The Microstructure of Diffusion-bonded Ti/Ni Interface

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The microstructure of diffusion-bonded Ni/Ti interface has been investigated by means of secondary electron microscopy, electron probe microanalysis and transmission electron microscopy. The α-Ti in the vicinity of the bonding interface is transformed into β-phase by the penetration of Ni atoms at temperatures between β-transus and eutectoid point. This transformation enhances the diffusivity of Ni atoms into Ti and results in the microvoid formation due to Kirkendall effect. Across the Ni/Ti bonded interface from the Ni- to Ti-side, the intermetallic compound layers, i.e., hexagonal TiNi₃ [and Ti(Ti₀.₁₁Ni₀.₈₉)₃], cubic TiNi, monoclinic TiNi, and hexagonal Ti₂Ni are formed. The region where the α-Ti transforms into bcc β-phase without intermetallic compound formation at the bonded temperatures decomposes into the lamellar Ti₂Ni eutectoid structure directly or after the proeutectoidal α-lath formation during cooling to room temperature.

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I. Introduction

The Ti–Ni binary alloy phase diagram shows that the mode of intermetallic compounds formed will change from Ti₂Ni to TiNi₃ via TiNi with increasing Ni content(1). This suggests that the microstructure in the vicinity of the diffusion-bonded Ti/Ni interface can be significantly complicated and is worth investigating to understand the mechanical properties of this type of joints.

The examination of the microstructural change within the Ti phase close to the interface is also of interest because the β-phase stability of Ti alloys is largely enhanced with increasing Ni content. In the present study, therefore, the structures at the diffusion-bonded Ti/Ni interface have been carefully examined by means of transmission electron microscopy.

II. Experimental Procedure

A commercial high purity Ni rod (99.5%) and a pure Ti plate (99.7%) were used for the diffusion bonding experiment. They were machined into the cylindrical specimens with the dimension of 8 mm in diameter and 6 mm in length. The flat surfaces were mechanically polished by a fine carborandum paper to keep the surface roughness constant.

The specimens were set to a compressive test machine in the vacuum chamber of 5×10⁻² Pa with the flat surfaces contacting to one another as shown in Fig. 1 and were heated up to temperatures in the range between 973 and 1123 K under the initial compressive stress of 58 MNm⁻².

The microstructures of the diffusion-bonded
specimens were examined by means of optical, scanning electron, and transmission electron microscopies. The specimens for optical microscope observation were etched with a 10% HF and 5% HNO₃ aqueous solution. The scanning electron microscopy was carried out in the back scattered electron image mode without etching to avoid the selective attack of Ni rich layers along the diffusion-bonded interface. The thin foils for the transmission electron microscopy (TEM) were prepared by a conventional twin jet polishing method using an electrolyte 90% CH₃ COOH and HClO₄. The diffusion of Ni and Ti elements across the bonded interface was examined by an electron probe microanalyser (EPMA) and a STEM/EDS mode of TEM.

III. Experimental Results

1. Microstructure of the diffusion-bonded interface

Figure 2 shows an optical micrograph of the Ti/Ni interface diffusion-bonded at 1123 K for 6 ks. The initial interface is shown by an arrow. Adjacent to the initial boundary, the layers consisting of a darkly etched region containing a large number of fine precipitates and the Widmannstätten structure (transformed β) can be seen between the fcc Ni and the hcp α-Ti. Such a layered structure was observed in the specimens bonded at temperatures above 1023 K, but was not recognized in the specimens bonded at temperatures below 973 K. Figure 3 shows an example of the back scattered electron images in the vicinity of the bonded interface. Three layers with different contrasts exist between the Ni and the transformed β layer of Ti (Fig. 3(a)). The X-ray intensity profiles of Ti(Kα) and Ni(Kα) across the interface show that each contrast corresponds to the composition of TiNi₃, TiNi, or Ti₂Ni respectively (Fig. 3(b)).

Microvoids are also observed to form along the TiNi₃/Ni interface (Fig. 3(a)). Figure 4 shows a matching pair of the fracture surface separated at the TiNi₃/Ni interface, (a) and (b) corresponding to the TiNi₃ and the Ni sides re-
spectively. A careful examination of these pairs of micrographs reveals that the corresponding dimples on each fracture are observed as concaves and that they have already existed prior to the final fracture as micro-voids.

2. TEM observation

The microstructure across the Ti/Ni interface diffusion-bonded at 1123 K for 0.6 ks are examined by a transmission electron microscope as in Fig. 5. From the right to the left of the micrograph, the metallic Ni, the layers of hexagonal Ti$_3$Ni and/or Ti(Ti$_{0.11}$Ni$_{0.89}$)$_3$, the cubic TiNi, the monoclinic TiNi, the cubic Ti$_2$Ni and the Ti/Ti$_2$Ni eutectoid structure are observed. The Ni concentrations at the points indicated by numbers on the micrograph in Fig. 5 were analysed by the STEM/EDS mode and the results are shown in Fig. 6. The Ni concentration both in the TiNi$_3$- and TiNi-layer slightly deviates from those of stoichiometric concentrations.

Within the intermetallic compound layer adjacent to the metallic Ni, an electron diffraction pattern from hexagonal TiNi$_3$ was obtained as in Fig. 7. In this layer an electron

Fig. 4 Matching pair of the fracture surfaces separated at TiNi$_3$/Ni interface: (a)TiNi$_3$ side, (b)Ni side.

Fig. 5 Transmission electron micrograph of Ti/Ni interface diffusion-bonded at 1123 K for 0.6 ks (1, 2, 3: points for STEM/EDS analysis).
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Diffraction pattern different from that of hexagonal TiNi₃ was also obtained. An example is shown in Fig. 8(b) with the bright field image (a) and the dark field image (c). The diffraction pattern is in good agreement with that from the rhombohedral Ti(Ti₀.₁₁Ni₀.₈₉)₃ with the symmetry of R3m. This phase can also be treated as the hexagonal system with the lattice constant of a₀ = 0.2549 nm and c₀ = 0.43648 nm.

In the TiNi-region, the structure is divided into layers as in Fig. 5. The Ni rich layer contains much less dislocations and can be identified as the cubic TiNi by the selected area electron diffraction pattern. While the Ni poor layer shows the martensitic structure with high dislocation density and can be identified as the monoclinic TiNi as in Fig. 9.

The next layer is fcc Ti₂Ni and the dislocation density within these grains is significant low as in Fig. 10. In the final layer, the pearlitic structure comprising Ti₂Ni and α-Ti form with

![Graph showing Ni concentration](image)

**Fig. 6** STEM/EDS analysis of Ni concentration at the points indicated by numbers in Fig. 5.

![TEM observation](image)

**Fig. 7** TEM observation of hcp TiNi₃ precipitated in the layer adjacent to the Ni: (a) bright field image, (b) diffraction pattern, (c) its schematic representation.
or without the formation of Widmannstätten 
\( \alpha \)-Ti lathes as in Figs. 11 or 12. However a 
specific crystallographic orientation relation- 
ship between \( \text{Ti}_2\text{Ni} \) and \( \alpha \)-Ti could not be ob-
tained in the present study.

**IV. Discussion**

1. **Diffusion across the bonded interface and microvoid formation**

Although the structure of Ti is hcp at temper-
atures below the \( \beta \)-transus, the diffusion of Ni 
atoms into Ti lowers the \( \alpha \)-\( \beta \) transformation 
temperature as can be expected from the Ti/Ni 
binary alloy phase diagram\(^{[1]}\). Thus the diffu-
sional aspects of Ni atoms or Ti atoms across 
the Ni/Ti interface should be closely exam-
ined. Since the mutual diffusion coefficient for 
Ti atoms in fcc Ni is extremely small, 
\( 3.0 \times 10^{-17} \text{ m}^2\text{s}^{-1} \) at 1073 K\(^{[2]}\), the mean diffusion 
distance of Ti atoms from the interface into 
Ni is almost negligible.

On the other hand, the diffusion of Ni atoms 
in \( \alpha \)-Ti is not well understood, but it is thought 
to be also very slow because \( \alpha \)-Ti is of a close-
packed structure. In order to explain rather 
wide transformed \( \beta \)-region in Ti where Ni 
atoms are enriched as in Fig. 3, the effect of the 
transformation into \( \beta \)-phase by the diffusion 
of Ni atoms should be taken into account. 
Whithin this bcc \( \beta \)-phase layer, the diffusivity 
of Ni atoms at 1073 K is largely enhanced and 
is given as about \( 9 \times 10^{-14} \text{ m}^2\text{s}^{-1} \), being 300

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Fig. 8 TEM observation of rhombohedral \( \text{Ti}(\text{Ti}_{0.11}\text{Ni}_{0.89})_3 \) precipitated together with \( \text{TiNi}_2 \): (a) 
bright field image, (b) dark field image using (01.1) reflection of \( \text{Ti}(\text{Ti}_{0.11}\text{Ni}_{0.89})_3 \), (c) and (d) 
diffraction pattern and its scheme representation.
times larger than that of Ti atoms in Ni\(^{(3)}\).

Such a situation will induce a quite large difference in mass balance across the Ni/Ti interface known as Kirkendall effect and will yield microvoids on the initial Ni/Ti diffusion-bonded interface as in Figs. 3 and 4, although the diffusivities of Ni atoms in the intermetallic compound layers which are not well established should be considered in the more precise sense.

2. Variation of microstructure across the Ti/Ni interface

The quantitative analyses by means both EPMA and STEM/EDS in Figs. 4 and 5 show that the compositions in the layers where the intermetallic compounds form approximately correspond to those of TiNi\(_{3}\), TiNi and Ti\(_2\)Ni respectively. The formation of those compounds can be expected from the Ti/Ni phase diagram. However in the layer where TiNi\(_3\) particles form adjacent to the fcc Ni, Ti(Ti\(_{0.11}\)Ni\(_{0.89}\))\(_3\) particles were indentified to precipitate by the selected area electron diffraction patterns as in Fig. 8. This R3m-type Ti(Ti\(_{0.11}\)Ni\(_{0.89}\))\(_3\) is reported as a high temperature phase in Ti-Ni binary alloys\(^{(4)}\). Pfeifer et al. showed that the valence electron concentration is a dominant factor to determine the stacking sequence of close-packed structures in Ti–Ni–Cu alloys and that the alloys between Ti\(_{25}\)Ni\(_{75}\) and Ti\(_{33}\)Ni\(_{67}\) contain the close-packed phases.

Fig. 9 TEM observation of monoclinic TiNi formed adjacent to a cubic TiNi layer: (a) bright field image, (b) dark field image using (110) reflection, (c) and (d) diffraction pattern and its schematic representation.
with various stacking sequences when quenched from the melt or from relatively high temperature. With increasing the valence electron concentration, the stacking sequence will change from $A^4$, $A^{10}$, $A^9$, to $A^{21}$, where $n$ in $A^n$ is the number of layers parallel to the basal plane of the hexagonal close-packed structures. Considering the composition gradient across the diffusion-bonded Ti/Ni interface and the non equilibrium nature of the diffusion bonding, various stacking variants such as TiNi$_3$ of $A^4$ and Ti(Ti$_{0.11}$Ni$_{0.89}$)$_3$ of $A^{21}$ can be expected to form and to be frozen by the subsequent cooling.

Within the next region of TiNi, both cubic and monoclinic TiNi particles form as layers, Fig. 5. The structure of equiatomic alloys is known to be very sensitive to the composition. For Ti-Ni alloys $M_s$-temperature at which martensitic transformation starts decreases from 350 K to 200 K with increasing Ni concentration. Thus the Ni-rich region will yield a stable CsCl type ordered structure (B2-type), but the decrease of Ni concentration will transform martensitically into monoclinic structure when cooled down to room temperature via $M_s$-temperature. This is in keeping with the observation where the monoclinic martensite forms in the Ti rich layer as in Fig. 9.

The fourth intermetallic compound layer from the fcc Ni consists of Ti$_2$Ni particles as demonstrated in Fig. 10. Next to this layer, the Ni enriched region is transformed into $\beta$-phase at the bonding temperatures by the penetration of Ni atoms and decomposes into Ti$_2$Ni/$\alpha$-Ti eutectoid structure directly or after proeutectoidal Widmannstätten $\alpha$-Ti laths precipitate during the subsequent cooling. Although the eutectoid structure like pearlite normally exhibits a specific crystallographic orientation relationship and a habit plane to minimize the interface energy, the lamellar structure comprising Ti$_2$Ni and $\alpha$-Ti does not show such a relationship. The reason for it is not clear at present.

Fig. 10 TEM observation of cubic Ti$_2$Ni layer: (a) bright field image, (b) and (c) diffraction pattern and its schematic representation.
V. Conclusion

(1) The $\alpha$-Ti phase is transformed into the $\beta$-phase in the vicinity of the Ti/Ni interface by the penetration of Ni atoms into Ti at temperatures slightly below the $\beta$-transus. The diffusion of Ni atoms in Ti at these temperatures occurs via the migration of the $\beta/\alpha$ boundary into the $\alpha$-Ti matrix.

(2) Although the diffusion coefficient of Ti atoms in the close-packed cubic Ni is extremely small, that of Ni atoms in the Ti phase at the temperatures blow the $\beta$-transus is significantly large, because the diffusivity of Ni in the Ti atoms is enhanced by the transformation into
$\beta$-phase induced by the Ni penetration. This induces Kirkendall effect and results in the microvoid nucleation at the initial Ni/Ti bonded interface.

(3) Across the Ni/Ti bonded interface from the Ni- to Ti-sides, the intermetallic compound layers, i.e., hexagonal TiNi$_3$ [and Ti(Ti$_{0.11}$Ni$_{0.89}$)$_3$], cubic TiNi, monoclinic TiNi, and hexagonal Ti$_2$Ni are formed.

(4) The region where the $\alpha$-Ti transforms into bcc $\beta$-phase without intermetallic compound formation at the bonded temperatures decomposes into the lamellar Ti$_2$Ni eutectoid structure directly or after the Widmannstätten proeutectoidal $\alpha$-lath formation during cooling to room temperature.

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