memory alloys*

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Rapidly solidified Ni-Ti bulk shape memory alloys have been manufactured using the suction method. The as-solidified rods have been characterized using DSC and internal friction methods. In the as solidified state it is shown that an inhomogeneous structure may occur due to the change in the cooling rate from the outer surfaces in contact with the cooled mold and the core. Two transitions are clearly observed on cooling the as-quenched sample while during heating only one distinct peak appears on both DSC and internal friction. The heat treatment applied to the rapid solidified specimen lead to a volume transformation, similar to the one observed in similar samples prepared via the classical path. The analysis of the relaxation peak is consistent with similar known results.

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1. Introduction

Shape memory alloys (SMAs) are under scrutiny for several years due to their wide spectra of properties that allows them to be used in various fields and applications. Most of the time they are manufactured as bulk alloys, but recently they have also been fabricated and investigated as ribbons and thin films. The ribbons and films bare a high potential for structural adjustment in the nanocrystalline state. An amorphous state can be obtained for films deposited on unheated substrates and a crystallization process leads to crystalline films and the shape memory properties [1]. Heated substrates also allow crystalline films to be obtained [2]. On the other hand, rapid solidification techniques have been used for several years to manufacture amorphous alloys, mostly as ribbons [3].

Shape memory alloy ribbons have been manufactured by melt-spinning and characterized for various compositions. Structural refinement and nanocrystalline clusters have been obtained in such ribbons and the shape memory effect has been observed [4].

More recently, the attention has been shifted toward rapid solidified bulk shape memory alloys. Such materials can be obtained if the melt is rapidly solidified in water cooled copper molds. Compared to ribbons, that are 20-30 μm thick and films that usually range between 0.5-10 μm in thickness, rapid solidified bulk alloys with round section allow the use of internal friction as a tool for characterization. Ribbons and films attached to substrates can only be tested in flexural internal friction tests whereas rods can be tested using classical forced torsion pendulum methods. This is an area where this paper intends to contribute.

In terms of composition, NiTi alloys are the most used shape memory alloys and their behavior is governed by a bcc B2-R19' monoclinic phase transition. Their properties can be better adapted to specific requirements by adding a third element to the basic composition [5,6,7].

While the martensitic transition occurring between martensite (the low temperature phase) and austenite (the

high temperature phase) is the main driving element in shape memory alloys, it is not uncommon to detect more than one type of transformation, depending on the alloy composition. For example, Ni-Ti-Cu are interesting shape memory alloys because - depending on their Cu content - they show two types of martensites. For lower Cu contents (less than 7.5 %) a B2-monoclinic transition governs the behavior, while for higher Cu contents the transition is B2-orthorhombic-monoclinic. Pre-martensitic effects have been reported initially in Ni-Ti-Fe alloys by Hwang et al. [8, 9] who found a sequence of second order "normal-incommensurable" followed by a first order "incommensurable-commensurable" transformation leading to a rhomboedral crystalline structure called R-phase. Thus, a typical transformation sequence on cooling in a Ni-Ti alloy with pre-martensitic effects would be: cubic B2 (austenite) \rightarrow incommensurable \rightarrow commensurable rhombohedral (R-phase) \rightarrow monoclinic B19' (martensite) [10]. In binary Ni-Ti alloys, it is rather frequent to observe the occurrence of an R-phase transition in Ni-rich alloys.

Internal friction (IF) and differential scanning calorimetry (DSC) are adequate tools that enable the characterization of phase transition in various conditions of shape memory alloys. The phase transformation in bulk alloys or thin films, crystallization of amorphous films can be made using IF and DSC spectra [e.g. 1,11]. This paper is focused on the characterization of the phase transition in rapid solidified Ni-Ti bulk alloys using internal friction as main investigating tool.

2. Experimental details

Ni-Ti samples have been manufactured by rapid solidifying the melt into water cooled copper molds. The alloys with the desired composition were melted in quartz crucible having a circular opening in the bottom part using a high frequency induction furnace. When the melting temperature is reached, an argon overpressure is used to eject the melt into the copper mold. Polycrystalline

samples with rod shape have been manufactured, with the dimensions ranging from 1.5 to 1.8 mm in diameter and 50 mm long.

The samples have been investigated in the as cast and heat-treated state. The heat treatment consisted on heating at 1000 K for 3600s in argon, followed by water quenching.

The samples were further investigated using optical microscopy, X-ray diffraction, differential scanning calorimetry (DSC) and internal friction (IF). A forced torsion pendulum was used for the measurement of internal friction as a function of temperature in the cyclic thermal range of 100-400 K. The strain amplitude used in the experiment ranged from 2×10^{-5} to 2×10^{-4} , with heating rates 1-5 K/min and frequency ranging from 0.1 to 5 Hz.

3. Experimental results

The composition $Ni_{51.04}Ti_{48.96}$ determined by EDX locates the samples in the Ni-rich range and the room temperature X-ray diffraction shows that the structure of the sample in the heat treated state shows austenitic (B2) and monoclinic martensite (B19') as well as R-phase reflections, while diffuse peaks appear to predict the heat treated ones, as described in Fig. 2.

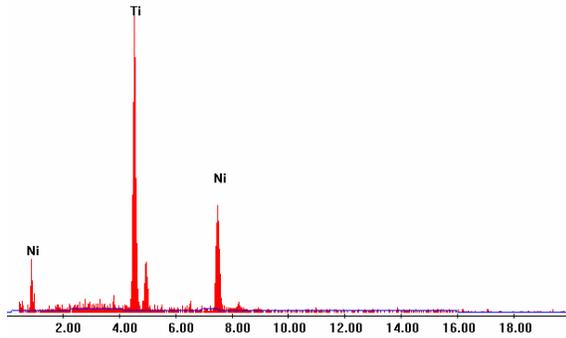


Fig. 1. EDX Spectrum of the as-solidified Ni-Ti alloy.

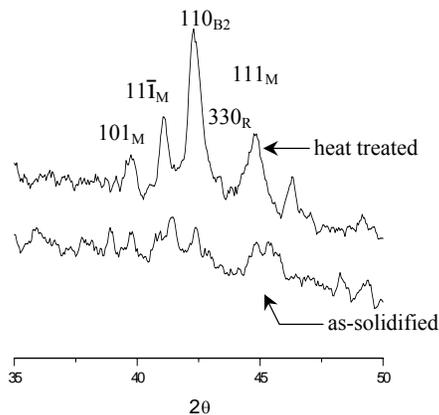


Fig. 2. X-ray spectra recorded at RT for the as-solidified and heat treated specimens.

The DSC data of the Ni-Ti sample is shown in Fig. 3. One large peak is observed on heating starting at 280.5 K, while on cooling two peaks are separated on the DSC spectra. One of the peaks on cooling starts at 317.91 K and develops in the same temperature range as the one shown on heating. The second peak recorded on cooling is located at lower temperature (starts at 272.41 K) and does not have a correspondent on the heating curve. Both peaks observed on cooling are of lower amplitude compared to the peak recorded on heating.

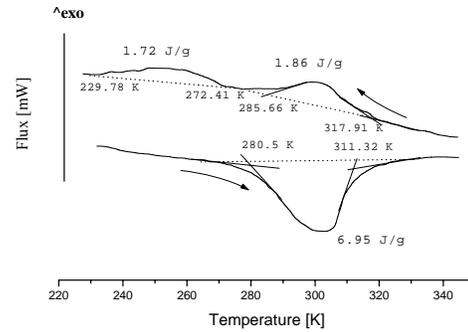


Fig. 3. DSC data of the Ni-Ti rapidly solidified bulk shape memory alloys.

Similar transitions have also been observed on the internal friction and modulus defect data, plotted in Fig. 4 a and b.

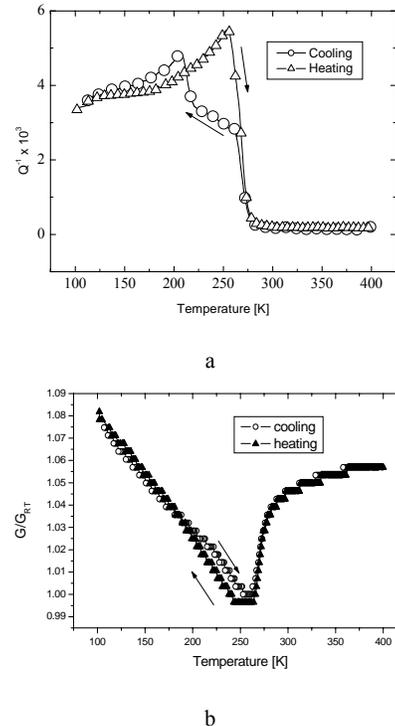


Fig. 4. Temperature dependence of internal friction (a) and shear modulus (b) of a Ni-Ti rapidly solidified bulk alloy after (1 K/min heating rate; 0.1 Hz frequency, around 2×10^{-5} amplitude).

Again, two peaks can be identified on the internal friction curves on cooling and only one on heating, suggesting similar transitions in the alloys studied by DSC and mechanical spectroscopy. On cooling, the first sharp increase in the internal friction around 300 K is continued by less steep slope and then – around 225 K by another sharp increase of lower amplitude compared to the first one. On heating, only one transition can be observed, similar with the DSC curve.

The internal friction measurements results obtained on bulk polycrystalline samples, annealed in argon at $T_{\text{ann}} = 630$ °C/1 h followed by water quenching are shown in fig.5. The temperature dependence of the internal friction of the bulk alloys, recorded as a function of temperature for several oscillation frequencies (0.1; 0.5; 1; 5 Hz).

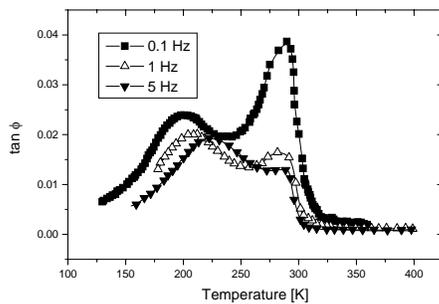


Fig. 5. Internal friction ($\tan\phi$) vs temperature spectra for rapid solidified bulk alloys, after annealing, recorded using various oscillation frequencies.

Two main peaks can be observed. A large one around 300K, associated with a sharp change in the internal friction, linking the very low region to the one with higher values. A second peak is less developed in height, but expanded over a larger temperature range is observed around 200K. This peak shifts toward higher temperatures as the oscillation frequency is increased.

4. Discussion

Mechanical spectroscopy is an effective tool to assess the phase transformation in shape memory alloys. Martensite – the low temperature phase - is usually softer and show higher damping properties compared to austenite – the high temperature phase, which is harder and associated to very low damping characteristics. This is true not only for bulk alloys, but also for thin films, including those attached to substrates, and the phase transition during crystallization of amorphous films shows gradual increase in damping as a function of the fraction of crystallized part [2].

It has been shown that the internal friction can provide information concerning the effect of the microscopic hysteresis during the transformation, and the study of the internal friction spectra peaks can provide information concerning the mechanisms of the macroscopic hysteresis [12]. On the other hand, the oscillation frequency vs. temperature data is effectively related to the behavior of the shear modulus G (f^2 proportional to G).

Rapid solidified alloys are known to have the structure influenced by various parameters, among which the cooling rate is the most important. Even melt-spun ribbons and thin films show inhomogeneous structures over the thickness. It has been shown that significant structural differences exist between the structure observed on the ribbon surface that is in contact with the wheel compared to the “free surface” [13]. Thin film structure is also influenced by the substrate’s properties [14].

Rapid solidified bulk alloys are also influenced by the cooling rate, which tends to be higher in the surfaces in contact with the mold, compared to the solidification areas located toward the center of a solidified rod. This is known in cast samples, however, for low diameter rods, the cooling rate of the external surface is less influenced by the mass of the alloy.

The as-solidified samples have shown a low absolute damping (in the range of 2×10^{-3}) and the phase transition detected by DSC only reveals phase transitions with low amplitude. There is however no doubt that a phase transition occurs, as proven by both internal friction data (low damping at high temperature, damping increase in the phase transition range and higher damping in the low temperature range) and modulus defect (slopes associated to the phase transition) as well as DSC. The low amplitude phenomena observed in the internal friction and DSC spectra suggest that only a fraction of the sample transforms, while the rest does not. If we consider the fact that the outer surface solidified with a higher cooling rate due to the contact with the cooled parts of the mold it is reasonable to consider that the phase transition occurred in a layer with the thickness in which the cooling rate was enough to induce the martensitic transformation. Since the cooling rate was high it allowed a layer with martensitic transformation comparable in dimensions to the inner volume fraction of the sample where the transformation did not occur, thus leading to a discernable effect on the internal friction.

The hypothesis is further confirmed for the samples that have been subject to a volume heat treatment. The internal friction increased by a factor of 10, and typical features are observed, such as the ones related to the intrinsic damping component (Q^{-1}_{int}), the phase transition (Q^{-1}_{PT}) and the (Q^{-1}_{TR}) [15]. They are associated with changes in both the internal friction and modulus defect occurring around 300 K. On the other hand, the 200 K peak is not associated with any other discontinuity on other physical characteristics, therefore it is considered not effectively related to a phase change and is considered a relaxation peak.

A relaxation peak is known to appear around 200K and has been previously reported in Ni-Ti bulk alloys. It has been related to the interaction of dislocations and point defects [16] and is independent of the martensitic and pre-martensitic transformations [17]. The analysis of the relaxation peak, depicted in Fig. 4 shows an activation enthalpy of about 0.64 eV, which is in the same range as the one reported before (0.53 eV [9] and 0.56 eV [18]). Shaposhnikov et al. [14] further concluded that such a relaxation peak argues well for a dislocation – point defect interaction, but is not related to a Granato-Lücke-type dislocation breakaway from point defects model.

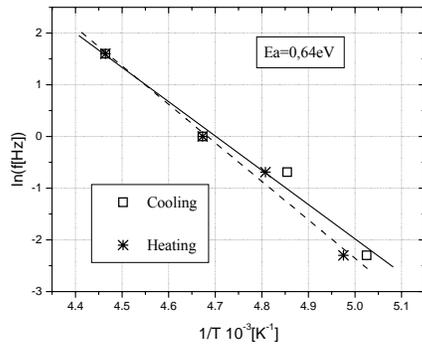


Fig. 4. Arrhenius plot for the relaxation peak of the internal friction.

By contrast to the heat treated sample, the one as-rapidly solidified appears to show two transitions on cooling on the internal friction spectra, confirmed on both the DSC and modulus dependencies. Multiple phase transitions are not uncommon for shape memory alloys. Ni-rich shape memory alloys in particular show and additional rhomboedrical (R-phase transition) in addition to the austenite (B2) – martensite (B19') transition. Since the type of transition disappeared after heat treatment it is considered that during annealing the sample homogeneity is increased, which is not the case for the rapid solidified one. In fact, a Ni-rich over-stoichiometric composition is susceptible to lead to a multiple phase transition sequence and it is not uncommon that multiple transitions reflected in corresponding peaks on cooling are replaced with single peaks including more transitions on heating [19].

5. Conclusions

In summary, it can be concluded that rapid solidified bulk alloys are influenced by the cooling rate that decreases from the outer surface (in contact with the mold) to the center of the sample.

It is suggested that if a martensitic transformation occurs in the outer layer, it can have a small influence on the internal friction with an amount proportional to the fraction of the phase change volume reported to the entire volume.

The heat treatment applied to the rapid solidified specimen lead to a volume transformation, similar to the one observed in similar samples prepared via the classical path.

Such a rapid solidification technique can be considered for manufacturing natural composites with a non-transforming core surrounded by a transforming layer. The ration between the components could be adjusted in technological limits by relating the total diameter with the cooling rate. The later would be responsible for inducing the martensitic phase transformation in the outer layer.

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♦ In memoriam I. Mihalca
