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Thermal stability and hardening behavior in superelastic Ni-rich Nitinol alloys with Al addition

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ABSTRACT

Ni-rich NiTi alloys exhibit high hardness of 58–65 HRC, comparable to tool steels. Ni-rich NiTi alloys combine hard, corrosion resistant, nonmagnetic and other attributes that makes them promising candidates for bearing and related applications. The high hardness has been associated with the precipitation of a large volume fraction of nano-sized Ni_4Ti_3 strengthening phase. In this work, a series of $Ni_{55}Ti_{45-x}Al_x$ (x = 4, 6, 8 at%) ternary alloys have been prepared to explore the microstructural evolution, hardening behavior and thermal stability in Ni-rich NiTi alloys with Al additions. For comparison purposes, the binary 55Ni-45Ti alloy was also examined. TEM results revealed that the Al additions refined the Ni_4Ti_3 phase to a few nanometers, as a result, the ternary alloys showed higher hardness than binary alloy. After aging for 96 h at 500 °C, the hardness of ternary alloy (55Ni-39Ti-6Al) remained above 820 HV, significantly superior to binary alloy was lower than 700HV. Upon aging at 600 °C for 96 h, the hardness of 55Ni-39Ti-6Al could reach over 700HV, while the binary alloy's hardness decreased dramatically to about 400HV. It was because there were still nano-sized Ni_4Ti_3 precipitates in ternary alloys while the Ni_4Ti_3 phase in binary 55Ni-45Ti alloy had completely decomposed. Thus, the Al additions increased the hardness of Ni-rich NiTi alloys by refining the strengthening phase Ni_4Ti_3 and improve the thermal stability of Ni_4Ti_3 phase. The study results enhance the hardness of Ni-rich NiTi alloys and raise the working temperature. Therefore, it would make contributions to the development of new generation NiTi based bearing alloy.

1. Introduction

NiTi based alloys are commonly known as the shape memory alloy for their shape memory and superelastic behaviors which have been deeply studied and widely used in biomedicine industry [1]. For NiTi binary alloys, researches focus on near equiatomic and Ti-rich variations for their shape memory behaviors at moderate thermoelastic martensitic transformation temperatures [2,3]. Recently, the Ni-rich NiTi alloys draw our attention for National Aeronautics and Space Administration (NASA) announcing on reusing 60NiTi alloy. 60NiTi contains 60 wt% Nickel and 40 wt% Titanium (the atomic ratio of Ni/Ti is 55/45). W.J. Buehler at the Naval Ordinance Laboratory first invented it in late 1950's. With high hardness and excellent corrosion resistance, 60NiTi was considered as bearing materials; however, difficulties on fabrication had buried 60NiTi's remarkable properties for decades. Nowadays, modern processing methods animate 60NiTi to be the most promising bearing material candidate [4–7]. For example, bearing balls and races can now be produced through modern powder metallurgy manufacturing methods. NASA has been exploring aerospace applications for 60NiTi inside the International Space Station's water recycling system with a highly corrosive, lightly loaded, low-speed bearing environment [8]. Bearing company Abbott Ball is also devoting into the application development of 60NiTi in various areas, such as kitchen knives for its high hardness and excellent corrosion resistance, and medical equipment like scalpels for its chemical and thermal stability as well as its nonmagnetic characteristic [9].

60NiTi's hardening mechanism is the precipitation of nanoscale Ni_4Ti_3 platelets that are coherent with the B2 NiTi matrix. With solid-solution treatment followed by water quenching, Ni_4Ti_3 precipitates could occupy up to 71% volume fraction [10,11]. However, increasing aging temperature or extending aging time may lead to the coarsening of Ni_4Ti_3 precipitates. Such Ni_4Ti_3 phase is metastable and is prone to decompose to Ni_3Ti_2 and Ni_3Ti phase with higher thermodynamic stability [12]. The coarsening and decomposition of Ni_4Ti_3 lead to the loss of hardness. According to the present study, the maximum application temperature of 60NiTi is 400 °C [7]. Thus, it is necessary to enhance the alloy's hardness and improve its thermal stability to access higher working temperature.

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The majority of studies on alloying of NiTi focus on shape memory behavior and superelastic characteristic. Derek Hsen Dai Hsu et al. investigated the effect of Al additions in NiTiHf shape memory alloys and revealed that the mechanical strength increased with Al additions [13]. Cong Wang et al. studied the microstructure evolutions of Ni-Ti-Nb-Al alloys with different Al addition and found that the increase in Al addition promoted grain refinement and increased the macro-hardness values [14]. In addition, there were also studies focusing on the alloying of NiTi to use it as a potential candidate for high-temperature structural material. NiTi-Al alloy was studied as high temperature intermetallic compound to evaluate the feasibility of replacing nickel-base superalloys. Y. Koizumi et al. found that the coherent precipitation of Ni_2TiAl produced by substituting a portion of the Ti in NiTi alloys with Al led to a sharp increase in compression strength at both high and room temperatures [15]. Li-Jing Zheng et al. studied $Ni_{43}Ti_4Al_2Nb_2Hf$ alloy produced by directional solidification and found that the micro alloying caused a negative effect on the high-temperature mechanical properties [16]. Li-Wen Pan et al. studied NiTi-Al-based alloys and found that the β-NiTi/β'-Ni_2TiAl structure contributed to increasing of the strength upon 800 °C [17]. However, there are limited studies on alloying study of Ni-rich NiTi alloys. NASA Glenn Research Center is working on alloying of 60NiTi and has already investigated the additions of Zr, Hf, and Ta [11,18]. They found that the Hf-containing alloys likely biased the Ni content needed for Ni_4Ti_3 to decompose by the co-precipitating of the H-phase. Therefore, the study work for the alloying of Ni-rich NiTi alloy with Al content is promising to enhance the mechanical properties and increase the working temperature , which may contribute to the development of this potential high hardness bearing material.

The purpose of this study is to investigate the effect on Ni-rich 55Ni-45Ti alloy's microstructure and hardenability after micro-alloying additions of Al and explore the thermal stability of 55Ni-45Ti alloy with Al additions. This study demonstrated the microstructures and hardenability of 55Ni-(45-x) Ti-xAl (x = 0,4,6, 8) ternary alloys under solution-treated and aged conditions. According to the previous study on NiTi-Al high temperature intermetallic alloys, Al would substitute Ti in NiTi alloys and had solution strengthening effect [15]. Once the content of Al reached to a certain amount, β-NiTi/β'-Ni_2TiAl structure, similar to the γ/γ' structure, would be generated in Ni-based alloys which contributed to the improved mechanical properties. The additions of Al could improve the mechanical properties of Ni-rich NiTi alloys and contribute to the development of NiTi-base bearing material. The strengthening mechanism of Ni-rich NiTi alloys is attributed to nanoscale Ni_4Ti_3 precipitates coherent with NiTi matrix and the Ni_4Ti_3 phase was a metastable phase which would coarse and decompose with increased aging temperatures and prolonged aging times. Therefore, the objectives of this paper are: (1) observe the influence of Al additions on 55Ni-45Ti alloy's microstructures and hardenability; (2) study the strengthening mechanism of Al additions in Ni-rich NiTi alloys; (3) extend aging temperature and time to investigate the effect of Al additions on alloy's thermal stability.

2. Experimental details

2.1. Materials synthesis

The ternary NiTi-Al alloys (55Ni-(45-x) Ti-xAl (x = 0,4,6, and 8)) were produced by arc-melting with high purity Ni (99.95%), Ti (99.99%) and Al (99.99%). Those raw materials were purchased from Trillian Metals. The alloy ingots were prepared by arc-melting on a water-cooled copper crucible in an argon atmosphere and the furnace chamber was vacuumed to $3{\sim}5\times10^{-3}$ Pa and then backfilled with high purity argon to a pressure of 0.05 MPa. Each ingot was melted four times to ensure composition homogeneity. The ingots were heated together with the furnace and homogenized at 1050 °C for 24 h in vacuum (approximately 10–6 Torr) followed by furnace cooling of 3 °C/min and then sectioned by wire electrical discharge machining into several $\phi 5 \times 5$mm cylinder specimens. The as-processed specimens were heat treated for 3hr at 1050 °C followed by water quench. Then They were aged at 400 °C for 3 h and 500 °C, 600 °C for 1 h, 24 h, 48 h and 96 h respectively, following by air cooling to room temperature. During all solution and aging treatments, the specimens were encapsulated within quartz tubes vacuumed to 10^{-3} Pa and then backfilled with ultra-high purity Ar to 0.3 MPa to reduce the amount of oxidation.

2.2. Microstructure characterization

After heat treatment, the microstructure of the alloy in different conditions was studied by JXA8100 electro-probe microanalyzer (EPMA) (JEOL, Japan) equipped with energy dispersive X-ray spectroscopy (EDS). There are two main signals collected in the scanning electron microscopy (SEM). One is secondary electrons (SEs), mainly providing information about surface topography; the other is backscattered electrons (BSEs), depending on the atomic number (Z) of the scattering elements and revealing sample composition primarily [19]. The samples were imaged with accelerating voltages of 17 and 18KeV and a probe current of roughly 5 nA at a working distance (WD) of 11 and 12 mm. The transmission electron microscopy (TEM) images of the thin foils were taken in a JEOL-2000 electron microscope. The thin foils were prepared by twin-jet electro polishing device. The acceleration voltage was 200KeV.

2.3. Hardness test

An FM800 microhardness tester equipped with a Vickers diamond pyramid was adopted to evaluate the alloying and aging effect on hardness variation. A load of 1 kg and 10 s dwell time was utilized for each of the ten separate hardness measurements from which an average and standard deviation were determined.

3. Results

3.1. The microstructures and hardness of the binary and ternary alloys

The BSE SEM image in Fig. 1 showed the microstructures of the binary alloy and three ternary alloys solution-treated at 1050 °C for 3 h followed by water quenching. The microstructure of the solution-treated 55Ni-41Ti-4Al alloy in Fig. 1(b) and 55Ni-39Ti-6Al alloy in Fig. 1(c) were similar to the binary 55Ni-45Ti alloy in Fig. 1(a). They were composed of homogenized NiTi matrix and Ti_2Ni precipitates except for finer Ti_2Ni precipitates with Al additions. However, the microstructure of 55Ni-37Ti-8Al alloy shown in Fig. 1(d) revealed the existence of Ni_2TiAl primary phase and Ni_3Ti phase. The portion of Al atoms in 55Ni-37Ti-8Al alloy was adequate for generating Ni_2TiAl primary phase [15,17]. With high content of Al component, Ni: Ti ratio increased and tended to precipitate Ni-rich phase like Ni_3Ti. The hardness values of all the alloys solutioned at 1050 °C for 3 h followed by water quenching and aged at 400 °C for 3 h followed by air cooling are presented as a function of the content of Al atoms in Fig. 2. With the increase in Al content, the hardness value of alloys increased both in solution treated and in aged condition. For the binary 55Ni-45Ti alloy, the hardness was about 740HV. This value is equivalent to a Rockwell hardness of 61HRC that within the standard range for bearing materials. After 400 °C aging, the hardness of 55Ni-41Ti-4Al alloy and 55Ni-39Ti-6Al alloy increased, especially the hardness of 55Ni-39Ti-6Al alloy was up to about 820HV. While 55Ni-37Ti-8Al alloy showed limited change after aging at 400 °C in hardness. The hardness of 55Ni-37Ti-8Al is comparable to that of 55Ni-39Ti-6Al alloy. Considering both microstructures and hardness, alloy with 6 at% Al content demonstrated to be the most promising candidate. Thus, we selected 55Ni-39Ti-6Al alloy as the key research object. 55Ni-41Ti-4Al alloy was used as the reference object to investigate the effect of Al content. Despite of