Chemical machined thin foils of TiNi shape memory alloy

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Abstract

$Ti_{50}Ni_{50}$ thin foils up to $10\,\mu m$ thickness are successfully fabricated from $100\,\mu m$ thickness thin plates using chemical machining. Ultrasonic agitation is applied to enhance the chemical etching process with mixed solutions of $HF/HNO_3/H_2O$. The higher the HF/HNO_3 volume ratio in the solution, the higher the etching rate and the smoother the surface will be. Thin foils can also be fabricated with the electropolishing process but with a much slower etching rate. Foil thickness by these processes can only be approximately $10\,\mu m$ due to the side-etching effect. The martensitic transformation peaks of thin foils shown on the DSC curve are broader for a thinner sample due to the effect of thermal resistance in the DSC sample pans. The enthalpy of transformation also decreases while the foil thickness is reduced due to the effect of the foil surface energy and the energy of plastic deformation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: TiNi shape memory alloy; Thin foil; Chemical etching; Electropolishing; Thickness effect

1. Introduction

In practical applications, shape memory alloys (SMAs) are usually first mechanically processed into wires or plates and then further fabricated to springs or other shapes [1]. The performance of the shape memory effect pertaining to the SMAs is closely related to the heating/cooling rate of fabricated shapes in the temperature range of A_f–M_f. Here, M_f is the finished temperature of the forward martensitic transformation, and A_f is that of the reverse martensitic transformation. Obviously, the fabricated shapes of SMAs having a larger ratio of surface area/cross-section area can achieve a higher heating/cooling rate and shorten the response time of their shape memory effect. Therefore, from the viewpoint of the response time, how to reduce the cross-section area of fabricated shapes becomes important in the practical applications of SMAs. For example, the thin foils of SMAs can be used as the microactuator because the microactuator of SMAs has a high work output and power density [2–4]. The microactuator device can be fabricated out by the assembly of individual SMA parts [2,5]. However, the thickness of these parts is limited by the conventional mechanical fabrication processes. According to our experience, the conventional cold-rolling/recrystallization process can reduce the thickness of TiNi alloy foil to approximately $30\,\mu m$ [6]. In this study, thin foils of TiNi alloy, however, can

be thinned to around $10\,\mu m$ using chemical machining processes. It is well known that the wet-chemical etching solution mixture of hydrofluoric and nitric acid can be used to electrochemically thin the TiNi foil. However, the details of this thinning process have not yet been reported [5]. In the present paper, the details of the chemical machining of the TiNi alloy is described and the martensitic transformation behavior of acquired thin foils is also discussed.

2. Experimental procedure

The TiNi equiatomic alloy was prepared from the raw materials of titanium (purity 99.7 wt.%) and nickel (purity 99.97 wt.%) using the vacuum arc remelting (VAR) technique. The weight loss of the VAR process is less than the order of 0.01%, thus the composition deviation from TiNi can be neglected. The ingot was then hot rolled at 850°C to 1 mm in thickness and wire-cut into pieces of 2 mm × 30 mm. The oxide on the surface of samples was removed by chemical etching. Then, the specimen was further thinned to 0.1 mm thickness using the alternate processes of cold rolling and recrystallization annealing. The reduction rate was 30% for each cold rolling process. The inter-annealing (recrystallization annealing) between each cold rolling process was conducted in an evacuated quartz capsule at 700°C for 30 min. The grain size of thin foils after the alternate processes of cold-rolling and anneal-
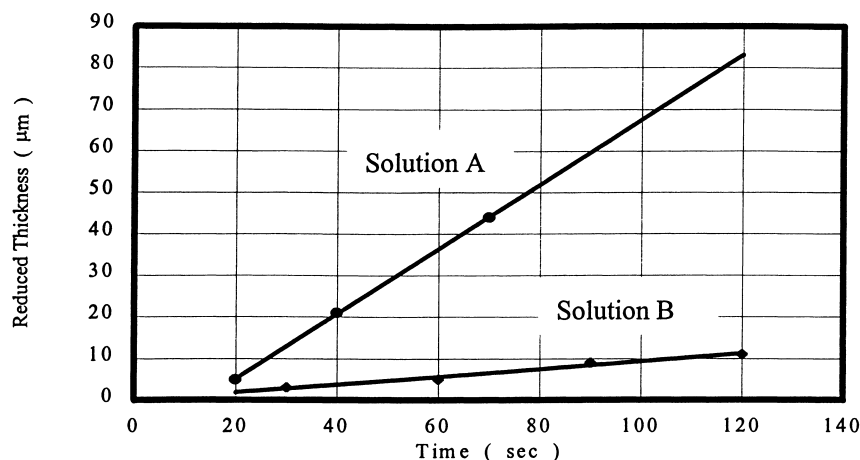
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Fig. 1. Etching rates of ultrasonic agitated chemical etching of Solution A and Solution B at room temperatures.

ing is about 10 μm. The final thickness of thin foils used in this study was chosen between 100 and 10 μm by the process of chemical machining, described as follows.

The chemical thinning process of the TiNi alloy is tested using two methods: the chemical etching with the assistance of ultrasonic agitation, and the electropolishing. There are two chemical solutions, Solutions A and B, for chemical etching. Both of them consist of the solutions of HF, HNO_3 and H_2O with different volume ratios, in which Solution A is HF : HNO_3 : H_2O = 1 : 4 : 5, and Solution B is 1 : 5 : 20. For the electropolishing process, the electrolyte is composed of H_2SO_4 and CH_3OH with 1 : 4 in volume ratio. The applied voltage is 5 V and the operation temperature is 20°C.

The shape memory effect of acquired thin foils is measured with the bending test [7] and their martensitic transformation temperatures are determined by the Differential Scanning Calorimetry (DSC) with a heating/cooling rate of 10°C min^{-1}. DSC measurement was conducted using a Dupont 2000 thermal analyzer equipped with a quantitative scanning system 910 DSC cell for controlling the heating and cooling rates in pure nitrogen gas.

3. Results and discussion

To avoid the effects of concentration polarization, ultrasonic agitation is applied to enhance the etching process. Fig. 1 shows the etching rate of ultrasonic agitated etching. Solution A has a higher concentration of HF/HNO_3 than solution B and thus the etching rate of solution A, 0.5 μm s^{-1}, is higher than that, 0.1 μm s^{-1} of solution B. Although the lower etching rate is preferred for thickness control, the surface of the thin foils etched by Solution A is much brighter than that etched by Solution B. The brightness contrast is so obvious that they can be easily distinguished visually. The plate thickness can be machined by ultrasonic agitated chemical etching to as thin as 10 μm or

so, which is difficult to achieve by a conventional rolling process [6].

Electropolishing can also be applied to chemically machine the TiNi thin plate. The advantage of electropolishing is that the thinning rate can be controlled by the applied voltage. Fig. 2 shows the thickness reduction rate of electropolishing under the condition of 5 V at 20°C. The polishing rate is about 2.5 μm min^{-1} (0.042 μm s^{-1}) which is much slower than that in the case of Fig. 1. The thin foil fabricated in this way is even brighter than that etched by Solution A.

All thin foils fabricated in this study have a shape memory effect in the bending test. The recovery percentages of foils with different thickness are shown in Fig. 3. The foils with thicknesses of 100 and 60 μm are all in excellent shape achieving 100% recovery. However, those with thicknesses of 40, 30 and 20 μm achieve only about 80% recovery. This feature may be due to the fact that, before or during the bending test, the folding induced plastic strain caused by manual operation is more significant in thinner foils.

In order to understand the effect of specimen thickness on the martensitic transformation of the TiNi alloy, thin foils with thicknesses of 100, 50, 20 and 10 μm are tested by DSC
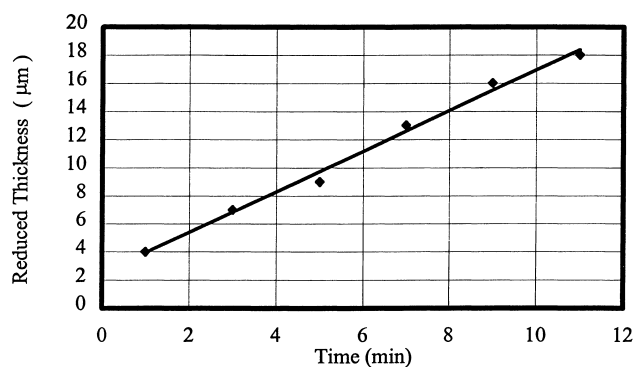

Fig. 2. Thickness reduction rate vs. time in the electropolishing process under the condition of 5 V at 20°C.
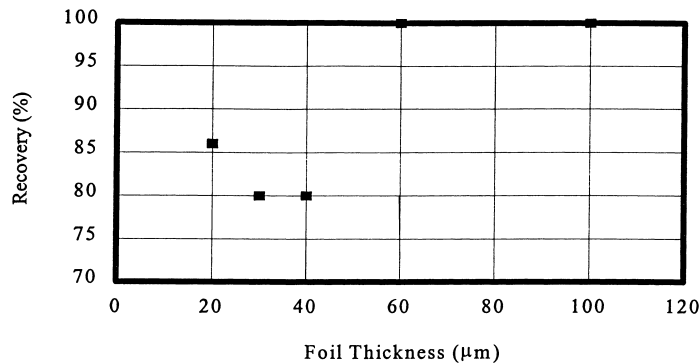
Fig. 3. Recovery of 100, 60, 40, 30 and 20 μm thickness thin foils. These foils are etched by Solution A with ultrasonic agitation.

and the results are shown in Fig. 4. Fig. 4 indicates that the temperatures of transformation peaks, M^* and A^*, do not change much for various foil thicknesses. However, the transformation peak broadens and the peak height decreases as the specimen thickness decreases. A similar situation also occurs in the transformation enthalpy, ΔH. Kuninori et al. [8] observed that the area of TiNi alloy thinner than approximately 100 nm in the thin foil of the TEM specimen did not achieve martensitic transformation even when the thin foil was cooled to 98 K. This feature indicates that the surface energy of thin foil can affect the martensitic transformation. Therefore, we suggest that the significant drop of the ΔH value of the foil of 10 μm thickness shown in Fig. 4 partly comes from the effect of the surface energy. The broadening of the transformation peak is related to the effect of the sample size (thickness × length × width) on the traces of the thermal analysis. It is well known that the

heavier sample will enhance the sensitivity of the thermal analysis more greatly [9]. It is difficult for the DSC apparatus to correctly detect the difference of heat flow when the sample is too small. The suggested minimum weight of the DSC sample used in this study is about 5 mg. In order to obtain the sample weight higher than the minimum value (weight 10~20 mg was used in this study), quite a number of thin foils pieces need to be folded into the same DSC pan. The thinner the foil is, the more folding of the foil is needed to put together to get the desired weight. This causes the DSC tracing be different from that of the bulk specimen. The face-to-face contact of folded foils in the DSC pan will induce thermal contact resistance [10]. This thermal contact resistance will delay the heat flow among the folded foils during the DSC test and cause the transformation temperature range become wider. Therefore, the thinner the foil is, the broader the transformation peak will be. These results are explicitly shown in Fig. 4. In addition, as shown in Fig. 3, if the thickness of the thin foil is below 40 μm, the recovery of the SMA is affected by the bending induced plastic deformation. We believe that the folded foils have plastic deformation energy caused by folding and thus decrease the measured ΔH value during the DSC test.

The thickness of TiNi thin foils fabricated by this study is limited by the edge etching attack effect as shown in Fig. 5. The specimen edges are found to be etched more rapidly than thickness reduction when the foil is as thin as 10 μm, even though the thickness reduction rate is as slow as 2.5 μm min^{-1} in the electropolishing process. Fig. 5 shows the zig-zags profile edge of the 10 μm thin foil. Therefore,

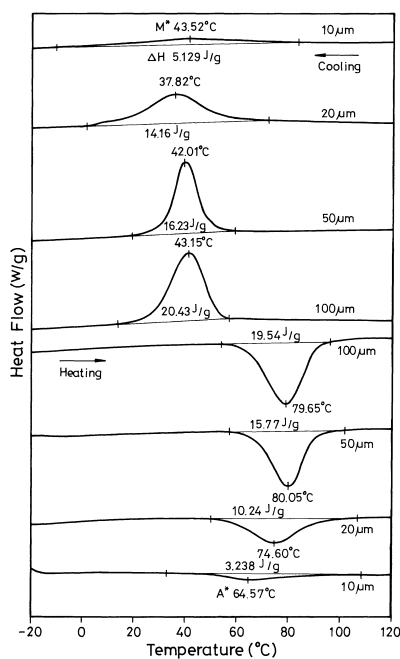Fig. 4. DSC transformation peaks of 100, 50, 20 and 10 μm thickness thin foils. These foils are etched by Solution A with ultrasonic agitation.
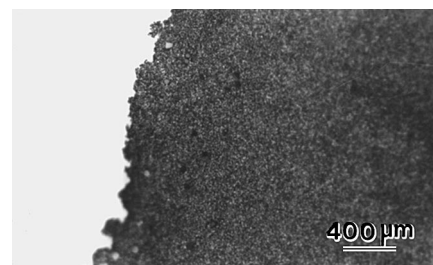

Fig. 5. The zig-zags appear on the edge of a 10 μm thickness thin foil.

the effect of the edge etching attack shown in Fig. 5 limits the further thinning of the TiNi alloy foil by chemical machining.

4. Conclusions

Chemical solution of $HF : HNO_3 : H_2O = 1 : 4 : 5$ in volume ratio with ultrasonic agitation can be applied for the fabrication of TiNi thin foils. The surface of thin foils fabricated by this solution is very bright and the etching rate can reach $0.5\,\mu m\,s^{-1}$. The electropolishing process with electrolyte of $H_2SO_4 : CH_3OH = 1 : 4$ in volume ratio can also be applied to fabricate TiNi thin foils with an even more brighter surface. When the applied voltage is 5 V at room temperature, the etching rate of electropolishing is only about $0.042\,\mu m\,s^{-1}$. The thickness of thin foils fabricated in this study is limited by the edge etching attack effect and the thinnest thickness obtained is approximately $10\,\mu m$.

All TiNi thin foils fabricated in this study exhibit shape memory effect. The proceeding of martensitic transformation is obviously affected by the surface energy and the folded foils if the foil thickness is approaching $10\,\mu m$. This feature appears on the decrease of the ΔH value and the broadening of transformation peaks in the DSC test.

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