Complex Oxide Layer at a Nickel/Steel Interface Bonded under a Moderate Vacuum Condition

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Microstructures of a nickel/austenitic-steel (AISI304) interface, which has been bonded through *in-situ* cold-rolling of clean surfaces (pre-sputtered by argon ion) within a vacuum apparatus ($\sim 10^{-3}$ Pa), then followed by an annealing at 500°C, are investigated by transmission electron microscopy. We frequently find significant traces of thin oxide layers of 5–10 nm in thickness, which commonly reveal complex microstructures composed of bi-layers of different types of oxides. Origin of such interface oxides is presumably due to a slight oxygen contamination of the sputtered-surface in the present moderate vacuum condition, and the oxide precipitation at the bonded-interface has been promoted during annealing. Concerning that the strength of the present Ni/steel cold-rolled interface remarkably increases during an early stage of the annealing at 500°C, it is concluded that their strong interface bonding is supported both by nanometric oxide-layers as well as direct metal/metal contacts.

KEY WORDS: interface structure; surface activated bonding (SAB); scanning transmission electron microscopy; diffusion bonding.

1. Introduction

Solid-state bonding has long been used for many applications, since it enables dissimilar metals/alloys to be joined together without significant changes of microstructures and/or shapes at the joints.^{1–4)} A solid-state bonding is generally composed of a pressurizing process and following annealing at high temperatures (*e.g.* 1/2–2/3 of melting temperature). During the pressurizing stage, the surface contact area largely increases by a rapid deformation localized around the joint interface. Then, during the annealing stage, bonding strength is increased by diffusional processes such as creep deformation, grain boundary migration and void elimination.¹⁾ Earlier studies pointed out that, for most cases, clean surfaces are essential to obtain strong joints between the metals and/or alloys, since surface contamination prevents an intimate contact between the surfaces; therefore, most solid-state bonding processes are conducted in a protective atmosphere such as a vacuum or an inert gas.^{1,2)} For an extreme example, it is shown that an ultra-high vacuum ($\sim 10^{-8}$ Pa) bonding achieves strong metal-metal bonding even at room temperature.^{5–7)} Contrary to the most solid-state bonding processes utilizing protective atmosphere, laminated steels constructed by brittle/ductile layers^{8–10)} are successfully fabricated by cold rolling in the air, followed by a short time annealing at around 1 000°C. The dissimilar steels are firmly bonded even without protective atmosphere, because surface oxide layers on the original steel

sheets are mostly crushed into small pieces due to a severe plastic deformation during cold-rolling (reduction in thickness $\sim 60\%$), and recrystallized grains grow and stride over the original cold-rolled interfaces during the annealing.^{11,12)} During systematic attempts of various roll-bonding procedures of the laminated steels, Nambu *et al.* have found that even the annealing below a recrystallization temperature is able to achieve a firm bonding when combined with a unique surface activated bonding (SAB) under a moderate vacuum condition ($\sim 10^{-3}$ Pa). The SAB is a solid-state bonding method via pre-surface polishing/activation by Ar-ion sputtering to obtain clean surfaces, followed by *in-situ* cold rolling with a small reduction in thickness ($\sim 1\text{--}3\%$); the both processes are performed in a pre-evacuated system. After the roll-bonding, the laminated sheet is then subjected for annealing at temperatures below recrystallization temperature. In the case of a SAB-processed Ni/austenitic-steel (AISI304) laminate, the bonding strength of the interface significantly increases and almost reaches at its maximum value in the relatively early stage of low-temperature annealing.¹³⁾ In this paper, we will investigate the detailed microstructures of the SAB-processed Ni/austenitic-steel interface by using transmission electron microscopy (TEM) and scanning transmission electron microscopy combined with energy dispersive spectroscopy (STEM-EDS), in order to elucidate the roll-bonding mechanism under the moderate vacuum condition.

Fig. 1. Bright field TEM image of a Ni/austenitic-steel interface. The insets show magnified images around the defects.

2. Experimental Procedures

Compositions of the original Ni and austenitic stainless steel (AISI304) are pure Ni (>99 mass%) and Fe-0.04C-0.49Si-0.90Mn-0.032P-0.003S-8.05Ni-18.17Cr (mass%), respectively. The Ni/austenitic-steel bi-layered sheets were bonded through the SAB process combined with *in-situ* cold rolling (thickness reduction ~1–3%); original surfaces were sputtered/activated by Ar radio frequency plasma etching, and then they were immediately bonded by cold rolling in a vacuum apparatus with several chambers (each chamber was pre-evacuated to at least 10^{-3} Pa before sputtering/roll-bonding). Original surface oxide layers should be fully removed by the Ar etching. Details of the SAB roll bonding process are described elsewhere.^{13,14} After the roll-bonding, the Ni/austenitic-steel sheets were annealed at 500°C for 100 minutes to obtain strongly-bonded interfaces.¹³ For TEM observations, cross sections were cut from the bulk sheets, polished by abrasive paper and diamond paste, and finally thinned by an Ar ion mill. TEM, STEM-EDS and high-resolution transmission electron microscopy (HRTEM) were performed by using a JEOL 2010F microscope operated at an acceleration voltage of 200 kV equipped with an EDS detector. Composition mapping analysis was constructed by using C–K, O–K, Fe–K, Ni–K and Cr–K lines. When calculating the O map, there is a considerable contribution from Cr–L lines to the O–K intensity (energy window: 440–550 eV), and therefore we corrected the O–K intensity by an estimated Cr–L contribution from Cr–K intensity. The ratio of the Cr–L contribution to the Cr–K was determined by Gaussian peak fitting of an EDS spectrum taken from the stainless layer (the estimated ratio: ~10%), and the calculated contribution of the Cr–L to the O–K has been subtracted.

3. Results and Discussions

Figure 1 shows an interface between Ni and austenitic-steel sheets bonded through the SAB method followed by annealing at 500°C. Most part of the interface is well-bonded (*i.e.* “defect-free”), except obvious few defects at the interface. As represented by the inset images in Fig. 1, these defects are voids or relatively large oxide blocks (~20–100 nm in thickness), both of which are probably inherited from the non-uniformly ion etched surface and/or the initial surface roughness. It is noteworthy here that volume diffusion of Fe and Cr is insignificant at 500°C, and hence void annihilations may not take place during the annealing (dif-

Fig. 2. Bright field TEM image of a Ni/austenitic-steel interface with strain-induced martensite in the stainless steel.

fusion coefficient of Fe and Cr in a Fe-17Cr-12Ni alloy are estimated to be an order of $\sim 10^{-18}$ m²/s at 500°C¹⁵). Another important feature is that both the Ni and austenitic-steel layers are slightly deformed, as confirmed by the traces of dislocation contrast in the layers (Fig. 1). At a few regions around the interface, it is also confirmed that the austenitic steel is partially transformed into strain-induced martensite laths as shown in **Fig. 2**. These facts indicate that there occurred the local large plastic strains around the interface, even though the given reduction in total thickness is only a few % for the present cold-rolling process.

The apparent defect-free interface area in Fig. 1 are actually divided into two types; one is the interface with a metal-metal direct contract, and the other is the interface composed of thin oxide layers with a thickness of 5–10 nm. For the case of the metal-metal contract, the interfaces seem to be firmly bonded as if they were ordinary grain boundaries, as shown in **Fig. 3(a)**. The corresponding HRTEM image of Fig. 3(b) reveals a clean boundary at an atomic-scale, confirming that the Ni and austenitic-steel layers are directly bonded without any intermediate layers or nano-sized precipitations. In addition, no significant oxygen segregation or oxide precipitation was observed at metal-metal direct contact interfaces by STEM-EDS (not shown), even though the EDS oxygen detection limit is more than 1 mass% under existence of Cr. Generally, this kind of metal-metal clean interface is known to be formed when the solid-state bonding is accomplished under an ultra-high vacuum condition; for example, $< 10^{-8}$ Pa for Al–Al bonding,⁵ otherwise the oxide layers essentially accompany with the interface bonded

Fig. 3. (a) Bright field TEM image of a Ni/austenitic-steel interface without any oxide layers, and (b) low-pass filtered high resolution image. The inset shows a Fourier transform of (b).

under the vacuum of an order $\sim 10^{-5}$ Pa⁵⁾ due to a surface contamination before bonding. For the present Ni/austenitic-steel case, the degree of vacuum for the SAB process is not sufficiently high ($\sim 10^{-3}$ Pa), and therefore the intermediate oxide layer originated from surface contaminations indeed occurs, as described in the last paragraph of this section. Nevertheless, the partial metal-metal direct contracts are found to be formed for the present Ni/austenitic-steel interface, which are probably due to dynamical formation of new clean surfaces by destroying the original contamination layers during the cold-rolling. Of course, the metal-metal direct contracts significantly contribute for the firm interface bonding.

Figure 4(a) shows the representative Ni/austenitic-steel interface with a thin oxide layer, together with elemental distribution maps obtained by STEM-EDS (Figs. 4(b)–4(e)). The Ni and austenitic-steel layers are bonded by sandwiching the oxide layer of 5–10 nm in thickness, which mostly consists of Cr and O. The composition profiles across the interface (Fig. 4(f)) are steeply changed at the interface with the small peaks of Cr and O, suggesting that there is no significant interdiffusion beyond the oxide layer. The oxygen intensity is slightly stronger for the stainless region, even though we subtracted the contribution from Cr–L lines. The apparent oxygen enrichment in the stainless layer may be caused by an underestimation of the Cr–L contribution, or by slight oxygen contamination occurred after the ion polishing of the TEM foil. In any cases, the high concentration of oxygen at the interface is evident since the O–K intensity is much higher than the neighbor layers. It may be noteworthy that Cr-rich small particles, which are identified to be a $M_{23}C_6$ -type carbide, are formed within the austenitic-steel layer near the interface region (see Fig. 4(e)). As discussed in the previous paper,¹¹⁾ carbide precipitation around the layered-steel interfaces is driven by a steep change of C chemical potential across the interface; *i.e.* C diffusion is sufficiently fast even at the present annealing temperature of 500°C (diffusion coefficient of C in an AISI316 austenitic stainless steel, whose composition is similar to that of the AISI304, is 10^{-16} m²/s at 453°C¹⁶⁾).

We find that the thin oxide layer (**Fig. 5(a)**) actually possesses a complex bi-layered structure; see the HRTEM image of Fig. 5(b). The oxide layer can be roughly divided into two parts, as represented by oxide-layer 1 and 2 in Fig. 5(b). The oxide-layer 1 attached on the austenitic-steel side seems to be grown from the austenitic steel, as implied by

the continuous lattice fringes between the oxide-layer and austenitic steel (Fig. 5(b)). Diffraction analysis (Figs. 5(c)–5(d)) shows that the structure of the oxide-layer 1 is identified to be the cubic (Fe, Cr)₃O₄-type (spinel), and confirms a certain lattice relationship between the oxide and the austenitic steel; $\langle 100 \rangle$ of the (Fe, Cr)₃O₄ is almost parallel to the $\langle 111 \rangle$ of the austenitic steel with a misalignment ~ 4 degrees. This orientation relationship is well supported by the remarkably small lattice mismatch between $\{400\}_{(Fe, Cr)_3O_4}$ and $\{111\}_{austenite}$, as estimated to be about 0.52% (their lattice constants are 0.8379 nm¹⁷⁾ and 0.361 nm¹⁸⁾ for the cubic FeCr₂O₄ (spinel-type) and the face-centered cubic (austenitic) steel, respectively).

As for the oxide-layer 2 attached on the Ni side, we were not able to identify its structure and a definite orientation relationship with the neighbor layers. Although no obvious lattice fringes are observed in Fig. 5(b), the oxide-layer 2 is considered to be not amorphous but crystalline phase, since a pair of residual diffraction spots (*i.e.* those not indexed by the austenitic steel or Ni) seem to be originated from this oxide area (Fig. 5(d)). It should be remembered here that the oxide-layer 2 at the Ni side is also composed of Cr and Fe as confirmed by the EDS analysis in Fig. 4(f). The reason for the Cr-rich content even for the Ni-side oxide is probably due to the stronger formability of Cr oxide than Ni or Fe oxide; the metal-oxygen bond formation enthalpies of Ni, Fe and Cr are –240, –272 and –383 kJ/mol, respectively.¹⁹⁾ Considering the fact that the most probable oxygen source for the oxide-layer 2 is contamination at the original Ni surface, growth of the oxide at the Ni side is primary governed by a Cr (and Fe) supply from the austenitic-steel surface.

Finally, we briefly discuss the formation mechanism of the intermediate oxide layer at the roll-bonded Ni/austenitic-steel interface. Most of the original surface oxide existed at the Ni and austenitic-steel sheets must have been removed by the Ar-ion sputtering, and hence these pre-existing oxides are hardly observed as shown in Fig. 1, except the few retained oxide blocks. Concerning the oxygen source to form the present thin oxide-layer (Fig. 5), we should remember that the present *in-situ* cold-rolling was made in a relatively low vacuum ($\sim 10^{-3}$ Pa) condition. That is, the oxygen may be supplied from the chamber atmosphere onto the cleaned, activated surfaces even after the Ar-ion sputtering, and these surface contaminations would still remain at the mechanically-bonded interfaces formed by the cold-rolling. Consequently, the as-rolled interface is assumed to be slightly oxygen-rich conditions, which would promote oxide precipitations during the annealing and form the (Fe, Cr)₃O₄ and Fe–Cr oxides (not fully identified) onto the austenitic-steel and Ni layers, respectively (Figs. 5(e)–5(f)). Because of a dynamical deformation process during the cold-rolling, clean surfaces to form direct metal-metal contracts (Fig. 3) are simultaneously generated. The complex bi-layered structure of the present oxide-layer (Fig. 5) can be explained by the far equilibrium growth of the oxides under a restricted Cr supply. That is, Cr supply from the austenitic-steel surface is limited by the diffusion from the relevant surface oxide, which may be immediately nucleated and started growing at the early stage of the annealing (*e.g.* less than 5 minutes to grow the (Fe, Cr)₃O₄ spinel on a Fe-18Cr (mass%) alloy surface at 800°C²⁰⁾). It is noteworthy

Fig. 4. (a) Bright field TEM image of an interface with oxide layers, and (b)–(e) element distributions for O, Fe, Ni and Cr, respectively; (f) averaged concentration profiles across the interface. The profiles are obtained by integrating the spectra over the ~ 100 nm area along the interface.

Fig. 5. (a) Bright field TEM image of an interface with oxide layers, (b) low-pass filtered high resolution image, (c) corresponding selected area diffraction pattern, (d) indexed diagram for (c), (e) schematic diagram of the interface in a cross section and (f) schematic diagram of the oxide layer morphology. The schematic of (f) represents the 2-dimensional distribution of the thin oxide layers at the bonded interface.

here that a bi-layered structure of two different spinels was observed for scale layers of a Cr steel,²¹⁾ where it was suggested that the Cr diffusion controls the growth of the layers. We note that growth of the present spinel oxides can be effectively enhanced when nucleated on the host austenite crystalline surface with favorable semi-epitaxial conditions, like the one described with Fig. 5(c). Although details of the Fe–Cr oxides formed onto the Ni layer are not fully identified, it is nevertheless concluded that the present Ni/austenitic-steel has been firmly bonded even sandwiching such oxide layers, where the microstructures appear to be seamless without any tiny voids. To further understand the relationship between bonding strength and interface microstructure, actual 2-dimensional distribution of the thin oxide layer (Fig. 5(f)) needs to be understood as well as the ratio between the oxide sandwiching interface and clean interface. We are planning so-called “plane-view” type observations by TEM for evaluating the 2-dimensional distribution and the ratio. In the future, we can discuss the relationship between the bonding strength and interface microstructure on the basis of a quantitative analysis.

4. Summary

In summary, the complex oxide layers as well as the metal-metal direct contracts are presented at the roll-bonded Ni/austenitic-steel interfaces. The complex bi-layered oxide is constructed by a spinel-type (Fe, Cr)₃O₄ and another type of oxide, where the microstructures are seamless without any voids. The (Fe, Cr)₃O₄ oxide layer, which was immediately grown from the austenitic-steel layer with semi-epitaxial conditions, presumably limits a Cr/Fe supply to the next oxide layer, consequently yielding the bi-layered structure.

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