Superelasticity of NiTi-Nb metallurgical bonding *via* nanoindentation observation

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Abstract:

Sandwich architecture with cross-shape periodic cellular cores is synthesized *via* eutectic reaction between NiTi and Nb powder, such forming metallurgical bonding between NiTi wires near eutectic reaction temperature. Superelasticity is investigated systematically *via* nanoindentation tests. The Ti-rich phase is weaker in superelastic recovery comparing with that of Nb-rich phase, lamellar and rod-like NiTi-Nb eutectic. Inconsistent Nb element distribution in the interface of eutectic area and NiTi wire enhances the martensitic transformation.

Keywords : titanium alloys; nanoindentation; interfaces; sintering; superelastic recovery

1. Introduction

Many approaches have been carried out to fabricate metal foams with open cell and stochastic structures [1-3]. Owing to the uniform and open architecture as well as isotropic performance,

cellular metals with truss-type inner structures have been studied for a long time [4]. According to the quasi-binary NiTi-Nb eutectic phase diagram, spontaneous contact melting appears once Nb comes in contact with NiTi at high temperature, such a quasi-binary liquid eutectic phase with a composition near Ni-36Ti-26Nb (at.%) is formed when NiTi and Nb are in contact with each other [5-7]. Grummon *et al* used Nb foils to bond NiTi foils, by creating a NiTi-Nb phase, into open-cell NiTi honeycombs with shape-memory properties [5]. Wang *et al* reported that high ductility and hardness can be obtained in NiTi-Nb eutectic region [6]. Comparing with superelasticity in NiTi titanium alloys [8-9], few literatures can be found focus basically on NiTi-Nb eutectic. Superelasticity of NiTi-Nb brazed NiTi wires with cross-shape architecture has not been systematically studied yet. In this study, sandwich architecture with periodic cellular cores is synthesized *via* eutectic reaction between NiTi and Nb powder. Superelasticity is investigated systematically *via* nanoindentation tests. Microstructure in the eutectic bonding region for cross brazed NiTi-Nb is also discussed.

2. Experimental

NiTi wires with a nominal composition of 50.5 at.% Ni were utilized for brazing. Pre-alloyed NiTi powders (44-63 μm , 48.6 at.% Ni) and pure Nb powders (99.8% purity, 1-5 μm) were used. We design the weight ratio of pre-alloyed NiTi and Nb powders as 2.3 and sinter the specimen at 1165 °C for 4 minutes in a high vacuum (10^{-5} torr) furnace. Figure 1(a) shows an example of sandwich framework with periodic cellular cores. In order to obtain this accurate structure, we prepare the cross-shaped bonded NiTi wires with NiTi/Nb slurry added at each node, as exactly indicated in Fig.1(b). Nanoindentation tests were carried out at room temperature using a nanoindenter with a Berkovich tip, performed with the continuous load up to a maximum value of 50 mN at a loading rate of 1.0 mN/s. A 30 s dwelling time was applied at the maximum load of about 50 mN followed by unloading at a

unloading rate of 1.0 mN/s. Scanning electron microscope (SEM) and energy-dispersive spectroscopy (EDS) observations were carried out using a Hitachi SU8030 microscope at 15 kV.

Fig.1 Schematic illustration of sample preparation: (a) Example of sandwich framework with periodic cellular cores; (b) Cross-shaped bonded NiTi wires with NiTi/Nb slurry added at each node.

3. Results and discussion

We prepare two perpendicular wires to produce NiTi/Nb eutectic at 1165 °C (near the eutectic temperature in the NiTi-Nb quasi-binary phase diagram [6]). Figure 2 shows the optical microstructure of as-polished surface of the brazed region, demonstrating an adequate metallurgical bonding *in situ* reaction processing, as exactly shown in enlarged micrograph of eutectic region in Fig.2(a). In region A (Fig.2(a)), martensite colonies appear at the interface of eutectic reaction (Fig. 2 (b)). The chemical composition for four different position (1, 2, 3, 4) in figure 2(b) were determined by EDS as follows: (1) 7.98Ti-7.65Ni-84.37Nb (wt.%) (Nb-rich phase), (2) 42.76Ti-33.65Ni-23.59Nb (Ti-rich particle), (3) 36.24Ti-51.37Ni-12.39Nb (proeutectic phase), (4) 43.64Ti-56.36Ni (NiTi matrix). It can also be determined that much more martensite transformation was obtained at the interface between NiTi and eutectic region. In region B (Fig.2(a)), a continuous change of Nb content from the reaction area to NiTi matrix is shown in figures 2(d) and (e), as measured by EDS in the marked region. Nb concentration is higher in the eutectic area (position 1), especially in the Nb-rich phase, and drops to zero in the NiTi wires (position 4), indicating that solid-state diffusion of Nb into the wires is very limited during the 4 minutes at 1165 °C.

Fig 2 Micrographs of polished surface of the brazed region for cross-shape wires: (a) Sintered specimen and enlarged micrograph of eutectic region; (b) micrograph of reaction interface between NiTi wire and eutectic region, as marked by A in (a) ; (c) EDS analysis of each phase composition in (b); (d) micrograph of reaction interface between NiTi wire and eutectic region, as marked by B in (a); (e) change of Nb content in (d).

Figure 3 shows the images of nanoindents on the bonded area. The proeutectic phase (P), eutectic region (E), and Nb-rich phase (N') are also visible (Fig.3(a)). Figure 3(b) shows the load–displacement curves obtained from the eutectic region (Fig.3(a)). Clear difference of the load–displacement curves for the nine indents in the eutectic region can be observed. The curves seem the same in the NiTi matrix region (Fig.3(c)). Complete unloading does not result in a full shape recovery as one might expect for a superelastic feature. Both the maximum depth and residual depth of indentation varies from each other due to the different indented locations (Fig.3(b)). For indents 1, 4, 7, and 9, located around the interface between eutectic and NiTi(Nb) proeutectic phase, the maximum depths are greater than 900 nm.

The relationships between the maximum indents depth at maximum load (h_{max}), residual depth during unloading (h_r), recovery ratio (η_d) and indents are shown in figures 3(d) and (e). As seen from Fig.3(d), superelastic recovery occurs and significant difference for those nine indenters is observed.

For indents 3, 6, and 8 in the eutectic region, the values of η_d are around 49%, and the values of others are relatively small ranging from 42% to 46%. However, comparing with the superelasticity in the bonded area, more strain recovery (ranging from 50% to 52%) is apparent after complete unloading for NiTi wire as indicated in figure 3(e).

For the indent 1, 4, 7, and 9, the depth is lower than that of the remanent indents. During unloading, the recovery curves associated with the stress-induced martensite transformation vary from each other. As shown in Ref. [10], martensite transformation is switched in which the slope of P(h) curve in the early stages of loading is not steep. Comparing with the eutectic region, a higher value of recovery ratio (50-52%) can be observed in NiTi matrix. It is concluded that much more phase transformation from stress-induced martensite to parent occurs which is caused by elastic strain energy stored around the martensite plates and matrix. While similar recovery ratio values to NiTi around 49% are obtained for the indents 3, 6, 8, and 9 (Fig. 3(e)), which distribute in the interface between eutectic phase and NiTi(Nb) proeutectic phase, where martensite transformation is also induced easily.

Fig.3 Nanoindents on polished surface sintered at 1165 °C for 4 minutes: (a) SEM micrograph of region C in Fig.2(a); (b) load–displacement curves obtained from the nine indents in eutectic region (numbers correspond to indents shown in Fig. 3(a)); (c) load–displacement curves of NiTi wire; (d)

recovery ratio for 9 indents in eutectic region, (e) recovery ratio for a NiTi wire.

The Hertzian elastic contact solution of nanoindentation tests can be calculated by [11]:

$$P = \frac{4}{3} (E_r R_i^{1/2} h^{3/2}) \quad (1)$$

where P is the applied load, E_r is the effective indentation modulus, R_i is the radius of the indenter tip, which was determined as 1 μm in this experiment, h is the indentation depth. Young's modulus and Poisson's ratio for the indenter and the tested specimen are taken as 1140 GPa, 0.07 [12] and 73 GPa, 0.3 [10], respectively. Figure 4 shows nanoindentation results obtained with Hertzian solution and magnified indentation curve at the position of the pop-ins for four different indents, including indent 1 in NiTi matrix, indent 1, 3, and 8 in eutectic, respectively. Hertzian elastic contact solution is presented as a red dash dot line (Fig.4). First pop-in is considered as the result of dislocation nucleation [13-14]. First pop-in occurs below 1.5 mN for indent 1 in NiTi matrix, while first pop-in events in other indents in eutectic region appear above 4 mN, and the largest value arrives around 8 mN for indent 8 in eutectic. The following pop-ins may be caused by martensitic transformation, as discussed by Ahn et al. [15]. Comparing with the three indents in eutectic, distinct pop-ins are detected during loading procedure, especially for indent 3 and indent 8, showing that martensite transformation occurs during the indentation. Furthermore, as shown in figure 4(d) about the superelastic recovery for the indents 1, 3, and 8, respectively, higher values are obtained for indents 3 and 8, which also confirms the fact that much martensite transformation takes place in indents 3 and 8.

Fig.4 Nanoindentation experiments conducted with Berkovich indent with Hertzian solution including an enlarged part of the indentation curve: (a) indent 1 in NiTi matrix, (b) indent 1 in eutectic, (c) indent 3 in eutectic, (d) indent 8 in eutectic. Arrows indicate the position of the pop-ins

4. Conclusions

Comparing with the superelasticity in bonding area, more strain recovery is observed for NiTi wire and the values range from 50% to 52%. Ti-rich phase is weaker in superelastic recovery comparing with Nb-rich phase, lamellar and rod-like NiTi-Nb eutectic. Lower values of recovery ratio are obtained in different phase in eutectic region comparing with the value of NiTi matrix. Inconsistent Nb element distribution in the interface of eutectic area and NiTi wire enhances the martensitic transformation, where martensite transformation is also induced easily.

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(a)

(b)

(a) Example of sandwich framework with periodic cellular cores; (b) Cross-shaped bonded NiTi wires with NiTi/Nb slurry added at each node

Nanoindentation experiments conducted with Berkovich indent