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Gas nitriding of an equiatomic TiNi shape memory alloy II. Hardness, wear and shape memory ability

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Abstract

$Ti_{50}Ni_{50}$ shape memory alloy was gas nitrided to modify the surface conditions. The surface hardness, wear characteristic, transformation temperature and shape memory ability of gas-nitrided $Ti_{50}Ni_{50}$ alloy were investigated. Experimental results indicate that the surface hardness is increased owing to the formation of TiN and $Ti_2NiH_{0.5}$ compounds. The $Ti_{50}Ni_{50}$ specimens nitrided at 700–900°C show improved wear characteristics, but those nitrided at 600°C cannot be effectively improved owing to surface cracks appearing in nitrided layers. Martensitic transformation temperatures are depressed slightly owing to the constraining effect originating from the nitrided layers, and/or the penetration of N and H atoms into the $Ti_{50}Ni_{50}$ matrix. The shape recovery is also slightly reduced because the nitrided layers do not exhibit a shape memory effect, and the constraining effect will also depress the shape recovery of the $Ti_{50}Ni_{50}$ matrix.

Keywords: Gas nitriding; TiNi shape memory alloy; Wear and shape memory ability

1. Introduction

Among the many shape memory alloys, TiNi alloys are the most popular because they possess superior properties of shape memory effect (SME) [1] and pseudoelasticity [2,3]. Most of their industrial applications may not involve any problems of wear. Nevertheless, for applications in orthopedic surgery, medical guide-wires and artificial bone-joints, wear resistance could be a very important property. Several investigations [4–7] have been performed on the wear characteristics of TiNi alloys. These studies concluded that the B2 phase (austensite parent phase) of TiNi alloys can exhibit good wear resistance as a result of its rapid work hardening and pseudoelastic properties. However, the wear resistance of the B19′ martensite phase of TiNi alloys is still too low and requires improvement. It is well known that nitriding techniques are commonly used to improve the fatigue and wear resistance of metals and alloys [8–10]. Moine et al. [11] have also tried to increase the wear resistance of TiNi alloys by N^+ implantation. In Part I of this study, the gas nitriding technique has been successfully used to form nitrided layers on the equiatomic TiNi alloy. The nitriding parameters and microstructural characterization of these nitrided layers have been discussed. In the present study, the surface hardness and wear characteristics of the nitrided layers will be investigated. Meanwhile, the experimental results of transformation temperatures and shape memory ability of the gas-nitrided $Ti_{50}Ni_{50}$ alloy are also reported.

2. Experimental procedures

The conventional tungsten arc-melting technique was employed to prepare the equiatomic TiNi alloy. Titanium (purity 99.7%) and nickel (purity 99.98%), totalling about 100 g in weight, were melted and remelted at least six times in an argon atmosphere. The as-melted buttons were homogenized at 1000°C in a 7×10^{-6} Torr vacuum furnace for 72 h, and then hot rolled into plates of thickness 1.5 mm. The details of the specimen preparation and the gas nitriding process have been described in Part I of this study [12]. The surface hardness was measured with a micro-Vickers tester with a load of 100 gf for 15 s. For each specimen,

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the average hardness value was calculated from at least five test readings. The wear tests were performed using a TE-53 type unidirectional sliding wear machine made by Plint and Partners Co. in England. JIS SKS-95 steel, with hardness Hv = 700, was used as the wear-resistant material. The tests were conducted at a constant wear load of 10 N and a sliding speed of 62.8 cm s^{-1}. The friction coefficient was automatically calculated during the sliding wear process using a digital computer. Differential scanning calorimetry (DSC) measurement was conducted to measure the martensitic transformation temperatures. A DuPont 2000 thermal analyzer equipped with a quantitative scanning system 910 DSC cell and a cooling accessory LNCA II were used. Measurements were carried out at a controlled cooling/heating rate of 10°C min^{-1}. Heats of transformation, ΔH, were automatically calculated from the areas under DSC peaks by means of an equipment software package. The SME was examined using a bending test [13]. The surface bending strain, ϵ_s, was 6% and the shape recovery, R_{SME}, was measured after a complete reverse martensitic transformation.

3. Results and discussion

3.1. Effects of gas nitriding on the surface hardness and wear characteristics of the $Ti_{50}Ni_{50}$ alloy

As discussed in Part I of this study, the $Ti_{50}Ni_{50}$ specimens nitrided at temperatures above 700°C consist of TiN and $Ti_2NiH_{0.5}$ compound layers, and those nitrided at temperatures below 650°C have two distinctive nitrided regions: a random mixture of TiN, $Ti_2NiH_{0.5}$ and Ni-rich phase and a columnar-like structure of mixed TiN and Ni-rich phase. We are interested in understanding the surface hardness and wear characteristics of these nitrided layers. Fig. 1 shows the surface hardness of $Ti_{50}Ni_{50}$ specimens after gas nitriding at various temperatures for 24 h. Because the hardness of TiN and $Ti_2NiH_{0.5}$ compounds is much higher than that of $Ti_{50}Ni_{50}$ martensite (Hv = 272), the surface hardness of gas-nitrided $Ti_{50}Ni_{50}$ specimens is increased, as shown in Fig. 1. However, the maximum surface hardness does not exhibit an expected high value of, say, 600 Hv, as shown in Fig. 1. This phenomenon can be explained as follows. For the $Ti_{50}Ni_{50}$ specimens nitrided at 700–1000°C, the nitrided layers of TiN and $Ti_2NiH_{0.5}$ compounds are quite thin (only a few microns) and hence the indentation of the hardness measurement will reach the soft $Ti_{50}Ni_{50}$ martensite. This feature causes the average hardness of the nitrided surface to be not as high as those of the TiN and $Ti_2NiH_{0.5}$ compounds. The $Ti_{50}Ni_{50}$ specimen nitrided at 800°C shows the lowest hardness increment because it has the thinnest nitrided layer (Fig. 3 of Ref. [12]). For the 600°C nitrided $Ti_{50}Ni_{50}$ specimen, the nitrided layer is thick enough (several tens of microns) and hence the indentation of the hardness measurement cannot reach the soft $Ti_{50}Ni_{50}$ martensite. However, owing to the existence of a great deal of Ni-rich phase in the 600°C nitrided layers, their surface hardness cannot exhibit an expected high value, either.

Fig. 2 shows the friction coefficients of $Ti_{50}Ni_{50}$ specimens after gas nitriding at various temperatures for 24 h. As shown in Fig. 2, the friction coefficients of 700–900°C nitrided $Ti_{50}Ni_{50}$ specimens are lower than that of specimens without gas nitriding. This result is due to the fact that wear interfaces are $TiN/Ti_2NiH_{0.5}$ compound layers and SKS-95 steel, and hence, the friction coefficient maintains a low value because of high surface hardness. This indicates that the wear characteristic of the $Ti_{50}Ni_{50}$ shape memory alloy can be effectively improved by gas nitriding because $TiN/Ti_2NiH_{0.5}$ compound layers contribute greatly to the improvement of wear resistance. However, the wear characteristics of the $Ti_{50}Ni_{50}$ shape memory alloy are hardly improved by gas nitriding at 600°C, because its friction coefficient has nearly the same value as that of a specimen without gas nitriding. This phenomenon can be attributed to the surface cracks appearing in the nitrided layer of the specimen gas nitrided at 600°C

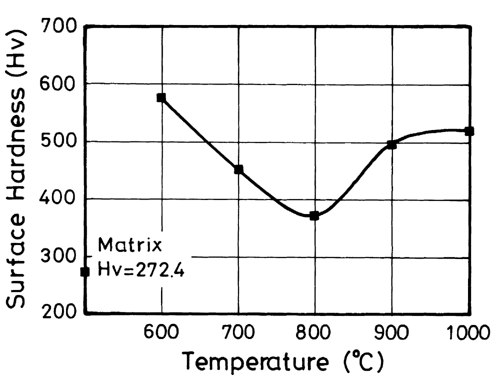

Fig. 1. The surface hardness of $Ti_{50}Ni_{50}$ specimens after gas nitriding at various temperatures for 24 h.

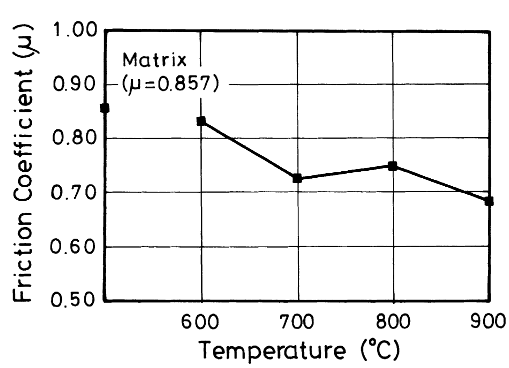

Fig. 2. The friction coefficients of $Ti_{50}Ni_{50}$ specimens after gas nitriding at various temperatures for 24 h.

(Fig. 2(a) of Ref. [12]). These surface cracks will propagate rapidly into the subsurface during the wear process, and then link together to cause fragmentation and pitting on the surface [7]. These pits will increase the friction coefficient and accelerate the wear rate. Hence, the $Ti_{50}Ni_{50}$ specimen gas nitrided at 600°C does not exhibit excellent wear characteristics although it has a high surface hardness.

3.2. Effects of gas nitriding on the martensitic transformation temperatures and shape recovery ability of $Ti_{50}Ni_{50}$ alloy

Fig. 3(a)–(c) shows the DSC curves of $Ti_{50}Ni_{50}$ specimens with and without gas nitriding at 600 and 900°C for 24 h, respectively. Fig. 3(a) represents a typical DSC curve of a stress-free $Ti_{50}Ni_{50}$ specimen in which the exothermic and endothermic peaks are associated with the martensitic transformation of B2↔B19′. The DSC curves for the gas-nitrided specimens, as shown in Fig. 3(b) and (c), exhibit similar martensitic transformation behaviors. However, the martensitic transformation temperatures are depressed slightly to lower temperatures. This phenomenon can be attributed to two factors. Firstly, the constrained stress on the $Ti_{50}Ni_{50}$ matrix originating from the gas-nitrided layers will depress the martensitic transformation. Secondly, the penetration of N and H atoms into the $Ti_{50}Ni_{50}$ matrix as the interstitial atoms during the gas-nitriding process will also potentially depress the transformation temperatures [14]. On carefully examining Fig. 3(b) and (c), one can easily find that the transformation temperatures of specimen nitrided at 600°C are more depressed than those of specimen nitrided at 900°C. This feature indicates that the specimen nitrided at 600°C has more constrained stress and/or more penetrated N and H atoms.

Fig. 4 shows the measured shape recovery, R_{SME}, after a complete reverse martensitic transformation (by heating to 300°C) for the gas-nitrided $Ti_{50}Ni_{50}$ specimens. From Fig. 4, the shape recovery is found to decrease slightly as a result of gas nitriding. This result is reasonable because the nitrided layers do not exhibit the SME and their constraining effect on the $Ti_{50}Ni_{50}$ matrix will also depress the shape recovery of the $Ti_{50}Ni_{50}$ matrix.

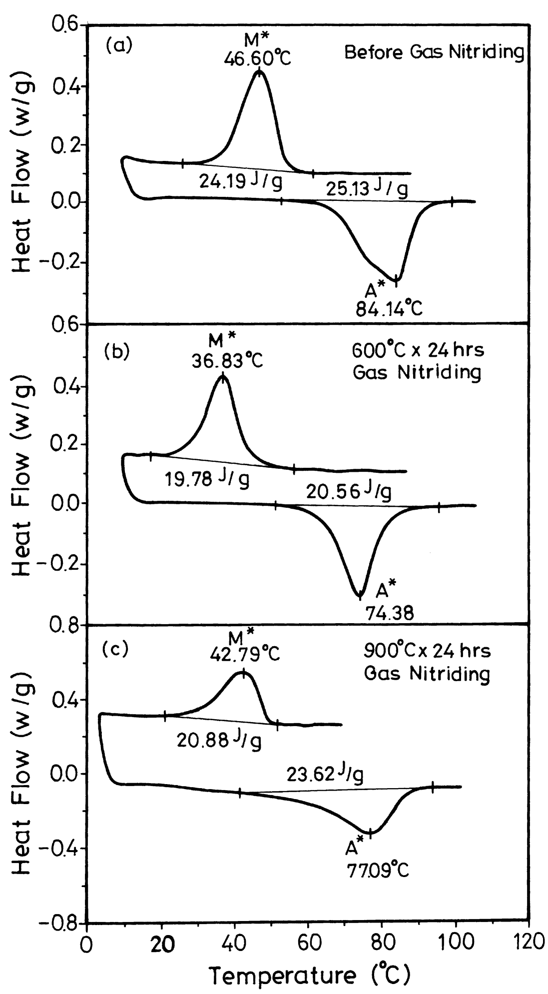

Fig. 3. DSC curves of $Ti_{50}Ni_{50}$ specimens: (a) without gas nitriding; (b), (c) with gas nitriding at 600°C and 900°C, respectively, for 24 h.

4. Conclusions

In this study, the surface hardness, wear characteristics, transformation temperature and SME of gas-nitrided $Ti_{50}Ni_{50}$ alloys were investigated. Experimental results indicate that the surface hardness of a gas-nitrided $Ti_{50}Ni_{50}$ specimen increases as a result of the formation of TiN and $Ti_2NiH_{0.5}$ compounds. The 700–900°C nitrided $Ti_{50}Ni_{50}$ specimens, being hardened by TiN and $Ti_2NiH_{0.5}$ layers, show improved wear characteristics. However, the wear resistance of the $Ti_{50}Ni_{50}$ specimen cannot be effectively improved by gas nitriding at 600°C owing to the surface cracks appearing in the nitrided layers. Martensitic transformation tem-

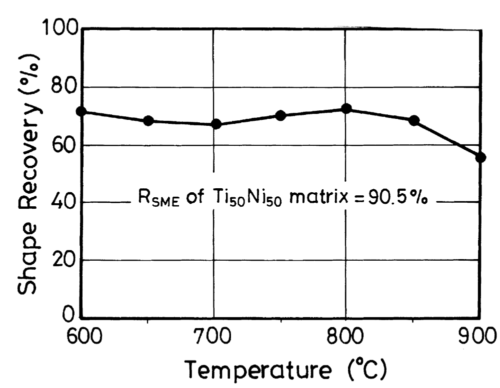

Fig. 4. The shape recovery ability of $Ti_{50}Ni_{50}$ specimens after gas nitriding at various temperatures for 24 h.

peratures are depressed slightly owing to the constraining effect originating from the nitrided layers, and/or the penetration of N and H atoms into the $Ti_{50}Ni_{50}$ matrix during the gas nitriding process. At the same time, the shape recovery of the gas-nitrided $Ti_{50}Ni_{50}$ alloy is also slightly reduced because the nitrided layers do not exhibit an SME and the constraining effect will also depress the shape recovery of the $Ti_{50}Ni_{50}$ matrix.

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