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Effects of Post Heat Treatment on the Mechanical Properties of Cold-Rolled Ti/Cu Clad Sheet

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Abstract: Titanium and titanium alloys have excellent corrosion and heat resistance, but weak electric and thermal conductivity. The weak conductivity of titanium can be overcome by cladding with copper, which has high conductivity. Although titanium is expensive, it is selected as a material suitable for applications requiring corrosion resistance such as in heat exchangers. This study was to investigate the effect of post heat treatment on the mechanical properties of the Ti/Cu cold-rolled clad plate by using the interfacial diffusion bonding. A titanium clad by cold rolling should be heat-treated after the rolling process to improve the bonding properties through the diffusion of metals and removal of residual stress due to work hardening, despite the easy formation of intermetallic compounds of Ti and Cu. As a result post-treatment, the elongation was improved by more than two times from 21% to max. 53% by the Ti-Cu interface diffusion phenomenon and the average tensile strength of the 450 °C heat-treated specimens was 353 MPa. By securing high elongation while maintaining excellent tensile and yield strength through post-treatment, the formability of Ti-Cu clad plate can be greatly improved.

Keywords: Ti-Cu clad; post heat treatment; rolling process; intermetallic compound

1. Introduction

There is a steady increase in the need for materials with improved functions and mechanical properties. When it is difficult to use a single metal in order to reduce costs and achieve complex properties, two or more metals may be welded to form a composite material. The commonly used clad composites include Ti/Cu, Ti/Cu/Ti, and Ti/Al/STS [1–3]. The advantage of the clad composite is that superior properties can be achieved through the combination of the excellent properties of different metals. For example, titanium exhibits high strength and good corrosion resistance, while copper exhibits high heat and electrical conductivity. The titanium clad formed by combining them is a high value-added composite sheet that can be used in heat exchangers, electrode materials, etc., which require high conductivity under severe corrosive environments [4–6].

Clad composites can be manufactured by various methods such as explosive welding, roll bonding, diffusion bonding, and electroplating. Explosive welding allows the fabrication of clad composites with a large surface area that are difficult to obtain by other processes, and it is a short time-consuming process that leads to less brittle compounds. However, this process is expensive and the size and shape of the welded sheets are limited. Moreover, residual stress and plastic deformation at the interface cause stress corrosion cracking, and the material requires stress relief through heat treatment. Diffusion bonding is a time-consuming process because of the need for atomic transfer and requires special considerations such as an appropriate interlayer and temperature to suppress the diffusion and interface degradation. Roll bonding is an efficient and economical process, and the temperature required for rolling can be reached in a relatively short time. Further, it can be easily automated for the high-speed continuous production of materials of various shapes and sizes, and is excellent in productivity [2,7].

In this study, a titanium clad plate was manufactured by a cold-rolling process. By performing heat treatment, the residual stress of the titanium clad plate was removed to improve the workability of the subsequent process, while the bonding properties were improved owing to interfacial diffusion. The purpose of this study was to investigate the effect of post heat treatment on the interfacial characteristics and mechanical properties of the clad plate.

2. Experimental Method

In this study, pure Ti (thickness: 2.0 mm) and Cu (thickness: 4.0 mm) were used, and a titanium clad plate (thickness: 3.0 mm) was manufactured by cold rolling. In order to improve the bonding characteristics at the interface of the titanium clad plate, heat treatment was performed under four conditions; the material was annealed at 450 °C for 0.5 h, 1 h, 2 h, and 4 h and then air-cooled.

The microhardness of Ti, Cu, and the interface was measured to evaluate the basic properties of the sheet shape according to the heat-treatment conditions. The surface of the specimen was ground to #2000 and maintained at a load of 100 gf for 10 s using a micro Vickers hardness tester (Mitutoyo, HM-200, Japan). The hardness of Ti and Cu were measured at intervals of 3 mm, and the hardness of the interface was measured at 5 mm intervals. After manufacturing the specimen with the ASTM E8M subsize specification, the room-temperature mechanical properties of the titanium cladding were evaluated at a tensile speed of 1.5 mm/min at room temperature using a universal testing machine (Instron, 5882, USA).

An X-ray diffractometer (Bruker, AXS D8-Discover, Germany) was used to confirm the presence of intermetallic compounds formed at the interface. To investigate the diffusion behavior of the titanium clad interface according to the heat-treatment time, the atomic concentration distribution around the interface was observed through line analysis using EDAX (Horiba, EX-250, Japan). The fracture analysis of the titanium clad was performed after the tensile test using a field-emission scanning electron microscope (Hitachi, S-4800, Japan).

3. Results and Discussion

A clad composite can have different mechanical properties according to the bonded material and the phase formed at the interface by diffusion through heat treatment. As can be seen from the background microstructures in Figure 1, the Ti-Cu interface under the as-rolled condition hardly exhibited microstructural interfacial bonding due to mechanical bonding by cold rolling. On the other hand, as the post-heat treatment time increases, a microstructure in which the interfacial bonding was gradually formed by atomic diffusion can be confirmed. The microstructure of the bonding zone in Figure 1f showed that the interface had an excellent bonding interface despite the marks of the interface caused by different etching solutions for Ti and Cu etching. In order to evaluate the metallic properties at the solid interface of the heat-treated titanium clad, line analysis was performed by EDS, and the results are shown in Figure 1. The heat-treated titanium clad shows a tendency of a gradual decrease in the Ti component from the Ti to Cu side, and the Cu component tends to decrease gradually from the Cu to Ti side. It can be seen that diffusion bonding occurred at the interface through the diffusion of each component at the interface [8]. In addition, as the heat-treatment time increases, the concentration gradient of each component at the interface is gentler.

The distance that Ti and Cu diffused across the interface upon heat treatment is summarized in Table 1. According to a previous study, the diffusion coefficient of Cu in α-Ti is $D_{Cu/Ti} = 3.8 \times 10^{-5}$ $\exp(-195\ \mathrm{kJ \cdot mol^{-1}}/RT) \cdot \mathrm{m^2 \cdot s^{-1}}$ [9], and the diffusion coefficient of Ti in Cu is $D_{Ti/Cu} = 0.693 \times 10^{-4}$ $\exp[-(196 \pm 2)\ \mathrm{kJ \cdot mol^{-1}}/RT] \cdot \mathrm{m^2 \cdot s^{-1}}$ [10]. The diffusion distance is expressed as follows:

$$x = \sqrt{(Dt)} \quad (1)$$

where *x* is the diffusion distance, *D* is the diffusion coefficient, and *t* is time. In this study, the diffusion distance measured by EDS and the theoretical value obtained from Equation (1) are shown in Figure 2. Although the experimental and theoretical values of the diffusion distance are different, they show a similar tendency; that is, the diffusion distance of both Ti and Cu gradually increases as the heat-treatment time increases. Comparison of the diffusion distance between Ti and Cu indicates that the diffusion distance of Ti is large, and that the diffusion speed of Ti in Cu is faster than that of Cu in Ti.

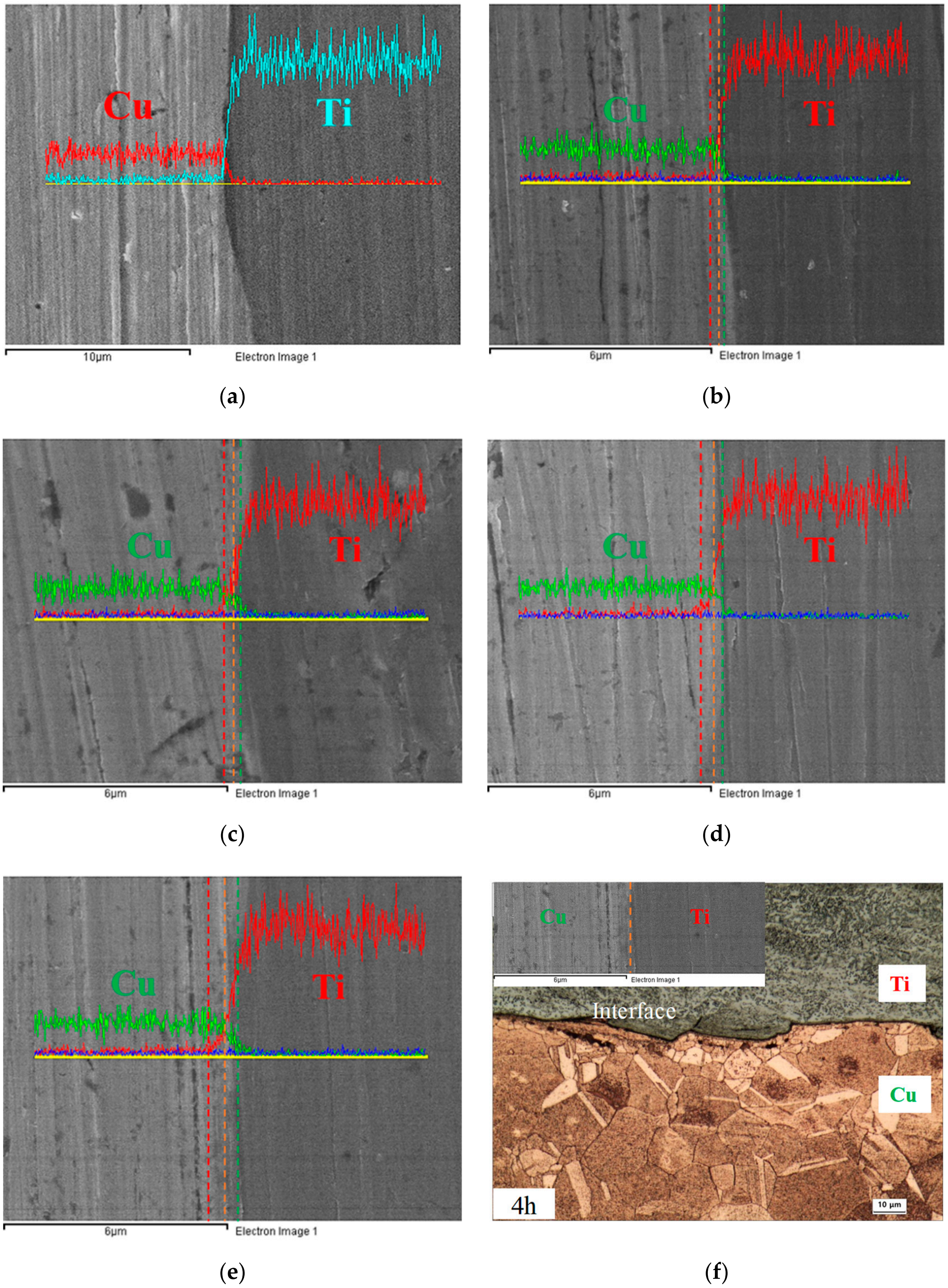

Figure 1. Line scanning analysis results of titanium clad materials: (**a**) as-rolled sample and samples annealed at 450 °C for (**b**) 0.5 h, (**c**) 1 h, (**d**) 2 h, (**e**) 4 h, and (**f**) interfacial microstructure for 4 h.

Table 1. Diffusion distance of each component from the interface layer.

Unit (nm) Specimens	Ti Distance	Cu Distance
0.5 h	219 ± 2.5	151 ± 4.2
1 h	260 ± 10	178 ± 3.7
2 h	329 ± 5.2	233 ± 6.4
4 h	453 ± 8.1	343 ± 6.1

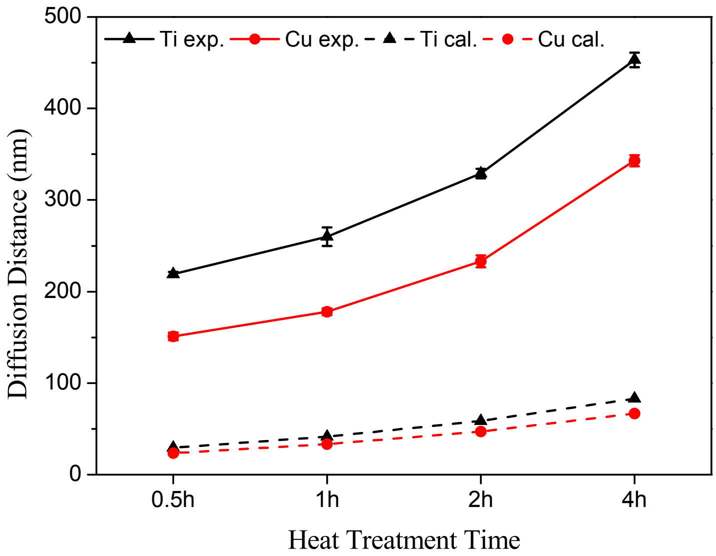

Figure 2. Experimental and theoretical values of diffusion distance.

Figure 3 shows the X-ray diffraction (XRD) patterns collected to identify the intermetallic compounds formed through diffusion induced by the heat treatment at the interface. Initially, only Ti and Cu peaks are observed in the XRD patterns of the as-rolled specimens. On the other hand, the annealed specimens show various peaks of Ti_xCu_y intermetallic compounds, as shown in the Ti–Cu binary diagram [11]. The intermetallic compound, $TiCu_2$, which is stable at high temperature, was not observed in any titanium clad because it is difficult to be formed at the heat treatment temperature of 450 °C used in this study.

If the hardness of the interface is too high, it acts as a crack initiation point at the interface during the forming process, which may lead to fracture; therefore, the hardness at the interface is an important factor. If the reaction layer thickness of the clad is thin, the analysis should be conducted carefully because it represents the average hardness value based on the area ratio of the hardness value of the nearby base metal as well as the reaction layer [12]. Figure 4 shows the Vickers hardness values of the base metal and the reaction layer of each of the as-rolled specimen and the titanium clad heat-treated at 450 °C. When the heat treatment was carried out for 0.5 h, the hardness of both the base metal and the reaction layer decreased. The reason is that the hardness is reduced owing to the removal of the residual stress accumulated in the titanium clad manufactured by cold rolling through heat treatment.

When the heat-treatment time was increased further, Ti and Cu base metals showed negligible change in their hardness values. However, the hardness of the interface increased gradually as the heat-treatment time increased. As can be seen from the EDS results shown above, the diffusion of the components at the joining interface increases with increasing heat-treatment time, thereby leading to the formation of intermetallic compounds and increased hardness. The hardness at the interface is slightly lower than the median value of the Ti and Cu base metals. Unlike the intermetallic compounds that exhibit high hardness at the interface of other dissimilar material clads such as Cu/Al/Cu and Mg/Al/STS, various Ti_xCu_y intermetallic compounds that formed between Ti and Cu exhibit lower hardness than the base metal and thus do not lead to brittleness [12–14]. Therefore, it is expected that the workability and plasticity will be improved in subsequent processes.

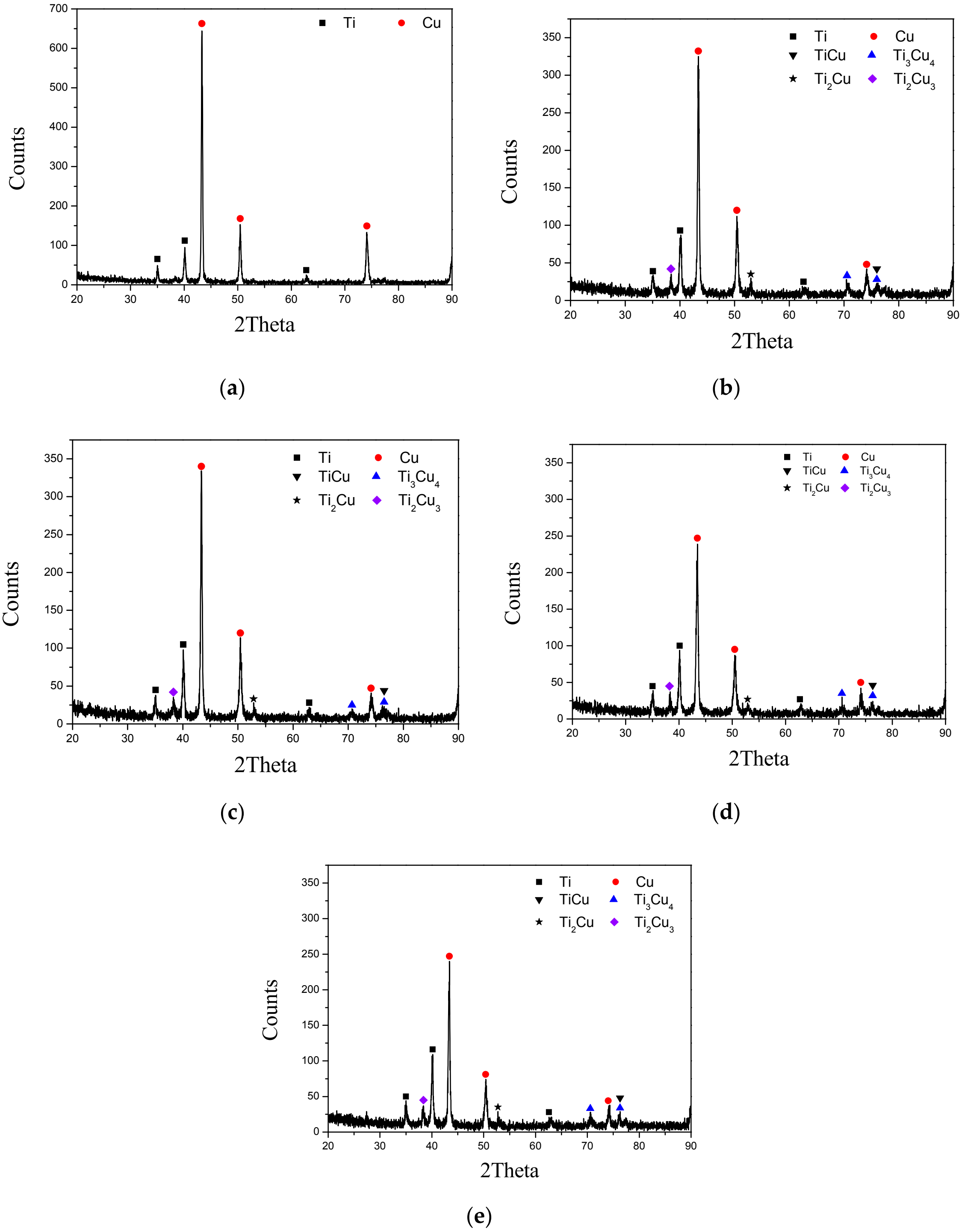

Figure 3. XRD patterns of titanium clad materials: (**a**) as-rolled sample, and samples annealed at 450 °C for (**b**) 0.5 h, (**c**) 1 h, (**d**) 2 h, and (**e**) 4 h.

A titanium clad manufactured by cold rolling should be heat-treated after the rolling process to improve the bonding properties through the diffusion of metals and removal of residual stress due to work hardening. Figure 5 and Table 2 show the results of the room-temperature tensile tests of the as-rolled titanium clad and heat-treated titanium clad. Figure 5 shows the stress–strain curves of the titanium clad, and Table 2 summarizes the tensile properties of Ti and Cu base metals along with those of the titanium clad. As shown in Table 2, the yield strength and tensile strength of the as-rolled titanium clad are 455 MPa and 507 MPa, respectively, and the elongation is ~21%. In general, the deformation behavior of the clad is along the stronger side, with elongation and strength determined by the thickness ratio [15]. The reason why the titanium clad is stronger and shows higher elongation than pure titanium at room temperature is because of the work hardening during the manufacture of cold rolling, and moreover, the Cu layer, which is more ductile during deformation, slows down the crack propagation and fracture of the Ti layer [16]. Thus, preparing and using the clad, rather than using a single metal, result in better mechanical properties.

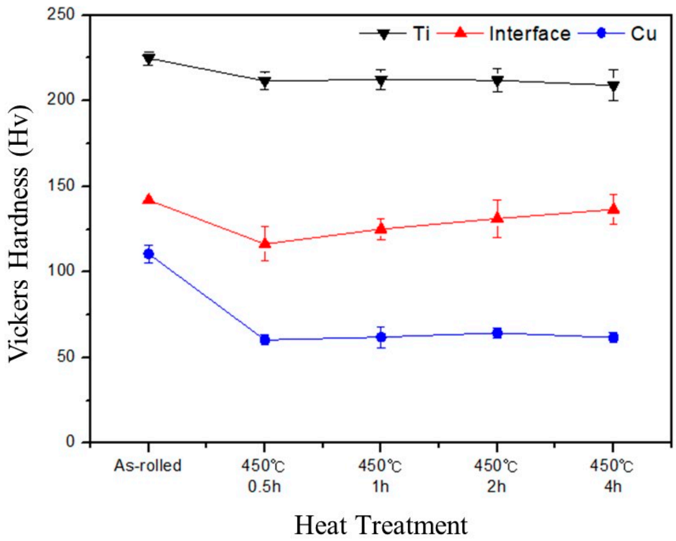

Figure 4. Vickers micro hardness of the component layers (Ti, Cu) and interface layers (Ti/Cu) for as-rolled and annealed clads.

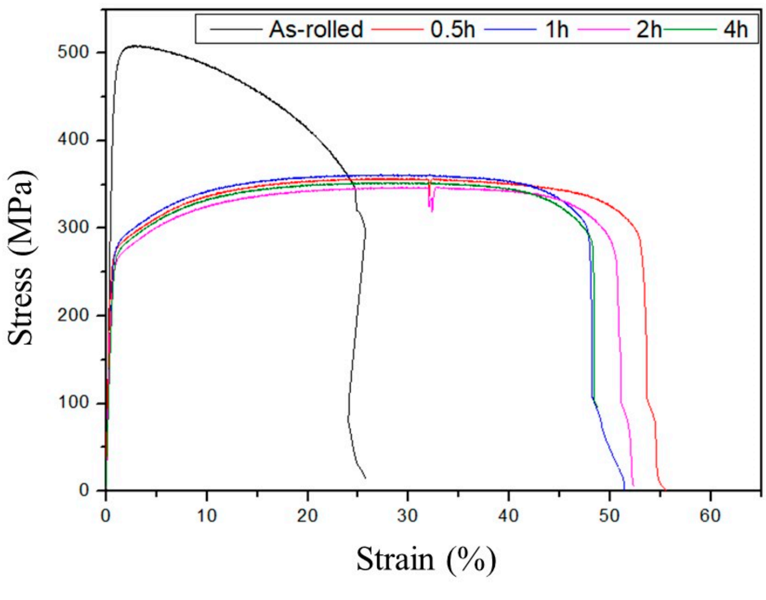

Figure 5. Stress–strain responses of as-roll-bonded clad metals annealed at 450 °C for different times.

As shown in Figure 5, the specimens did not fracture immediately, and a load drop occurred before the final fracture. This is because Ti and Cu act separately due to peeling at the interface, as shown in Figure 6, and the Ti layer fractures first followed by the fracture of the Cu layer [16,17]. According to previous reports, a rapid load drop in the stress–strain curve was also observed in the STS/Al/STS clad [18] and Mg/Al/STS clad [19]. This phenomenon has been explained in relation to the separation of the materials by interfacial crack and independent fracture of the metals that make up the clad. Titanium clad, on the other hand, similar to Cu/Al/Cu clad [12], shows a rapid load drop followed by a final fracture, because both Ti and Cu have good ductility.

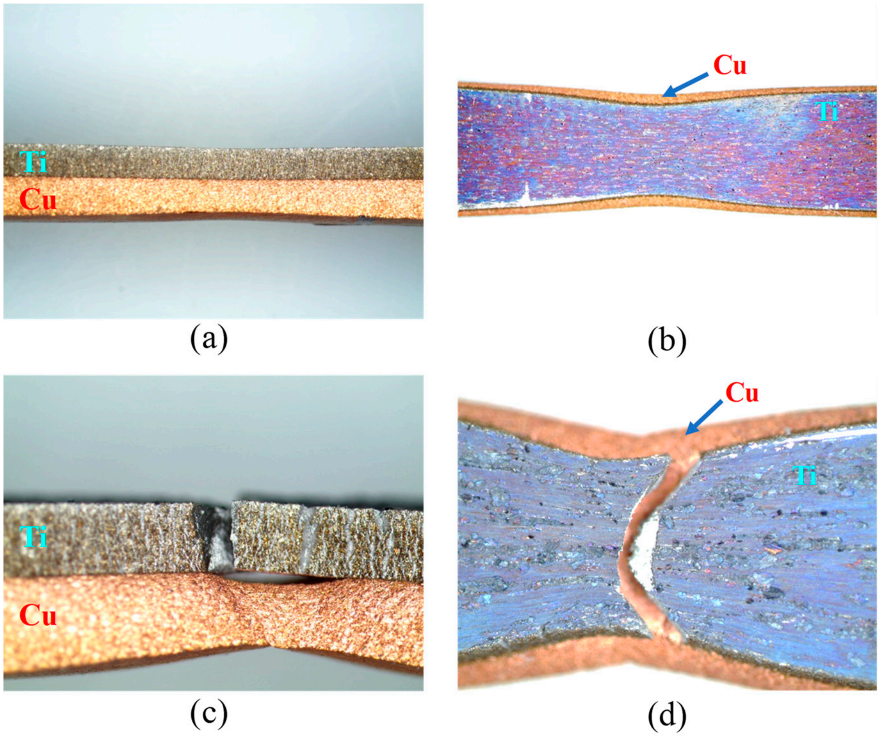

Figure 6. Top-view and side-view of the titanium clad during the tensile test: (**a**,**b**) 1 h and (**c**,**d**) 2 h; (**a**,**c**) side-view and (**b**,**d**) top-view.

After the heat treatment at 450 °C, the mean yield strength and tensile strength of the annealed clad were reduced to 265 and 353 MPa, respectively, compared to those of the as-rolled titanium clad, but the elongation rate was significantly increased by more than twice. Interfacial bonding can be reinforced by atomic diffusion at the interface between dissimilar materials along with strength softening by post heat treatment after work hardening by cold rolling. Due to this, the soft Cu layer may slow down the crack propagation in the Ti layer during tensile deformation. Upon annealing for 2 h, the strength decreased and the elongation increased owing to the general heat-treatment effect. Further, the titanium clad heat-treated for 4 h showed slightly higher strength but lower elongation. The reason is that as the heat-treatment time increases, the diffusion of the components increases and an increased amount of intermetallic compounds is formed, and the strengthening effect of the intermetallic compounds exceeds the softening effect of the heat treatment.

Figure 7a,c,e show the fracture surface of both Ti and Cu at low magnification, the upper part is Ti region and the lower part is Cu region. Figure 7b,d,f show the fracture surface of Ti at high magnification. At low magnification, Ti region showed the typical ductile fracture shape of the cup and cone, and Cu region showed a highly ductile fracture. Dimples were observed in the Ti fracture surface of the as-rolled specimen (Figure 7b) and the specimens heat-treated at 450 °C, 2 h and 4 h (Figure 7d,f). In order to investigate the improvement in the bonding force at the interface, the end of the fracture surface was cut and the cross-section of the fracture surface was observed by SEM, as shown in Figure 8. After the tensile test, Cu with low strength and high elongation shows a rougher surface than Ti. In addition, when the fracture surface inside the Ti interface-section was observed, a rougher surface compared to the as-rolled was observed as the heat-treatment time increased to 450 °C, 2 h and 4 h (Figure 8a,c,e). This phenomenon was observed in the fracture surface inside Cu interface-section (Figure 8b,d,f). Through this, it can be confirmed that the bonding strength at the interface was improved owing to diffusion induced by the heat treatment.

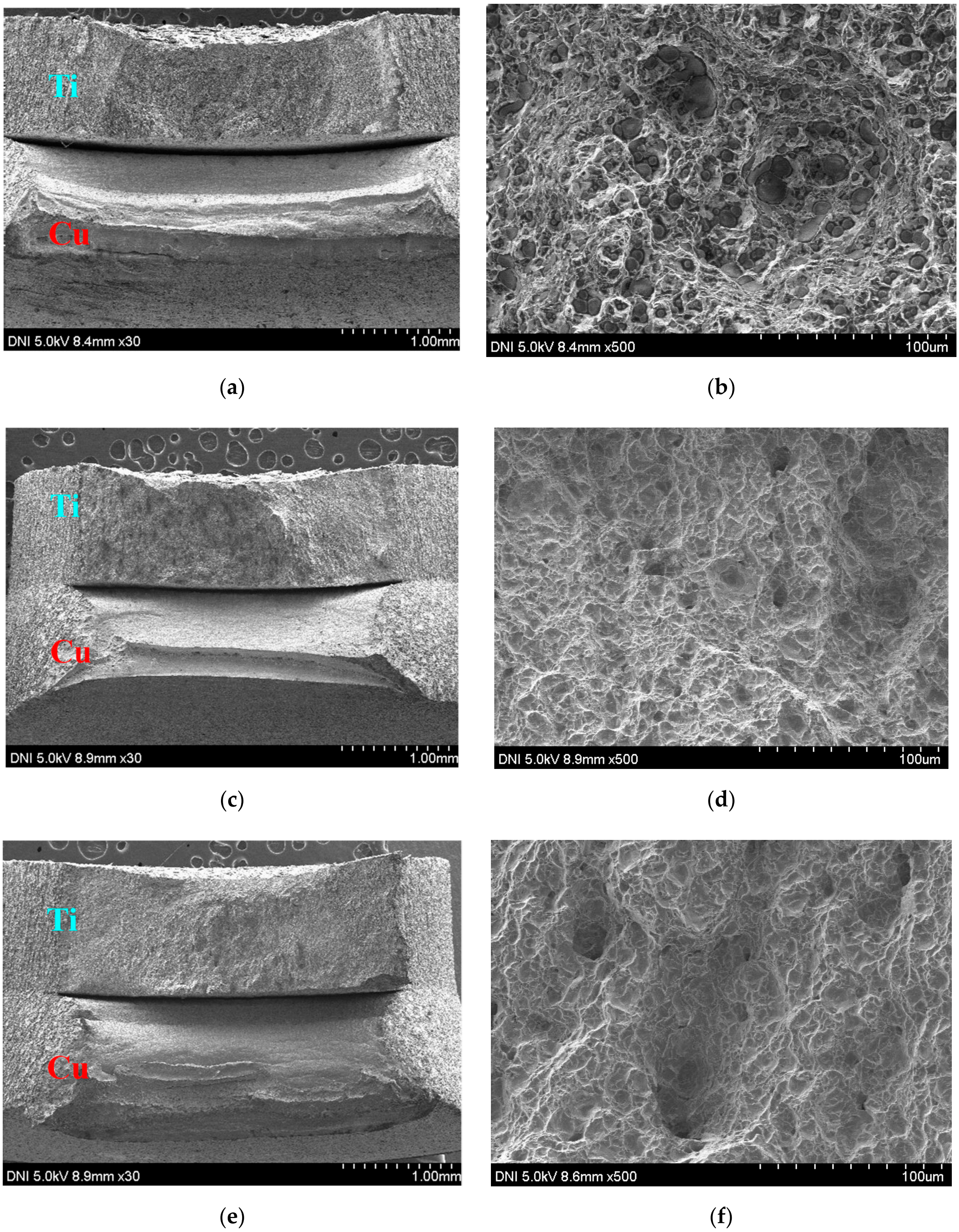

Figure 7. SEM images of fracture surfaces: (**a**,**b**) as-rolled sample; samples annealed at 450 °C for (**c**,**d**) 2 h and (**e**,**f**) 4 h.

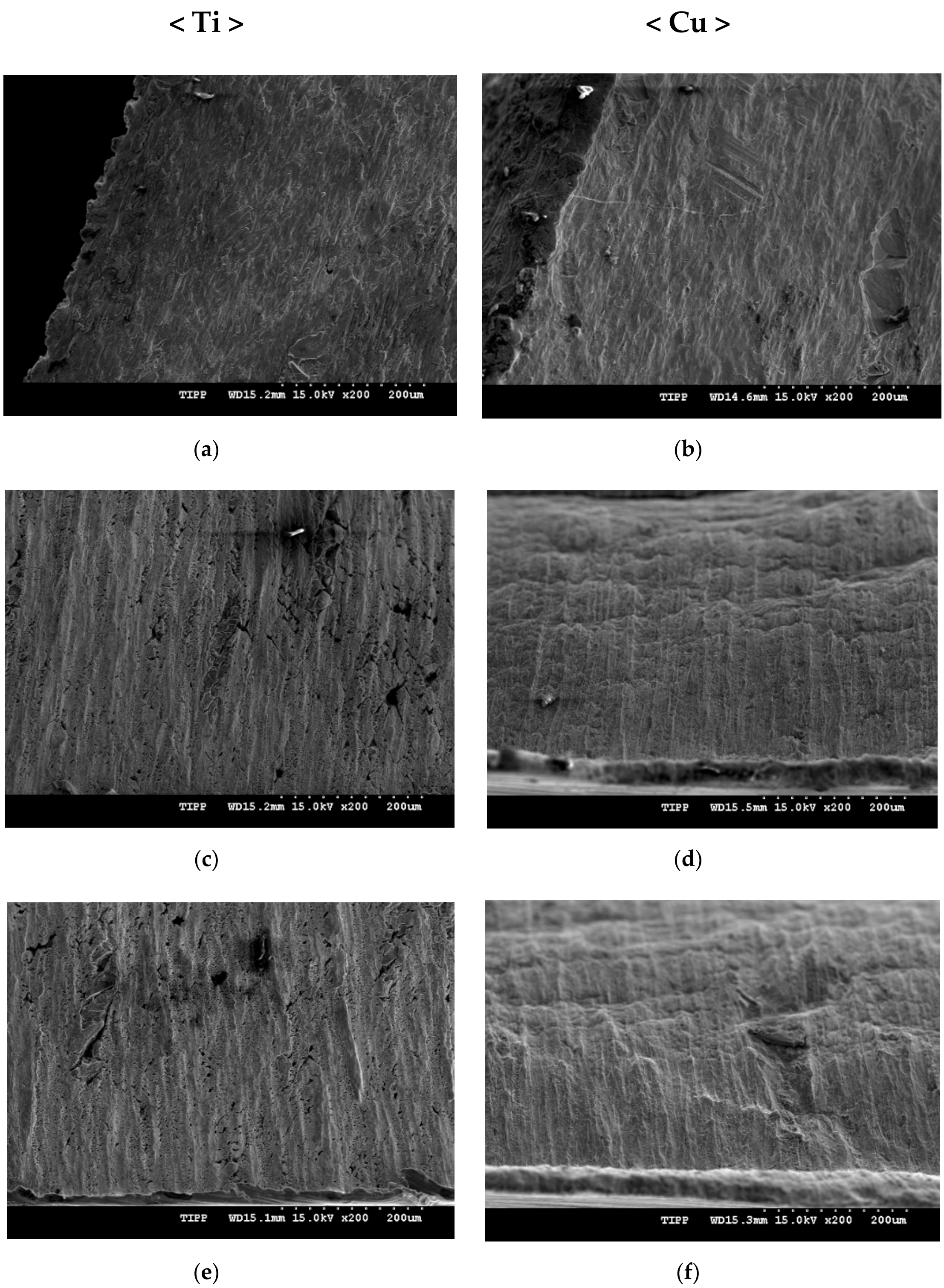

Figure 8. SEM images of the fracture surface in the interface-section of the clad after the tensile test: (**a**,**b**) as-rolled Ti, Cu sample; Ti, Cu sample annealed at 450 °C for (**c**,**d**) 2 h and (**e**,**f**) 4 h.

Table 2. Tensile properties of base metals (Ti and Cu), as-rolled titanium clad, and annealed titanium clad.

Properties Specimens	YS (MPa)	UTS (MPa)	El (%)
Ti	310	344	20
Cu	254	277	36
As-rolled	455 ± 14	507 ± 3	21.4 ± 2.9
450 °C 0.5 h	270 ± 13	357 ± 1	53.3 ± 2.7
450 °C 1 h	272 ± 1	360 ± 1	47.8 ± 1.3
450 °C 2 h	254 ± 6	346 ± 1	50.4 ± 1.2
450 °C 4 h	266 ± 7	352 ± 2	47.9 ± 1.1

4. Conclusions

The mechanical properties of a two-ply titanium–copper clad and the diffusion layer at the bonding interface were analyzed to investigate the effects of post heat treatment, and the following conclusions were drawn:

1. Titanium clads were successfully fabricated and the bond strength at the interface was improved through heat treatment. The average tensile strength of the heat-treated clad was 353 MPa while maintaining excellent tensile and yield strength, and the elongation was improved by more than two times from 21% to max. 53%.
2. In the titanium clad, Ti and Cu components diffused into each other across the Ti/Cu interface during the post heat treatment, and diffusion bonding occurred at the interface. In addition, the thickness of the diffusion layer increased with an increase in the heat-treatment time, and much stronger interface bonding of the Ti/Cu clad occurred.
3. Hardness at the interface increased gradually with increasing heat-treatment time. The tensile strength of the clad decreased slightly after the heat treatment, whereas the elongation increased significantly. This can greatly improve the forming processability of the Ti-Cu dissimilar clad plate.

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Conflicts of Interest: The authors declare no conflict of interest.

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