Microstructure, martensitic transformation and superelasticity of Ti$_{49.6}$Ni$_{45.1}$Cu$_5$Cr$_{0.3}$ shape memory alloy

Q.Y. Wang $^a$, Y.F. Zheng $^{a,b,*}$, Y. Liu $^c$

$^a$ Center for Biomedical Materials and Engineering, Harbin Engineering University, Harbin 150001, China
$^b$ Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, Beijing 100871, China
$^c$ School of Mechanical Engineering, The University of Western Australia, Crawley, WA 6009, Australia

A R T I C L E   I N F O

Article history:
Received 10 August 2010
Accepted 13 September 2010
Available online xxxx

Keywords:
Shape memory materials
Martensitic transformation
Mechanical properties
Metals and alloys

A B S T R A C T

The aim of this study is to investigate the microstructure, martensitic transformation behavior, shape memory effect and superelastic property of Ti$_{49.6}$Ni$_{45.1}$Cu$_5$Cr$_{0.3}$ alloy, with Cu and Cr substituting for Ni. After annealing, the alloy showed single step A→M→A transformations within the whole annealing temperature range of 623 K to 1273 K even in the presence and Ti$_2$(Ni, Cu) precipitates. With the increase of the annealing temperature, the transformation temperatures exhibited three stages: increasing from 623 K to 873 K, decreasing from 873 K to 1023 K and unchanging from 1023 K to 1273 K. Meanwhile, the critical stress for stress induced martensitic (SIM) transformation decreased to a minimum value and increased after that, exhibiting a V shape curve. The alloy annealed at 623, 773 and 923 K exhibited shape recovery ratio more than 90% when the deformation strain was below 20%.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In order to achieve good superelasticity and shape memory properties, thermomechanical treatments such as work hardening and precipitation hardening are considered to be effective ways for NiTi alloys. Such processes usually induce the A→R transformation [1,2]. Besides, the addition of third elements substituting for Ni can also change the transformation route. For example, TiNiCu alloys exhibit B2→B19→B19$^*$ transformations when the content of Cu exceeds 7.5 at.% [3]. Furthermore, the addition of third alloying elements is also beneficial for tailoring the transformation temperature and the mechanical properties for specific applications. When Cu is added to substitute for Ni, the transformation temperatures become less sensitive to composition compared with binary NiTi alloy [3]. This makes the casting, processing and controlling of shape memory properties easier. Moreover, the stress hysteresis becomes smaller, with the increase of Cu [4], which means more mechanical energy could be stored and utilized.

NiTi alloys have been used as an orthodontic arch wire material for decades. This kind of alloy can exert light and continuous force, and archwires made of this alloy are ideal for the initial stage of orthodontic treatment [5]. Recently, orthodontic archwires made of TiNiCuCr have been marketed as Copper NiTi™ (Ormco, Glendora, CA, USA) [5–7]. The addition of Cu could increase the unloading strength (corresponding to the orthodontic force) and reduce the energy loss by reducing the stress hysteresis; however, these benefits occur at the expense of increasing its phase transformation temperature above that of the ambient oral cavity [5]. To compensate for this unwanted effect, 0.2–0.5% Cr is added to regulate the $A_t$ temperature to achieve superelasticity (27 °C Copper NiTi™) or shape memory effect when hot foods are ingested (35 °C and 40 °C Copper NiTi™) [5].

Chemical analysis showed that 40 °C Copper NiTi™ consisted of 45.1%Ni, 49.6%Ti, 4.97%Cu and 0.29%Cr (atomic percentage) [7]. Our previous work investigated the corrosion behavior of Ti$_{49.6}$Ni$_{45.1}$Cu$_5$Cr$_{0.3}$ alloy, which contained similar element content with 40 °C copper NiTi™, and found that the addition of Cu and Cr did not impair the good corrosion resistance of NiTi alloy [8]. However, as an orthodontic alloy, the martensitic transformation and the related superelastic characteristics are still unrevealed, although its in vitro and in vivo performance have been widely studied [9–11]. Therefore the present study is to investigate the microstructure, the martensitic transformation characteristics and the superelasticity of Ti$_{49.6}$Ni$_{45.1}$Cu$_5$Cr$_{0.3}$ alloy, with Cu and Cr substituting for Ni on the basis of near-equatomic Ti$_{49.6}$Ni$_{50.4}$.

2. Materials and methods

Sponge titanium (99.95% in purity), bulk nickel (99.995% in purity) and copper (99.95% in purity) and sheet chromium (99.98% in purity) were used to fabricate the experimental Ti$_{49.6}$Ni$_{45.1}$Cu$_5$Cr$_{0.3}$ (TiNiCuCr, in atomic percentage) alloys by arc-melting in an argon atmosphere. The ingots of 30 g each were remelt four times to ensure chemical homogeneity. Before cold rolling, all of the ingots were solution treated at 1173 K for 2 h and quenched to water. The samples were
hot-rolled to certain thickness first, and then cold-rolled by 35% thickness reduction to achieve 1.5 mm final thickness. The samples for mechanical tests were cut along the rolling direction of the plates with an electro-discharge machine. The annealing treatments were performed in the range of 623 K to 1273 K for 1.8 ks and quenched to water at room temperature. DSC measurements were conducted on a Perkin Elmer Diamond DSC machine with a temperature scan rate of 20 K/min. All the mechanical tests were carried out on an Instron universal testing machine model 3365 with a strain rate of 0.01 min⁻¹ at 310 K. The critical stress for SIM was determined by extrapolating the elastic part and the SIM plateau on the stress–strain curve. XRD tests were conducted on an X’pert Pro diffractometer at 40 kV and 100 mA. The shape memory effect was evaluated with a bending test [12]. The strain was estimated by \( \varepsilon_t = \frac{h}{h+d} \), where \( h \) is the thickness of the specimen, and \( d \) is the diameter of the cylinder. The recovery ratio was calculated as \( R = \frac{\theta_d - \theta_h}{\theta_d} \times 100\% \), where \( \theta_d \) is the residual angle after unloading below \( M_f \) and \( \theta_h \) is the angle after heating the specimen above \( A_f \).

3. Results and discussion

Fig. 1(A) shows the optical micrograph of the 1123 K annealed sample and the X-ray diffraction patterns of samples annealed for 1.8 ks at different temperatures. The alloy exhibited fully equiaxed grains, with an average grain size below 50 \( \mu \)m. All the X-ray diffraction measurements were conducted at room temperature (298 K) which was higher than the \( M_s \) of the tested samples (as can be seen in Fig. 2). The annealing temperatures were indicated in Fig. 1 (B). The samples predominantly consisted of austenite regardless of the annealing temperature. Besides, \( Ti_2(Ni,Cu) \) precipitates were also found.

Fig. 2 shows the DSC curves and the corresponding transformation temperatures of cold-rolled TiNiCuCr alloy annealed at different temperatures. All the specimens exhibited direct A-to-M transformations upon cooling and M-to-A transformations upon heating, which was similar with fully annealed binary near-equiatomic NiTi alloys. The presence of \( Ti_2(Ni,Cu) \) precipitates did not change the transformation routes. This is different with binary NiTi alloys, which usually exhibit A-to-R phase transformation in the presence of precipitates [2]. It is believed that this is corresponding to the addition of Cu, which prefers A-to-B19 transformation instead of A-to-R transformation [13].

The critical temperatures of the transformations were plotted in Fig. 2(B) as a function of the annealing temperature. It is seen that the transformation temperatures strongly depend on the annealing temperatures, and there were three evolution stages as indicated in the figure. With the increase of the annealing temperature, in stage 1,
the transformation temperatures increased to maximum at around 873 K. This stage corresponds to a dislocation recovery process, in which dislocation annihilation occurred. The lower transformation temperatures at the initial stage of annealing were attributed to the resistance of high density of dislocations introduced by cold rolling to the lattice distortion of martensitic transformation [13,14]. The dislocation density decreased with the increasing annealing temperature, therefore the hindered martensitic transformation recovered and occurred at a higher temperature [2].

With the increase of the annealing temperature, during stage 2, the transformation temperatures decreased until it reached 1023 K. The evolution during this stage seems to be related with the grain growth after recrystallization. After that, the transformation temperatures became almost constant regardless of the annealing temperature. Above 1023 K, the specimen was fully annealed and free of dislocations, therefore annealing did not change the transformation temperatures. 

Fig. 3(A) shows a set of stress–strain curves of annealed specimens. The specimen annealed at 623 K exhibited uniform deformation as indicated by the absence of Lüders-type deformation plateau, whereas the other specimens exhibited typical Lüders-type deformation during the SIM transformations. Moreover, the modulus of this specimen was slightly lower than that of the other specimens. Due to the higher $A_f$ temperatures of specimens heat treated at 823 K, 873 K and 923 K, they showed large residual strains more than 4%. However, with the increase of the annealing temperature, the residual strain increased, due to the loss of work hardening effect after recrystallization. 

Fig. 3(B) shows the critical stress for SIM as a function of the annealing temperature and the corresponding Gauss fit curve. It is noted that the V shape stress–temperature curve exhibited firstly a negative temperature dependence of stress. At around 870 K, which was close to the recrystallization temperature, the stress reaches a minimum value of about 140 MPa. After that, it increased with the increasing annealing temperature till 1023 K. According to the Clausius–Clapeyron relation [15,16], the difference between $M_t$ temperature and the testing temperature (310 K) partially resulted in the progressive evolution of the stress.

The shape memory recovery ratio decreased with the increasing deformation strain for the three annealed specimens as can be seen in Fig. 4. With the increase of the deformation strain, the recovery ratio decreased but still more than 90%. The 923 K annealed specimen exhibited the best shape memory effect, of which the recovery ratio was more than 98%.

4. Conclusions

The annealed samples exhibited single stage A–M/M–A transformations throughout an annealing temperature range of 623 K to 1273 K even in the presence of Ti$_2$(Ni,Cu) precipitates. With the increase of the annealing temperature, the transformation temperatures exhibited three stages: increasing from 623 K to 873 K, decreasing from 873 K to 1023 K and unchanged from 1023 K to 1273 K. It is believed that dislocation recovery and recrystallization dominated this evolution. Specimens annealed below 773 K exhibited superelasticity. Meanwhile, the critical stress for SIM transformation decreased until 870 K and increased after that. The alloy annealed at 623 K, 773 K and 923 K exhibited shape recovery ratio more than 90% when the deformation strain was below 20%.

Acknowledgment

This work is supported by the Fundamental Research Funds for the Central Universities (HEUCFZ1017).

References