Materials & Design 130 (2017) 175–182

Contents lists available at ScienceDirect

Materials & Design

journal homepage: www.elsevier.com/locate/matdes

Intermetallic formation and mechanical properties of Ni-Ti diffusion couples

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ARTICLE INFO

Keywords:
Intermetallic
Diffusion
Interfaces
Ni-Ti
Shear strength

ABSTRACT

Samples of Ni-Ti diffusion couples were prepared by hot pressing in a furnace with a vacuum of 10^{-1} Pa. Scanning electron microscopy (SEM) investigations indicated that three intermetallic compounds, namely, $NiTi_2$, NiTi, and Ni_3Ti, were formed at the Ni-Ti interface at 650 °C. Ni_3Ti first grew at the Ni substrate because of the diffusion of Ti into Ni, $NiTi_2$ subsequently appeared, and NiTi finally developed between the $NiTi_2$-Ni_3Ti interface. As the thickness of the diffusion layers increased, a part of Ni_3Ti was also consumed by Ti to form NiTi. The interfacial microstructure was changed by the current at 900 °C. A columnar crystal initially formed inside the Ni_3Ti matrix, which was immediately adjacent to NiTi, and this crystal then elongated at a direction perpendicular to the plane of the joint. Ni_3Ti vanished, and pure Ti was finally produced. The observed strength variations were discussed in relation to interfacial microstructures. Shear experiments showed that fractures were observed in Ni_3Ti for the sample prepared at 650 °C. For the sample prepared at 900 °C, fractures were detected in $NiTi_2$.

1. Introduction

Titanium and its alloys are widely used in industries because of their excellent properties that include relatively high-yield strength and good corrosion resistance. In chemical, nuclear, and aerospace industries, bonding Ti and Ti alloys with stainless steel, Ni alloys, or other materials is necessary [1,2]. Ti and Ni films are also often used as interlayers to bond other metals or ceramic materials [3–5], but brittle intermetallic phases usually form in joints and may consequently decrease the plasticity and toughness of these joints. Hence, the interfacial microstructure of Ni-Ti joints and its formation mechanism should be investigated.

Among shape memory alloys (SMA), NiTi is the most widely used in engineering and medical applications because of its excellent physical and mechanical properties, such as good corrosion resistance, good wear resistance, high hardness, good biocompatibility [6,7], super-elasticity, and good damping properties [8]. The microstructural transformation behavior of this material has been extensively investigated. Chun [9] examined the effect of Ag on the microstructure and martensitic transformation behavior of NiTi prepared by arc melting technology. Kim [10] prepared a NiTi alloy through spark plasma sintering and evaluated its microstructural transformation behavior. Pan [11] found that rapid solidification produces equiaxic grains after large ingots of NiTi alloys are casted. NiTi, along with $NiTi_2$ and Ni_3Ti, can be fabricated on the surface of some alloys to improve oxidation resistance [12–16]. NiTi can also be used to prepare composites, which exhibit an excellent combination of strength and ductility [17].

Various synthesis techniques, such as reactive gas laser atomization [18], diffusion from Ni-Ti layers [19,20], mechanical alloying [21], ion implantation [22], powder metallurgy [23], cold deformation [24], laser cladding [25], and self-propagating high-temperature synthesis [26], have been developed to synthesize these compounds. The mechanism of mechanical alloying has also been explored. Laeng [7] studied the phase formation of Ni-Ti via solid-state reaction by using elemental powders and inferred that $NiTi_2$ and Ni_3Ti, and three intermetallic compounds form in the following order: Ni_3Ti, $NiTi_2$, and NiTi. However, this assumption has yet to be experimentally verified. Ghadimi [27] observed that single-phase NiTi can be obtained by mechanical alloying of Ni and Ti elemental powders for 60 h, but $NiTi_2$ phases can also be formed during annealing. MohdZaki [28] successfully produced single-phase NiTi by sintering equiatomic Ni-TiH_2 powders.

Ni-Ti diffusion couples have been widely investigated because reactive Ti and Ni multilayers are potentially useful for intermetallic compound synthesis or composite material fabrication [29]. Ni-Ti bimetals can also be applied to electrolyzers for chlorine production. The diffusion bonding of Ti to Ni can ensure good electric conductance between individual electrolyzer modules, such as between a nickel cathode and a titanium anode. However, compounds formed at the interface can affect the conductivity of electrolyzers [30]. Garay and

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http://dx.doi.org/10.1016/j.matdes.2017.05.055
Received 22 March 2017; Received in revised form 17 May 2017; Accepted 21 May 2017

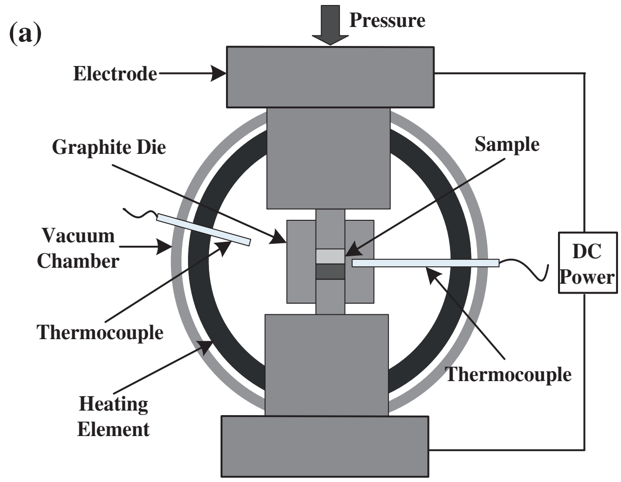

Fig. 1. Schematic of apparatus and structure of the chamber.

Zhou [31,32] found that the growth of intermetallic compounds is parabolic and current can significantly increase the growth rate of these compounds. Guo [33] examined the effects of surface roughness on the diffusion bonding behavior of Ti and Ni. Zhang [34] observed that only $NiTi_2$ layers and NiTi layers are preserved after 36 h of diffusion. Zhang [35] further demonstrated that the thickness of Ni_3Ti layers increases as the thickness of NiTi layers decreases when annealing time is prolonged.

The reaction mechanism of Ti and Ni, their microstructure evolution, and the phase transformation of Ni-Ti couples have yet to be fully understood. As such, these aspects should be elucidated to facilitate the fabrication of NiTi SMA and the bonding of Ni-Ti couples. In this study, the effects of diffusion on interfacial microstructures were investigated, and current was used to produce heat and promote diffusion. By applying current, we could shorten the diffusion time and thus accelerate the experimental process [31]. The mechanical strength of Ni-Ti diffusion couples in relation to microstructure was also examined.

2. Experimental

Fig. 1 shows a schematic of our experimental apparatus that consists of two graphite electrodes and a molybdenum mesh. The graphite electrodes can carry current and provide mechanical load to the diffusion samples, and a molybdenum mesh was used to heat the furnace. The samples were simultaneously heated by the current and the furnace. A type K thermocouple 1 mm in diameter was placed in the hole of the graphite die to monitor the temperature of the sample. A thermocouple was also used to monitor the temperature of the furnace. Experiments were conducted at different time points (5–60 min), currents (1000–1200 A), temperatures (650 °C–900 °C), and pressure (30 MPa). According to the Ni-Ti phase diagram, NiTi does not exist below 630 °C. At > 882 °C, α-phase Ti (h.c.p.) transforms into β-phase (b.c.c). Our experiments revealed that the pressure of 30 MPa and the diffusion time range between 5 and 60 min were sufficient to form the desired thickness of the diffusion layers. Therefore, these experimental parameters were chosen. When the current flowed through the graphite die and the sample, a high amount of Joules heat was generated. During the experiment, the heat generated by the applied current was inadequate to heat the sample to the required temperature. Thus, the furnace was first heated to 500 °C, and current was then used to heat the sample.

The raw materials used in the experiments were pure Ti foil and pure Ni foil at a thickness of 0.04 mm. Ti and Ni foils with a purity of > 99.9% were rinsed with concentrated HNO_3 and 10% HCl solution, respectively, to remove the oxide film and then rinsed with water. To prepared the Ni-Ti diffusion couples, these foils were cut into a round shape with a diameter of 20 mm and subsequently fabricated into a graphite mold with a 20 mm inner diameter (Fig. 1). A Ni foil was placed between the two layers of Ti and a Ti-Ni-Ti sample was prepared to investigate the effect of the direction of current.

The foils were subjected to hot pressing in a furnace at a vacuum of 10^{-1} Pa. Afterward, the test samples were prepared by conventional metallographic methods, ground with SiC paper of up to 2000 grit, and polished with diamond paste. The polished samples were chemically etched with 4% Nital solution (96 ml of ethanol and 4 ml of HNO_3) and examined under a scanning electron microscope (SEM; JEOL JSM-6390) equipped with an energy-dispersive spectrometer (EDS, INCA, Oxford).

Ti and Ni plates with a thickness of 5 mm were used instead of foils to prepare the samples for shear strength evaluation. The shear strength of the diffusion couples were examined in a material testing machine (Galdabini, SUN 1000) at a head movement rate of 1 mm/min. The surface topography of the fractured samples was also characterized by SEM. For each experimental parameter, three samples were tested.

3. Results and discussion

3.1. Effect of diffusion time on the diffusion zone

Fig. 2 shows the relationship of standard Gibbs energies with temperature for Ni-Ti system. This phenomenon was plotted by the software HSC Chemistry. Gibbs energies decreased in the following order: NiTi, $NiTi_2$, and Ni_3Ti. According to the thermodynamic conditions, the first phase formed is Ni_3Ti because its Gibbs free energy is the lowest. $NiTi_2$ and NiTi are subsequently produced.

Fig. 3 provides the SEM images of the Ni-Ti diffusion joints prepared at 650 °C and 30 MPa activated at 1000 A at different diffusion times. As the diffusion time was prolonged, more layers were formed at the Ni-Ti interface. According to the atomic ratio shown in Table 1, the phases indicated by numbers 1, 2, 3, 4, and 5 are Ni_3Ti, Ni_3Ti, $NiTi_2$, $NiTi_2$, and NiTi, respectively, which are presented in the Ni-Ti equilibrium phase diagram. Garay and Zhou [31,32] also found that the three layers formed in the Ni-Ti diffusion couples, and this result is in good agreement with our experimental findings. The three intermetallic compounds formed in the following order: Ni_3Ti, $NiTi_2$, and NiTi, and this observation is consistent with the thermodynamic conditions.

During hot pressing, pressure is necessary because it can ensure good contact between Ti and Ni foils. An intimate contact is also essential for the initial diffusion. The stress imposed to the sample was very uneven and could result in different degrees of diffusion. According to sectional observation, diffusion was not uniform. Diffusion first occurred in the location of close contact, that is, the surface asperities [36], and subsequently expanded to its periphery, which may lead to inhomogeneous thickness of the three phases

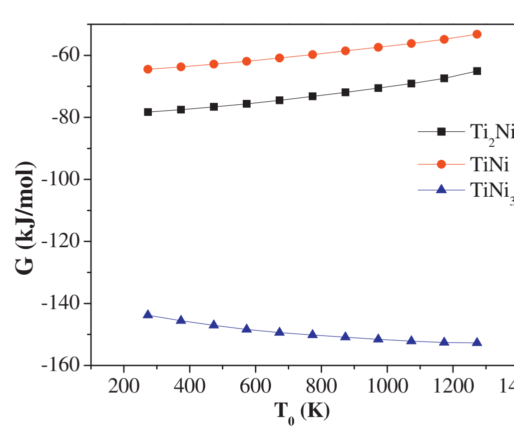

Fig. 2. Relationship of standard Gibbs energies with temperature for Ni-Ti system.