Polskie Towarzystwo Materiałów Kompozytowych
Polish Society for Composite Materials

Kompozyty 8: 2 (2008) 168-171

KOMPOZYTY
COMPOSITES

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Otrzymano (Received) 01.02.2008

STRUCTURAL CHANGES DURING FORMATION OF LAMINATED TITANIUM-INTERMETALLIC COMPOSITE

Well-bonded and almost fully dense laminated composites have been fabricated successfully by reactive sintering in vacuum using Ti and Cu foils. Since the copper layers were completely consumed by forming phases, the final microstructure consisted of alternating layers of intermetallic phases and unreacted titanium. Effects of treating time at 900°C and the microstructural changes were studied by interrupting in steps the reaction progressing after 0.5, 1, 2, 3, 4 and 5 hours. With the liquid phase appearance a fast growing of the layers containing intermetallic phases was observed. Because the structure resulting from solidification of locally melted reaction zone contained phases rich in copper (especially $TiCu_4$), melting consumed more copper than titanium. For this reason, the boundary between the intermetallic layers and copper migrated toward the copper side. Microstructural investigations by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) showed that after 0.5 hour of heat treatment at 900°C intermetallic compounds: Ti_2Cu, TiCu, Ti_3Cu_4, Ti_2Cu_3, $TiCu_4$ and solid solution αTi were formed. After the completely consumption of Cu, the intermetallics layer consisted of thin layers of Ti_2Cu (adjacent to eutectioid layer and titanium), thick layers of TiCu and the reaction zone consisting of $TiCu_4$ particles in Ti_3Cu_4+Ti_2Cu_3 matrix. The particles were probably produced by stresses resulting from the growth of the intermetallic layer. Since titanium could diffuse through the Ti_2Cu and TiCu layers to the reaction zone, it leaded to the growth of TiCu at the expense of $TiCu_4$, Ti_3Cu_4 and Ti_2Cu_3. As a result, the TiCu compound became dominant phase if the treating time was longer than 1 hour. After 5 hours of treating the intermetallic layer was transformed almost wholly into TiCu, but with a thick Ti_2Cu interphase layer. The formation of the TiCu phase is thermodynamically favoured over the formation of the other phases and can be understood from the steps occurred through a series of solid-liquid and solid state reactions involving $TiCu_4$ as one of the starting phases.

Keywords: **laminated composite, titanium, copper, intermetallic compounds**

ZMIANY STRUKTURY PODCZAS FORMOWANIA KOMPOZYTU WARSTWOWEGO TYTAN-FAZY MIĘDZYMETALICZNE

Używając folii tytanowej i miedzianej, wytworzono kompozyt tytan-fazy międzymetaliczne, charakteryzujący się dobrym połączeniem warstw i bardzo nieznaczną porowatością. W wyniku reakcji syntezy warstwy miedzi kompletnie przereagowały z częścią tytanu i utworzyły fazy międzymetaliczne. Badano wpływ czasu wygrzewania kompozytu w temperaturze 900°C na jego strukturę. Reakcje syntezy faz przerywano po 0,5, 1, 2, 3, 4 i 5 godzinach. Wraz z pojawieniem się fazy ciekłej zaobserwowano szybki wzrost grubości warstw faz międzymetalicznych. Ponieważ powstałe fazy były bogate w miedź (zwłaszcza faza $TiCu_4$), reakcja pochłaniała więcej miedzi niż tytanu. Z tej przyczyny granice pomiędzy warstwami faz międzymetalicznych i miedzią migrowały w głąb warstw miedzi. Badania z użyciem mikroskopu skaningowego i mikroanalizatora rentgenowskiego wykazały, że w kompozycie wygrzewanym przez 30 minut i następnie chłodzonym razem z piecem (prędkość chłodzenia 0,16°C/s) występowały fazy: Ti_2Cu, TiCu, Ti_3Cu_4, Ti_2Cu_3,$TiCu_4$ oraz roztwór stały miedzi w tytanie (α). Po całkowitym przereagowaniu miedzi warstwy faz międzymetalicznych składały się z cienkich warstw fazy Ti_2Cu (przyległych do warstw eutektoidu (Ti_2Cu+α) i nieprzereagowanego tytanu), grubych warstw fazy TiCu i obszarów zawierających cząstki fazy $TiCu_4$ w osnowie z mieszaniny faz Ti_3Cu_4+Ti_2Cu_3. Cząstki fazy $TiCu_4$ powstały prawdopodobnie na skutek naprężeń występujących podczas wzrostu warstwy faz międzymetalicznych. Ponieważ tytan mógł dyfundować przez warstwy faz Ti_2Cu oraz TiCu, powodowało to wzrost ilości fazy TiCu kosztem faz $TiCu_4$, Ti_3Cu_4 oraz Ti_2Cu_3. W rezultacie tego TiCu stała się dominującą fazą, gdy czas wygrzewania kompozytu w temperaturze 900°C był dłuższy niż 1 godzina. Po pięciu godzinach wygrzewania warstwy faz międzymetalicznych składały się prawie wyłącznie z fazy TiCu i cienkich warstw fazy Ti_2Cu (przyległych do warstw eutektoidu). Formowanie fazy TiCu jako dominującego produktu podczas reakcji pomiędzy tytanem i miedzią jest uzasadnione termodynamicznie i przebiega na drodze kolejnych etapów przemian z udziałem fazy ciekłej i w stanie stałym, a jedną z pierwszych powstających faz jest $TiCu_4$.

Słowa kluczowe: **kompozyt warstwowy, tytan, miedź, związki międzymetaliczne**

INTRODUCTION

Metal-intermetallic composites offer an attractive combination of physical and mechanical properties distinct from the separate constituent phases, e.g. high toughness of the metal coupled with low density, high modulus and high strength of the intermetallic. Methods for the production of laminated composites, consisting of at least one brittle phase, include diffusion bonding [1], magnetron sputtering [2], vacuum plasma spraying [3], vapour deposition [4] and synthesis reactions between dissimilar elemental metal foils [5-9]. Reaction synthesis of multilayers using foils has some advantages over some other methods. The obvious economic benefit in using this technique lies in the ease of processing. Furthermore, the process uses readily available elemental foils, which can easily be shaped prior to the initiation of the synthesis reaction, resulting in the potential to produce near-net-shaped composites. The objective of the present study is to synthesise Ti-intermetallic phases laminated composite through reactive sintering in vacuum using Ti and Cu foils. The microstructure will be characterised by optical and scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Progress of the synthesis process with prolonged time of reaction (0.5÷5 h) between elemental components will be investigated.

EXPERIMENTAL PROCEDURE

Commercially pure Ti (150 μm thick, 99.1 wt. %) and Cu (50 μm thick, 99.99 wt. %) foils were used to fabricate laminated titanium-intermetallic composites. Foils with dimensions of about 30 mm x 10 mm were cut from the titanium and copper sheets and polished on 800 grade abrasive paper. After rinsing in water, rinsing in ethanol, and then drying rapidly, foils were laminated alternately into titanium/copper multilayer samples (8 Ti and 7 Cu layers) and then placed in a vacuum furnace. A pressure of 5 MPa was applied at room temperature to ensure good contact between foils. The temperature was initially raised to 850°C and then the pressure was released to avoid an expulsion of liquid phases. Next, the temperature was raised to 900°C, which was necessary for the start and rapid development of structural process at the interface of titanium and copper [5, 6]. The samples were held at a temperature of 900°C for 0.5, 1, 2, 3, 4 and 5 hours and then were finally furnace-cooled to room temperature (cooling rate of 0.16°C/s). Progress of the synthesis reaction was determined by measuring of the thickness of the intermetallics layer using optical microscopy. After fabrication, the specimens were cut and mechanically polished using standard metallographic techniques. Microstructural observations were performed using an electron microscope JMS 5400 and an optical microscope NEOPHOT 2. For the study of the structure using an optical microscope, the samples were etched with solution of 5 pct HF in water to reveal the titanium grain boundaries and the structure of intermetallic layers. The chemical composition of the phases was determined by comparing an electron microprobe measurements using ISIS 300 Oxford Instruments with the Ti-Cu binary phase diagram [10].

RESULTS

After processing, the composite microstructure consisted of alternating, well-bonded Ti and intermetallic layers. No unreacted Cu was detected in any of the processed composites. Figure 1 shows layers formed in the titanium/copper multilayer samples, which were held for 0.5, 1 and 2 hours at 900°C.

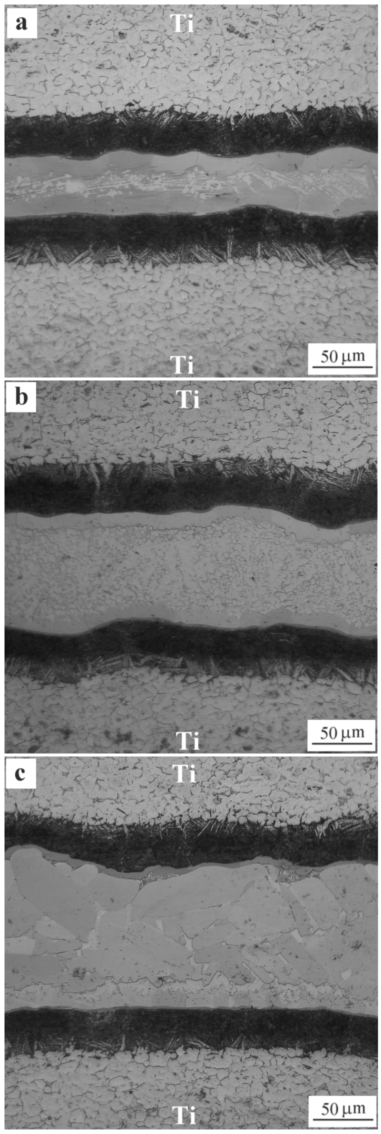

Fig. 1. Microstructures of the intermetallic layers treated at 900°C for: a) 0.5 h, b) 1 h and c) 2 h

Rys. 1. Mikrostruktury warstw faz międzymetalicznych uzyskanych po 0,5 h (a), 1 h (b) i 2 h (c) wygrzewania w temperaturze 900°C

The thickness of intermetallic layers was measured as a function of treating time at a temperature of 900°C. Results of the measurements are shown in Figure 2.

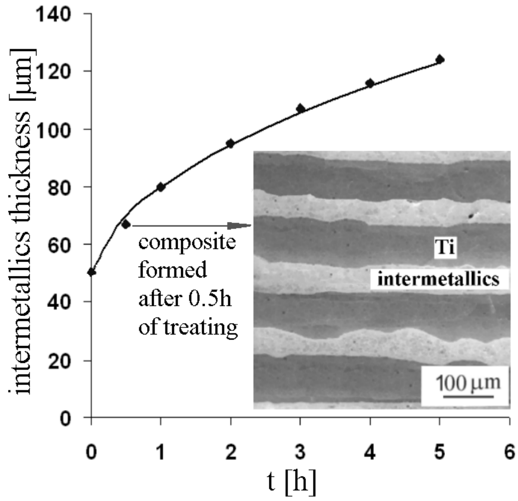

Fig. 2. The thickness of intermetallic phases layer as a function of annealing time

Rys. 2. Grubość warstwy faz międzymetalicznych jako funkcja czasu wygrzewania

The thickness of the elemental copper foil affects the final thickness of the resultant intermetallic layer. If the copper layer (initially 50 μm thick) is transformed completely into intermetallic phases the thickness of intermetallic layer can be expressed as

$$x = 35t^{0,5} + 45 \quad (1)$$

where x is the thickness of the intermetallic layer and t is the treating time. The reaction-diffusion growth kinetics of intermetallic layers is usually described using generally accepted parabolic equation

$$x = A\,t^n \quad (2)$$

where A is the layer growth-rate constant and n is the time exponent. The value of the time exponent $n = 0.5$ indicates the bulk diffusion with the liquid phase contribution [11]. The final structures of the laminated composite with different intermetallic volume fraction depend on the original metal thickness ratio. Intermetallic volume fraction V_i is expressed as

$$V_i = \frac{r}{(1-w)\cdot\frac{\rho_i}{\rho_{Cu}} + (1-w\cdot\frac{\rho_i}{\rho_{Ti}})\cdot r} \quad (3)$$

where r is ratio of the original copper to titanium thickness, w is titanium weight percent in the intermetallic product, ρ_i is the density of intermetallic layers, ρ_{Cu} and ρ_{Ti} are the density of copper and titanium, respectively [12].

An identification of the chemical composition of synthesised phases was performed by a scanning electron microscope equipped with a system for microprobe analysis. Figure 3 shows the typical microstructure of the sample held at a temperature of 900°C for 0.5 hour. The elemental analysis performed by the X-ray spectroscope was made for areas marked A, B, C, D, E and F.

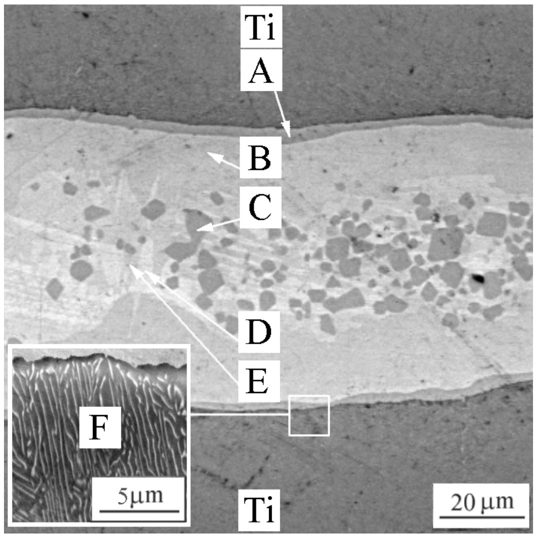

Fig. 3. Microstructure formed after treating for 0.5 hour

Rys. 3. Mikrostruktura utworzona w kompozycie po 30 minutach wygrzewania

A study of above structure was based on the Ti-Cu binary phase diagram [10]. In principle, six intermetallic products would be produced during the reaction. However, only five compounds were observed in the sample. Using X-ray microanalysis, it was found that the A-marked area, containing 67.7 at. % Ti and 32.3 at. % Cu is the Ti_2Cu intermetallic compound. Adjacent to Ti_2Cu, the deeply shaded B-marked area, consists of 51.7 at. % Ti and 48.3 at. % Cu is TiCu. The dark shaded C-marked island with composition of 20.9 at. % Ti and 79.1 at. % Cu is the $TiCu_4$ intermetallic compound. The lightly shaded D-marked region consisting of 42.8 at. % Ti and 57.2 at. % Cu is perhaps Ti_3Cu_4. The E-marked area containing 40.1 at. % Ti and 59.9 at. % Cu is presumably Ti_2Cu_3. According to the phase compositions it is easy to determine that the dark F-marked region containing 89.9 at. % Ti and 10.1 at. % Cu, adjacent to titanium, is the eutectoid mixture of two phases: Ti_2Cu and solid solution of copper in titanium (αTi). A similar analysis was performed for the samples treated at temperatures of 900°C for 1, 2, 3, 4 and 5 hours. Results of the investigations for the samples treated for 1 and 5 hours are shown in Figures 4 and 5.

It is obvious that temperature and time are vital to the formation of different intermetallics. If the treating time is longer than 1 hour the predominant part of the formed structure is the TiCu phase. After 5 hours of treating the intermetallic layer is transformed almost wholly into TiCu (with very thin layers of the Ti_2Cu phase adjacent to eutectoid). Colinet et al. [13] have recently made a thermodynamic assessment of a binary Ti-Cu system measured the enthalpies of formation for various intermetallic phases and claimed that the formation of the TiCu intermetallic compound is thermodynamically favoured over the formation of other phases. However, formation of TiCu as the almost only product during reaction between titanium and copper can be understood from the steps involved in another phases formation, which occur through a series of solid-liquid and solid state reactions involving $TiCu_4$ as one of the starting phases. The thickness of eutectoid layer is almost the same after 0.5, 1, 2, 3, 4 and 5 hours of heat treatment time and equals approximately 40 μm.

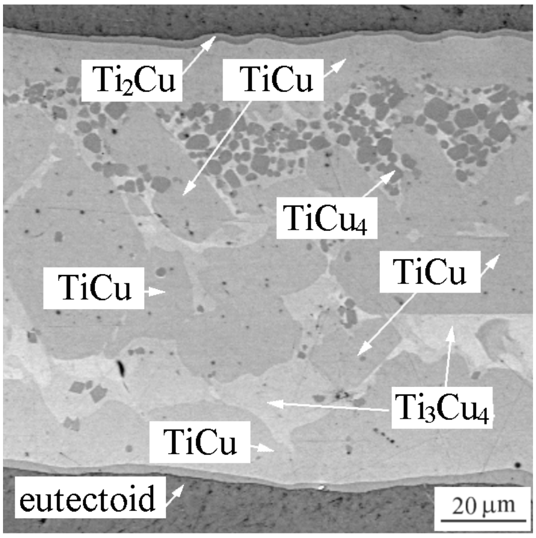

Fig. 4. Microstructure formed after treating for 1 hour

Rys. 4. Mikrostruktura utworzona w kompozycie po godzinie wygrzewania

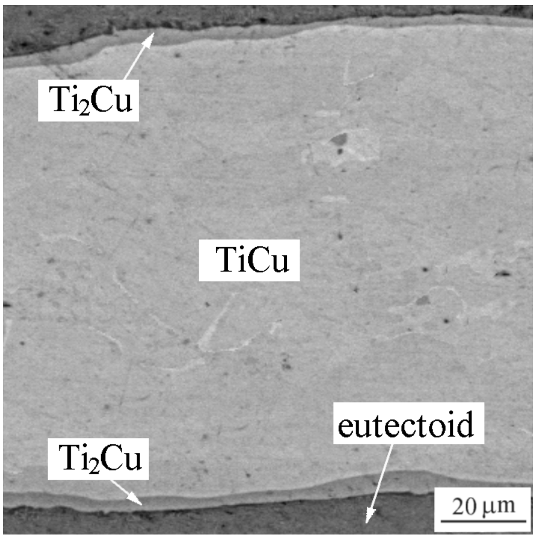

Fig. 5. Microstructure formed after treating for 5 hours

Rys. 5. Mikrostruktura utworzona w kompozycie po pięciu godzinach wygrzewania

CONCLUSIONS

Ti-intermetallic laminated composites have been successfully synthesised by reactive sintering technique in vacuum using Ti and Cu foils. The laminated structure is well bonded, almost fully dense and can be easy designed and controlled. Microstructural characterisation by SEM and X-ray microprobe analysis indicated that TiCu is the predominant intermetallic phase after more than 1 hour of treating. The formation of the TiCu phase is thermodynamically favoured over the formation of other phases such as: Ti_2Cu, TiCu, Ti_3Cu_4, Ti_2Cu_3, $TiCu_4$ and can be understood from the steps involved in another phases formation, which occur through a series of solid-liquid and solid state reactions. The structure of the composites depends on heat treatment time at 900°C. After 5 hours of treating the intermetallic layer is transformed almost wholly into TiCu.

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