Abstract

As the size of grains in polycrystalline materials is reduced to nanoscale, the properties of these materials will be dominated by grain boundaries and surface effects. Nanostructured NiTi Shape memory alloys (SMAs) were fabricated by cold-rolling melt-spun near equatomic NiTi. SMAs represent a unique class of materials that undergo a reversible phase transformation allowing these materials to display dramatic stress-induced and temperature-induced deformation that is recoverable. Changes in shape memory effect and pseudoelastic behavior are expected as the grain size is reduced to the nanoscale regime. Mechanical behaviors of both as-received and cold-rolled melt-spun ribbons were investigated. Shape memory behavior was observed in the melt-spun ribbons, and pseudoelastic behavior was observed after the melt-spun ribbons were subjected to cold rolling.

1. Introduction

Nanostructured materials (NsM) have attracted considerable attention in recent years [1] because new materials behavior is expected as surface effects and grain boundaries play a more important role. A NsM may be categorized according to its morphology: layer-shaped crystallites, rod-shaped crystallines (with layer thickness or rod diameters in the order of nm), and equiaxed nm-sized crystallites. Generally, a NsM consists structurally of the following two components: the crystallites and the boundary regions. In the boundary regions, the average atomic density and the coordination between nearest neighbor atoms deviate from the ones in the crystallites. The presence of these two structural components (crystals and boundaries), with comparable volume fractions and having typical crystal size of a few nanometers, plays a crucial role in determining the properties of a NsM. Thus, the properties will depend on the size of the crystalline regions and on the atomic structure of the solid characterized by the average atomic density and the coordination between nearest neighbors.

This research explores the fabrication of a NsM with shape memory behavior. Shape memory alloys (SMAs) represent a unique class of materials that undergo a reversible phase transformation allowing these materials to display dramatic stress-induced and temperature-induced deformation that is recoverable. These materials are still being explored as functional materials in a variety of aerospace, biomechanical, and microelectronics industries [2-4]. Among the known shape memory alloys, NiTi is the most commonly used because of its excellent mechanical properties, corrosion resistance and biocompatibility.

A variety of methods have been attempted in order to create finer-grained shape memory alloys. These include ultrarapid melt quenching, ball milling followed by powder metallurgy, inclusion of microalloying elements, recrystallization of thin films deposited by pulsed laser deposition, melt spinning, and plastic deformation followed by recrystallization. The majority of these studies have been successful at producing micron scale grain sizes, however virtually all of the nanoscale grain size NiTi reported in the literature has been in the form of thin films prepared by physical vapor deposition. Unfortunately work on thin films has shown the correlation between shape memory behavior and grain size is confounded with the grain-size-to-sample thickness ratio [5]. Only a few reports concerning synthesis and characterization of bulk shape memory alloys having nanoscale grain size are available in the literature [6-7]. Xu and Thandhani [6] used ball milling to produce 44-58 nm grain size NiTi and showed that this decrease in grain size increased the temperature at which Martensitic transformation starts (Ms) as compared to micron scale powder. They proposed that this was a result of increased internal stresses arising from greater anisotropy in the material, rather than and increase in the local elastic energy between Martensites and grain boundaries.

The research reported here explores new methods for producing nanostructured NiTi shape memory alloy material in bulk form and investigates the influence of the nanostructured nature of the material on its mechanical behavior. We have undertaken mechanical fabrication approaches to creating nanostructured shape memory alloys, including melt-spinning and cold rolling techniques.

2. Experimental Procedures

2.1 Melt-spinning

Rapid solidification technique (RST) is an important method for producing metals with improved mechanical and/or physical properties. This technique employs a very high cooling rate (up to 10^6 °C/s). In general, such a high cooling rate has the advantage of refinement of grain sizes [8]. One
Near equiatomic NiTi ingots were prepared with element Ni and Ti by arc melting. Then they were cut into small pieces, each of which has a weight in the range of 10 to 30 grams. One piece was placed in a quartz crucible with Y2O3 coating. The orifice of the crucible has a diameter of 2mm. The melt spinning chamber is pumped down to a pressure <10^{-3} torr prior to melting the ingot. The NiTi alloy was then melted with the RF heating. This process can be observed through the window of the melt-spinning chamber. When the NiTi alloy was observed to be fully molten, the copper wheel was rotated with a speed between 40 and 55m/s. Argon gas was then forced into the crucible to control the flow rate of the molten NiTi alloy through the orifice of the crucible. Droplets of molten NiTi fall down on the cold wheel and solidify with a very high cooling rate (up to 106/s). With this high cooling rate, it is possible to achieve a bulk NiTi ribbon with very fine grain structure or amorphous material.

### 2.2 Cold-rolling

In the cold rolling operation, layers of melt-spinning ribbons were stacked together and subject to thickness reduction of one half of the original layer thickness. In practice, the cold-rolling process was aided by stacking layers of ribbons between two pieces of 0.015'' thick 1010 steel. The as-rolled array was then folded, placed between the steel sheets, and the above procedure was repeated. Each rolling and folding cycle is termed as one F&R pass, as shown in Figure 1.

![Figure 1 Schematic of the cold rolling procedure.](image)

### 2.3 Mechanical testing

Tensile tests of as-received melt-spinning ribbons were carried out on an Instron 5548. This machine is equipped with a temperature chamber that can be used in the range of 20 to 80°C and a 10N load cell. Cold-rolled melt-spinning ribbons samples were tested on an Instron 5566. Testing on this machine was performed with heated grips that maintain a constant sample temperature through heat conduction.

The test samples of as-received melt-spinning ribbons were cut into a rectangle shape with length and width ratio larger than 10. Hard epoxy (Titanium-filled epoxy adhesive, ARALDITE®) was applied to the end of the rectangle samples to promote gripping and avoid slipping between the end of samples and grip, therefore reducing the chances of artifacts in the mechanical testing. The cold rolled melt-spinning ribbons samples were cut in the shape of the rectangle and their edges were ground parallel with the 400-grit SiC grinding paper prior to mechanical testing.

### 2.4 Material characterization

Several characterization techniques have been employed to identify the composition, grain size, and mechanical behavior of the melt-spinning NiTi ribbons produced. The nominal composition of melt-spun ribbons was determined to be 51.2 at% Ni by the Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) technique.

Low voltage high resolution scanning electron microscopy (SEM) was employed to investigate the microstructures of the as-received and cold-rolled NiTi melt-spinning ribbons. The average grain size of as-received melt-spinning ribbons was determined by scanning electron microscopy to be 5 μm. After cold rolling the average grain size was reduced to 280 nm.

### 3. Results

#### 3.1 Mechanical behavior of as-received melt-spinning ribbons

The as-received melt spun ribbon displayed the shape memory effect, which was easily observed by bending a ribbon and watching it return to its original shape upon heating. This was quantified by Differential Scanning Calorimetry. The temperature at which the material completely transformed to Austenite upon heating (A_f) was found to be 95°C and the temperature at which the material started to transform to Martensite upon cooling (M_s) was 56°C.

The mechanical behavior of as-received melt-spinning ribbons was investigated by tensile testing. All the mechanical tests were conducted in the environmental chamber with an aqueous bath at a temperature range of 303K to 358K. Samples for mechanical tests were carefully selected to minimize flaws and obtain a reasonable width to length ratio, however the melt-spinning ribbon is inherently nonuniform.

Figure 2 summarizes results for a melt-spun ribbon sample tested at various temperatures. There were several interesting features in the tensile behavior of as-received melt-spinning ribbon. First, almost all curves show nonlinear loading before the elastic region. This behavior was previously thought to be due to the soft epoxy used in the gripping region of the sample. However, a harder epoxy didn’t eliminate this region completely in later trials with additional samples. Saburi [9] showed that slip can occur after the re-arrangement of the martensite phase if the testing temperature is below the A_s, which is the case in our study. Therefore a possible explanation of nonlinear region is due to the re-arrangement of residual martensite produced in the formation of melt-spinning ribbons with a very high cooling rate. However, it may be also due to no uniformity of the ribbons or engagement of the grip teeth into the sample.

Secondly, the stress level was quite low and this was thought to be due to an overestimate in the width and thickness of the samples. Finally, signs of a distinct plateau may be identified at high temperature when the elastic behavior changes to constant stress as the strain increase.
3.2 Mechanical behavior of heat treated melt-spun ribbons

The mechanical behavior of melt-spun ribbons was further studied after heat treatment. The as-received melt-spun ribbons were heat treated at different temperatures for one hour and quenched in water. Following heat treatment, tensile tests were conducted in air at room temperature.

The mechanical properties of four heat-treated samples are compared to the as-received melt-spun ribbons in Figure 3. Little change in the mechanical behavior was observed with the exception of the peak stress level attained. This may be a result of inaccuracy in the cross section area measurement. Some indication of R-phase transformation can be observed. Following the mechanical tests shown in Figure 3, the samples were observed to be slightly bowed after the crosshead was returned to the zero position. This indicated incomplete recovery of the induced deformation. The sample heat-treated at 350°C was then heated to 80°C with a water bath, and shape memory recovery was observed.

3.3 Mechanical behavior or cold-rolled melt-spun ribbons

A collection of melt-spun ribbons weighing approximately 0.5 gm was subjected to repeated cold rolling passes (10 R&F). The mechanical behavior of the cold-rolled melt-spun ribbon sample was then studied at temperatures ranging from 25°C to 90°C, as showed in the Figure 4.

In contrast to the observations for the melt-spun ribbon, pseudoelastic plateaus were observed after cold rolling. The critical stress of the plateaus increases with increasing test temperature at a rate of approximately 3.6 MPa/°C. This is in the range of values reported for NiTi [10]. The elastic modulus at unloading is approximately 18 GPa, which is lower than expected for NiTi. Some plastic strain is induced with each cycle however, as indicated by the permanent strain shown after unloading in Figure 4. This strain is unrecoverable even upon further heating. It is also observed that the ability for strain recovery decreases with increasing temperature. Another important feature observed in the behavior of cold rolled melt-spun ribbon is the small hysteresis stress. This difference between the loading and unloading plateaus for strain above 2% are minimal. Samples loaded beyond 5% strain tended to fail before the limit of the transformation was attained. This is hypothesized to be a consequence of flaws introduced in the process of cold rolling.

4. Discussion

There are several aspects of material fabrication that distinguishes cold rolled melt-spun ribbon from commercially produced NiTi alloy. It is expected that the nanoscale grain size will influence shape memory properties and it is also known that mechanical work history plays an important role in the pseudoelastic behavior displayed by NiTi.

There are two effects present in this work which have been reported to have an influence on the Ms temperature in NiTi. Cold work has been reported to decrease Ms [11], while grain refinement has been reported to increase Ms [6]. It is unclear at this time which one has a more pronounced influence however.

Cold work has also been reported to have a substantial impact on the critical stress for slip in NiTi [11]. This is clearly demonstrated by the results presented above. Both the melt spun ribbon samples and the cold rolled melt spun ribbon samples display the shape memory effect, but pseudoelastic behavior is only observed after a significant amount of cold
work is imparted to the material. This effect is depicted graphically in the stress vs. temperature diagram of Figure 5. The pseudoelastic region in the diagram can only be obtained after the critical stress for slip is increased above the critical stress to induce martensite at temperatures greater than the $A_s$ temperature.

![Figure 5](image)

**Figure 5** Stress-temperature diagram for shape memory and pseudoelastic effects in NiTi.

Cold work, and possibly the grain refinement produced by the melt spinning and cold rolling processes, also have a substantial impact on the magnitude of the hysteresis stress. If the area under the loading curve in the stress/strain diagram (Figure 4) is defined as $E_1$, and the area under the unloading curve as $E_2$, then $E_1 - E_2$ represents the energy density per unit volume that is dissipated during loading, while $E_2$ is the energy density per unit volume that is stored and available to release upon unloading. These parameters can be used to describe the energy storage capacity of the pseudoelastic behavior [11]. A parameter $\eta = E_2 / E_1$ is introduced to describe the efficiency of the energy storage.

Lin and Wu [11] showed that both $E_2$ and $\eta$ increase with increased cold rolling, which is also observed in cold-rolled melt-spun ribbon investigated. Additionally, it was determined that cold rolling does not have an effect on the reversibility of the transformation, which is supported by our findings. For the results reported above, $\eta$ ranges from as high as 85% for the test conducted at 25°C to 70% for the test conducted at 90°C. The reduction in efficiency with increasing temperature is caused by slip. These results are lower than that achieved by Lin and Wu's [11] study, but the efficiency would be enhanced it plastic deformation could be avoided.

5. Conclusion

The nanostructured shape memory alloys were fabricated by cold rolling of melt-spun NiTi ribbons. The mechanical behavior of the as-received and cold rolled melt-spun ribbons were investigated by tensile testing. Improved pseudoelastic behavior was found and small hysteresis effects were observed in the cold rolled melt-spun ribbon. These changes in behavior were confirmed to be induced by the cold rolling treatment.

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References