Interfacial reactions and structural properties of explosively welded titanium/copper plates

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Abstract. In this study, the effect of post-processing heat treatment on the interface morphology and kinetics of intermetallic phase growth in titanium/copper bimetallic sheets were analyzed using a scanning electron microscopy and mechanical testing. Ti/Cu composite was fabricated by explosive welding. Then, clads were subjected to the post-welded annealing at 973 K for times ranging between 15 min and 100 h. In the as-bonded state, the interface shows a wavy character with a limited number of melted zones, which are mostly composed of phases that are not observed in the Ti-Cu equilibrium phase diagram. Short-term annealing is shown to transform non-equilibrium phases into equilibrium ones, such as TiCu4 and Ti2Cu4. For longer annealing times, the growth of four intermetallic sublayers (Ti2Cu, TiCu, Ti3Cu4, and TiCu3) distributed along the entire interface is detected. However, the growth kinetics of particular sublayers was different. Volume fraction estimation of intermetallic phases at annealing times under study revealed the largest thickness for TiCu and TiCu4 phases. The nano-hardness of intermetallic sublayers was found to drop with the Ti content.

1. Introduction

Explosive welding (EXW) is one of the promising and industrially applicable technologies for the fabrication of titanium/copper (Ti/Cu) clads. This is a joining method that enables welding of two dissimilar plates under very high pressure resulting from controlled detonation of explosive charge. Following the explosion, the upper plate (here, Ti) collapses onto the bottom plate (Cu) and a jet of heated gases is formed at the impingement line between two plates [1, 2]. An increase in temperature near the collision line leads to local melting. During solidification, melted zones undergo extremely rapid cooling. This leads to the formation of intermetallics with various chemical compositions and structures. During annealing, the morphology and chemical composition of the solidified melted zones change significantly. Near the bonding interface, the nucleation and growth of new intermetallic phases with various chemical compositions [3-5] is observed. These processes strongly determine the composite properties.

Although numerous bi-layered Cu/Ti composites have been successfully fabricated by EXW, only a few publications have been focused on the Cu/Ti explosive cladding interface behavior [3-5]. To the best of the authors’ knowledge, there are no reports on the interfacial transformations during
annealing.
Therefore, the main goal of this study was to investigate the effect of annealing of EXW clads on the phase transformations in layers near the bonding interface. Short annealing times (below 1 hr) at 973 K were applied to analyze the changes during stress relief annealing, typically applied before technological operation of straightening, whereas longer ones (>1 h) simulated the effect of working conditions on the nucleation and growth kinetics of intermetallic phases near the bonding interface. The interface morphology after annealing was compared to that obtained just after EXW (as-welded state), in order to highlight the effect of post-welded annealing on the structural and chemical composition changes near the interface. Evolution of microstructure was examined using SEM equipped with an energy dispersive spectrometer (EDX) followed by nano-hardness measurements and the Charpy test.

2. Experimental
EXW was performed by High Energy Technologies Works ‘Explomet’ (Opole, Poland). The welding conditions were tailored through the parallel geometry route with a stand-off distance of 1.5 mm (figures 1(a) and 1(b)). The flyer plate and the base plate with dimensions of 200 mm (width) × 350 mm (length) × 3 mm (thickness) were made of deoxidized high phosphorus (DHP) copper and commercial pure (cp) titanium, respectively. The explosive used was ammonium nitrate with fuel oil (ANFO). The use of such an explosive charge led to a detonation velocity of ~ 2500 m/s. Then, explosively welded clads were subjected to the post-welded annealing at 973 K for times in the range between ¼ h and 100 h. The analyses of the interface morphology and chemical composition changes were carried out with the use of a high resolution SEM (FEI Quanta 3D) equipped with an energy-dispersive X-ray spectrometer (EDX). The properties of phases formed during annealing were carried out via nano-indentation with the Berkovich tip. The measurements were conducted on polished surface using Hysitron Triboindenter TL-950 under a load control condition. The maximum load of 10000 µN with a constant loading rate of 400 µNs⁻¹ was applied. In order to study the mechanical properties of as-welded and annealed Cu/Ti bimetallic plates and evaluate the influence of solidified melt zones on the joint integrity, the bending test during dynamic loading was performed. The specimens with no V-notches were tested from the Ti-side using the Charpy hammer - Zwick/Roell RKP450.

Figure 1. Schematic illustration of the explosive cladding set-up. (a) Parallel arrangement of the sheets before welding. (b) The shape changes of the flyer plate during the impact on the base plate after explosion. (c) Typical microstructure close to the interface analyzed in this work. (d) Large melted zone inside the wave vortex was formed in the Cu plate. ED and ND – explosive and normal directions, respectively.
3. Results and discussion

3.1. The as-bonded state, morphology and chemical composition changes inside melted zones

The SEM investigations confirmed a high quality of the joint. No fractures and discontinuities were noted in the parent materials along the interface (figures 1(c) and 1(d)). A wavy morphology of the interface on the longitudinal, i.e. ND/ED section is revealed, where ED and ND are explosive and normal directions, respectively. The average period of wave was ~ 200 µm, whereas the average amplitude ~ 70 µm. The formation of wavy interface coincides with the occurrence of solidified melt zones. Figures 2(a) and 2(b) show the internal structure of solidified melt zone, which is mostly composed of mixture of amorphous volumes, extremely fine-grains, small dendrites and columnar grains. For all analyzed cases non-uniform distribution of different chemical composition, with even pure Ti or Cu inclusions inside the solidified melted zones was observed. Moreover, the concentration of both elements and the occurrence of a given phase inside the solidified melt do not depend on the distance from the parent materials. The distribution of areas with similar chemical composition (similar SEM/BSE contrast) confirms an intense stirring in the reaction zone during wave formation (figure 2(a) and 2(b)), as previously reported experimentally in Zr700/carbon steel [6], Cu/Al [7], Ta/austenitic steel [8] clads and numerically predicted by Bataev et al. [9].

![Figure 2](image_url)

**Figure 2.** (a) Internal microstructure of solidified melt zone of 5 µm, (b) Internal microstructure of solidified melt zone of 3 µm and (c) Typical SEM/EDX line scan along ND showing chemical composition changes inside zone of solidified melt. SEM/BSE imaging and SEM/EDX chemical composition measurements.

In the as-bonded state the phases have tendency to form small, rather irregular, volumes instead of layers (figure 1(d)). The point SEM/EDX analyses show that chemical composition of the large solidified melted zone is strongly diversified; Cu and Ti contents ranged between Cu_{0.18-0.92}Ti_{0.08-0.82}, but in most analyzed cases, the range was between Cu_{0.5}Ti_{0.5} and Cu_{0.5}Ti_{0.5}. This indicates the dominance of Cu-rich phases. Most of these phases do not appear in equilibrium phase diagram. The prevalence of non-equilibrium phases over equilibrium ones can be attributed to a very high cooling rate and high pressure that were imposed on melted volumes during EXW [9-11]. Since the solidification conditions are far from equilibrium, ultra-fine-grained and amorphous phases predominates the zone of solidified melt in the post-welding state. Although most of phases differed from those observed in the equilibrium Cu-Ti phase diagram, there were small areas of chemical compositions corresponding to six equilibrium phases (mostly Cu_{0.5}Ti, Cu_{1}Ti, or CuTi and, to a smaller extent, CuTi, Cu_{1.5}Ti_{1.5}, and Cu_{2}Ti_{3} ), as shown in figure 2(c).

3.2. Phase transformations upon annealing

Structural transformations during annealing are predominantly related to (i) changes occurring inside the pre-existing zones of solidified melt and to (ii) growth of newly formed intermetallic layers of various chemical compositions and structures.
3.2.1. Phase transformations inside the pre-existing zones of solidified melt. For annealing times of $\frac{1}{4}$ and $\frac{1}{2}$ h at 973 K, the most drastic morphological and chemical composition changes were observed in the solidified melt zones. During the first period, the formation of specific lamellar structure of alternatively arranged platelets was observed (figure 3(a)). The kinetics description of the supersaturated (Cu) solid solution during annealing is based on the spinodal decomposition accompanying the precipitation of alternatingly Ti-enriched and Ti-depleted phases with a disordered structure [12, 13]. For longer annealing times the layered structure of platelets systematically disappears and after 1h of annealing occurs only accidentally. SEM/EDX analysis shows that chemical composition of darker and lighter platelets differs slightly, but in both cases of platelets the concentration of Cu is always higher (up to 10%) than of the one observed inside the TiCu$_4$ phase (figure 3(b)). After annealing for 1 h, the structure of platelets was almost completely replaced by nearly equiaxed grains of TiCu$_4$ phase, whereas the ‘average’ chemical composition of the remaining platelets approached Ti$_{0.2}$Cu$_{0.8}$.

3.2.2. The growth of equilibrium phases near the interface. The nucleation and systematic broadening of layers composed of equilibrium phases is observed along the entire length of interface. In principle, six intermetallic products may be formed during annealing, as it is visible on the Ti–Cu binary phase diagram [14]. However, only four compounds were observed in EXW samples annealed at 973 K for times ranging between $\frac{1}{4}$ h and 100 h. The microstructural characterization using SEM/BSE imaging and SEM/EDX analysis indicates that the diffusion controlled processes lead to the formation of a strictly defined sequence of intermetallic phases, i.e. the phases enriched with Ti are formed closer to the Ti plate, whereas those enriched with Cu closer to the Cu plate. Additionally, titanium is a dominant diffuser [15, 16]. Near the Ti plate, a very thin layer of the Ti$_2$Cu phase enriched with Ti was detected.

Next, the formation of a thick TiCu layer, followed by a layer of Ti$_3$Cu$_4$ phase of average thickness and finally a thick TiCu$_4$ phase were detected near the Cu plate (figures 4(a)-4(d)). The TiCu$_2$ and Ti$_2$Cu$_3$ phases, clearly observed near the boundary of diffusion bonded Cu/Ti-6Al-4V composite annealed at higher temperatures 1148 K - 1173 K for $\frac{1}{4}$ h – 1 h [15] are not formed near the interface of EXW cp-Ti/Cu clads. The plot showing kinetics of particular sublayers growth at 973 K is presented in figure 4(e). The total width of reaction layer in the specimen annealed for 1 h was around 5 µm. The thickness of the reaction layer increased to about 35 µm as the time was increased to 100 h of annealing. For very short annealing times the width of the TiCu and TiCu$_4$ phases increases rapidly, whereas the thickness of Ti$_2$Cu and Ti$_3$Cu$_4$ phases increases only slightly and their width reaches very quickly saturation rate. After 1 h and 10 h of annealing the broadest sublayer is formed by the TiCu$_4$ phase. For longer annealing times a systematic growth of the TiCu phase is observed. The reason why

![Figure 3](image-url)
after 100 h of annealing, the thickness of both layers, i.e. TiCu and TiCu₄, is comparable.

**Figure 4.** (a) Formation of the diffusion (sub) layers near the flat part of the interface. Sample annealed at 973 K for 100 h. (b, c) SEM/EDX chemical composition maps showing the Ti and Cu elements distribution near the interface. (d) SEM/EDX line scan along ND (marked in ‘b’) across the interface. (e) The width of the diffusion (sub)layers near the interface after annealing at 973 K for times ranged between ¼ h and 100 h. SEM/BSE imaging and SEM/EDX chemical composition measurements.

### 3.3. Mechanical testing

The results of the nano-hardness measurements show that the indentation depth is much smaller in the intermetallic layers as compared to the Cu and Ti matrix, regardless if the sample is just after EXW or after further annealing. The nano-hardness of the Ti₂Cu phase was evaluated at the level of 4.1 GPa, whereas for other phases was as follows: TiCu – 4.3 GPa, Ti₃Cu₄ – 5.6 GPa and TiCu₄ – 8.6 GPa. The nano-hardness of Cu and Ti is about 1.1 GPa and 2.2 GPa, respectively. From this can be concluded that nano-hardness of given phase decreases as the content of Ti increases. These results are qualitatively similar to those obtained by Konieczny [17], who assessed the micro-hardness of TiCu, Ti₂Cu, eutectoid mixture, and Ti as 783, 681, 342, and 273 HV, respectively. Thus, it is expected that the titanide phases (especially TiCu₄) have the highest contribution to hardness and stiffness of the composite [17].

In order to study the mechanical properties of the Cu/Ti bimetallic plates and to evaluate the influence of macro-/micro-cracks on the integrity of the joint, the three-point bending test at high loading rates (using a Charpy impact hammer) was performed. The impact energy required to fracture a sample (figure 5(a)) and the maximal load (figure 5(b)) in all annealed samples were lower as those measured in the as-welded state. Although no macro-separations of the sheets were observed in all bended samples, a network of macro- and micro-cracks developed more intensively in samples annealed for longer times. The role of the solidified melt zones in the as-welded state is twofold. On the one hand the presence of hard and brittle intermetallic compounds increases the hardness and improves the clad strength properties. On the other hand, the existence of micro- and macro-crack network, which appears due to the shrinkage during solidification of molten materials give rise to crack propagation. The diffusion processes during long-term annealing (10 and 100 h) lead to a significant broadening of intermetallic layers, which contribute to the mechanical strength of the clad but also significantly decrease the ability of clad shaping.
4. Conclusions

The formation of complex, net-like structure near the bonding interface of explosively welded Ti/Cu clads was analyzed using SEM in as-welded and annealed samples. The microstructural changes of the interface region were characterized as a multi-step process. The most important phase transformations upon EXW took place in the weld interface as a result of local melting and formation of solidified melted zones during extremely fast cooling. This gave rise to the formation of ultra-fine-grained or even amorphous phases that mostly do not appear in the equilibrium phase diagram. Upon further annealing, all amorphous phases are transformed into crystalline ones. Triggering diffusion processes during annealing led to the formation of equilibrium phases and to homogenization of chemical composition inside the solidified melt zones, whereas the transfer of atoms across the interface led to the formation of four intermetallic layers (Ti$_2$Cu, TiCu, Ti$_3$Cu$_4$, and TiCu$_4$) distributed along the entire length of interface.

It was found that nano-hardness of intermetallic layers decreases with the content of Ti. The nano-hardness of the Ti$_2$Cu phase was evaluated at the level of 4.0 GPa, whereas for TiCu – 4.3 GPa, Ti$_3$Cu$_4$ – 5.6 GPa and TiCu$_4$ - 8.6 GPa. The Charpy impact test did not provoke macro-separations the plates in all bended samples. However, a network of microcracks developed more intensively in the samples annealed for longer times.

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