STRUCTURAL TRANSFORMATIONS AT THE Cu-Ti INTERFACE DURING SYNTHESIS OF COPPER-INTERMETALLICS LAYERED COMPOSITE

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This article is mainly devoted to examination of the structure formed at a Cu-Ti interface. Investigations were concerned with the structural transformations of a Cu-Ti couple at a temperature of 890 °C because this was the lowest temperature sufficient for the formation of the Cu-intermetallic phases composite. Holding for a few minutes, the Cu-Ti couple results in the formation of a thin layer at the interface. Prolongation of the heating time leads to reactions in the liquid state. Using X-ray microprobe analysis, the intermetallic compounds: Cu_4Ti, Cu_4Ti_3, CuTi, and $CuTi_2$ were identified in the reaction zone. The predominant part of the dendritic structure is the mixture of Cu_4Ti and Cu_4Ti_3, copper rich phases, therefore a liquid front of reaction is moving into the copper. The microhardness of the reaction products and of the elemental Cu and Ti components was measured. Finally, it was shown that the copper-intermetallic layered composites can be formed by high temperature reactions from copper and titanium sheets.

Key words: intermetallic phases, metal-intermetallic phases composite

ŠTRUKTÚRNE TRANSFORMÁCIE NA ROZHRANÍ Cu-Ti V PRIEBEHU PRÍPRAVY VRSTEVNÉHO KOMPOZITU MEĎ-INTERMETALICKÉ FÁZY

Článok sa venuje najmä skúmaniu štruktúry, ktorá sa vytvára na rozhraní Cu-Ti. Výskum sa týka štruktúrnych transformácií dvojice Cu-Ti pri teplote 890 °C, ktorú sme určili ako najnižšiu teplotu postačujúcu na prípravu kompozitu Cu-intermetalické fázy. V dôsledku niekoľkominútovej výdrže na tejto teplote sa vytvorí tenká vrstva na rozhraní. Predĺženie času ohrevu vedie k reakciám v tekutom stave. V reakčnej zóne sme pomocou röntgenovej mikroanalýzy určili intermetalické zlúčeniny: Cu_4Ti, Cu_4Ti_3, CuTi a $CuTi_2$. Keďže hlavnou časťou dendritickej štruktúry je zmes fáz bohatých na meď Cu_4Ti a Cu_4Ti_3, front reakčnej taveniny sa posúva smerom do medi. Merali sme mikrotvrdosť reakčných produktov a základných komponentov Cu a Ti. Nakoniec sa ukázalo, že z pásov medi a titánu môžeme pomocou vysokoteplotných reakcií pripraviť vrstevný kompozit meď-intermetalické fázy.

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1. Introduction

Copper is commonly used as a very good electrical conductor, but its conductivity is conditioned by retaining high purity. Unfortunately, pure copper has a very low abrasion resistance. On the other hand, the copper-based alloys have high level of hardness and wear resistance, but their electrical conductivity is much lower in comparison with copper. For example, tin bronze, silicon bronze and manganese bronze have an electrical conductivity lower than 10 $\mathrm{m}/\Omega\cdot\mathrm{mm}^2$ while pure copper has 59.7 $\mathrm{m}/\Omega\cdot\mathrm{mm}^2$ [1].

It appears that a composite consisting of layers – copper partitioned by hard intermetallic phases – could meet the opposed requirements. Certainly, the maintenance of high purity copper in the layered composite is necessary to obtain its high electrical conductivity. We intended to synthesise the layered composite based on copper and copper-titanium intermetallic phases. The intermetallic phases were formed by high temperature reactions between copper and titanium in solid and liquid state.

Metal-intermetallic composites are unique structures, as they offer an attractive combination of properties from both component phases. The process of forming intermetallic compounds from reaction between elemental powders has been widely used to produce intermetallic and ceramic powders and *in situ* two-phase composites [2–6]. Recently, it was shown that metal-intermetallic phases layered composites can be processed on the way of self-propagating high temperature synthesis of intermetallic compounds at the interface between Ni and Al, Al and Fe and also Al and Ti foils [7–9]. The primary purpose of this study was to recognise the effect of a high temperature on the structure and development of the interfacial zone between copper and titanium. In order to do it, a microscopical examination of the reaction zone was performed to identify the intermetallic phases. Progress of the synthesis process with prolonged time of reaction between elemental Cu and Ti components was also investigated. Finally, the structure of the composite containing layers of copper metallurgically bonded with alternately located layers of intermetallic, was presented.

2. Experimental procedure

Series of attempts allowed us to find that a temperature of at least 890 ℃ was necessary for the start and rapid development of structural processes at the interface of Cu-Ti couple. Materials used in this experiment were M1E copper (containing 99.9 % Cu) and WT-0 titanium containing impurities: oxygen 530 ppm, nitrogen 100 ppm, carbon 200 ppm, aluminium 2700 ppm and iron 900 ppm. The 10 × 10 mm specimens were cut from 2.5 mm thick copper and 2.0 mm thick titanium sheets. The joining surfaces were polished on 600 grade abrasive paper just before bonding, and a sample (Cu-Ti couple) was placed in a vacuum furnace.

Pressure of 5 MPa that was used to ensure a good bonding was released at a temperature of 850 ℃. For the study of the structure forming at the Cu-Ti interface (using an electron microscope JMS 500), the sample was held at a temperature of 890 ℃ for 10 minutes and then was furnace-cooled to room temperature. The chemical composition of the phases was determined by an electron microprobe analysis using ISIS 300 Oxford Instruments. The Cu-Ti couple specimens prepared for the study of intermetallic layer growth were held in a vacuum furnace at a temperature of 810 ℃ under a pressure of 5 MPa to obtain initial contact between Cu and Ti components (but not to start rapid synthesis reaction). The joined Cu-Ti samples were maintained at a constant temperature of 890 ℃ for different times and then air-cooled. Progress of the reaction was determined by measuring of the thickness of the intermetallic phases layer using optical microscopy. For this purpose, the specimens were mechanically polished and etched to reveal the structure of the intermetallic layer. Vickers (HV0.065) measurements were performed by Hanemann microhardness tester mounted on Neophot 2 microscope.

3. Results and discussion

Examinations of the Cu-Ti couple specimens that were held at a temperature of 890 ℃ for different times allowed us to find that two successive processes took place at the reaction zone. At the beginning, the thin layer was formed at the Cu-Ti interface, which appeared to be rather uniform if carefully etched samples were observed by an optical microscope. This stable diffusion process was followed by a sudden onset of structure transformation, which in effect yielded a heterogeneous dendritic structure. The structures observed for these two processes are shown in Figs. 1 and 2. Figure 1 shows a thin layer formed at the boundary between copper and titanium after holding a Cu-Ti couple at a temperature of 890 ℃ for 5 minutes. Figure 2 shows a layer formed in Cu-Ti sample, which was held for 10 minutes at the same temperature. The dendritic structure of the layer indicates that this stage of the Cu-Ti reaction proceeds in the liquid phase. The thickness of the reaction zone was measured as a function of the holding time at a temperature of 890 ℃ for the Cu-Ti couple. Result of the measurements is shown in Fig. 3. The dependence can be expressed by the equation $d = At^n$ with the time exponent value $n > 1$ (d – thickness of the layer, t – holding time, A – constant). So, the rate of synthesised layer growth exceeds a parabolic growth [10–12] of intermetallic phases due to interdiffusion of the components in solid state. The microhardness of the dendritic layer was 510–550 HV. Comparatively measured, the microhardness of copper and titanium were 72 and 220 HV, respectively (indentations are shown in Fig. 4).

A structural analysis of the Cu-Ti reaction zone was performed by a scanning electron microscope equipped with a system for microprobe analysis. There were two aims of these examinations:

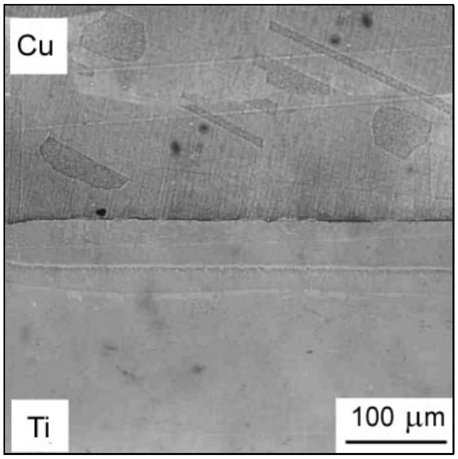

Fig. 1. A copper-titanium couple forming at 890 °C for 5 minutes.

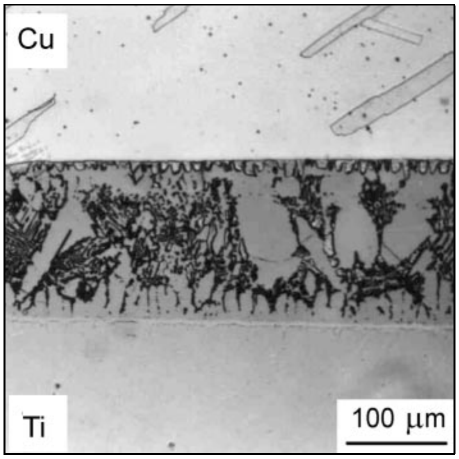

Fig. 2. Reaction zone formed after holding a copper-titanium couple at 890 °C for 10 minutes.

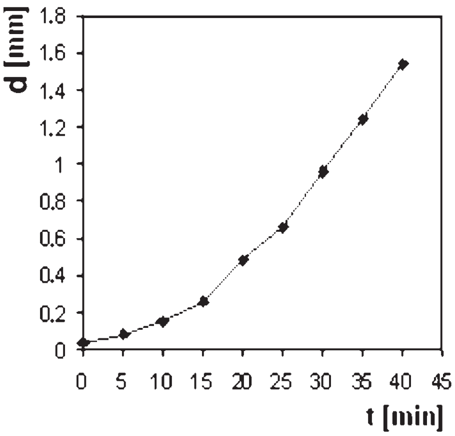

Fig. 3. Thickness of intermetallic phases layer *d* vs. time of holding *t* of Cu-Ti couple at temperature of 890 °C.

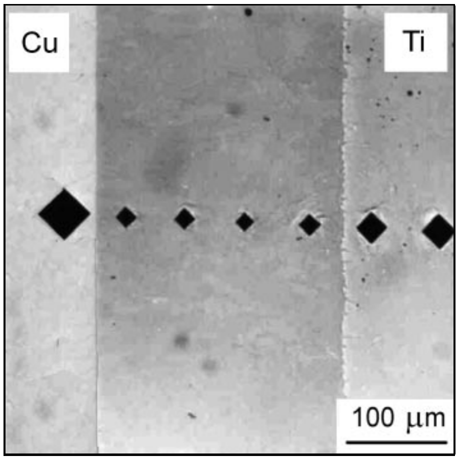

Fig. 4. Indentations of the Vickers penetrator in copper, intermetallic phases and titanium layers.

– identification of the chemical composition of phases synthesised at the reaction zone,

– determination of the titanium concentration profile across the interface between the layer of copper and the layer of Cu-Ti reaction products.

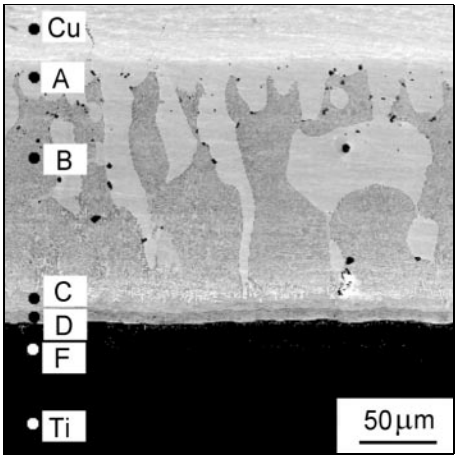

Fig. 5. Microstructure formed at the front of the reaction between Cu and Ti elements.

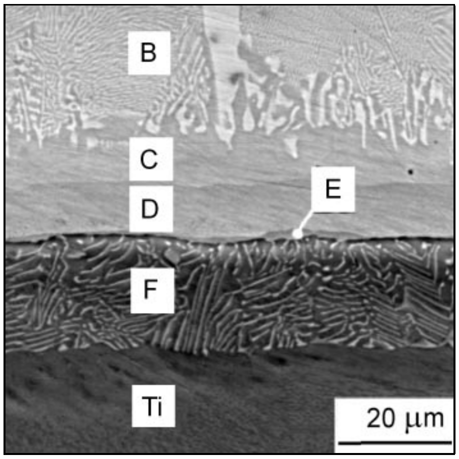

Fig. 6. Microstructure formed at the front of the reaction between Cu and Ti elements.

Figures 5 and 6 show the microstructure of the reaction zone between Cu and Ti components. On the copper side, we can distinguish the heterogeneous zone formed during solidification (region marked B), the homogeneous A, C, D, and E regions, and the two-phase structure (region F) in the neighbourhood of titanium. A study of the above structures was based on the Cu-Ti binary phase diagram presented in Fig. 7.

The elemental analysis performed by the X-ray spectroscope was made for areas marked A, B, C, D, E, and F in the micrographs shown in Figs. 5 and 6. An example of X-ray diffraction spectrum for A-area of the specimen is given in Fig. 8. The Cu : Ti ratio, about 4 : 1, suggests a Cu_4Ti intermetallic compound. Using X-ray microanalysis, it was found that for single-phase areas marked C, D and E, C is Cu_4Ti_3, D is CuTi and E (very thin layer) is $CuTi_2$. The chemical composition of the zone marked B was 67 at.% Cu and 33 at.% Ti. It should be mentioned that in the case of B area X radiation was simultaneously emitted by two phases of the structure. This result indicates, according to the phase diagram of Cu-Ti system (Fig. 7), a mixture of Cu_4Ti and Cu_4Ti_3 phases. A similar analysis allowed us to find that a two-phase structure observed in the neighbourhood of titanium (area F in Fig. 6) containing 93 at.% Ti is the eutectoid mixture of two phases: $CuTi_2$ and solid solution of copper in titanium.

The above results indicate that the structure between Cu and Ti plates is formed due to solid state transformations and liquid phase reactions. We can easily distinguish the boundary between these regions. It is evident from metallographical examinations that the predominant part of intermetallics is synthesised in the re-

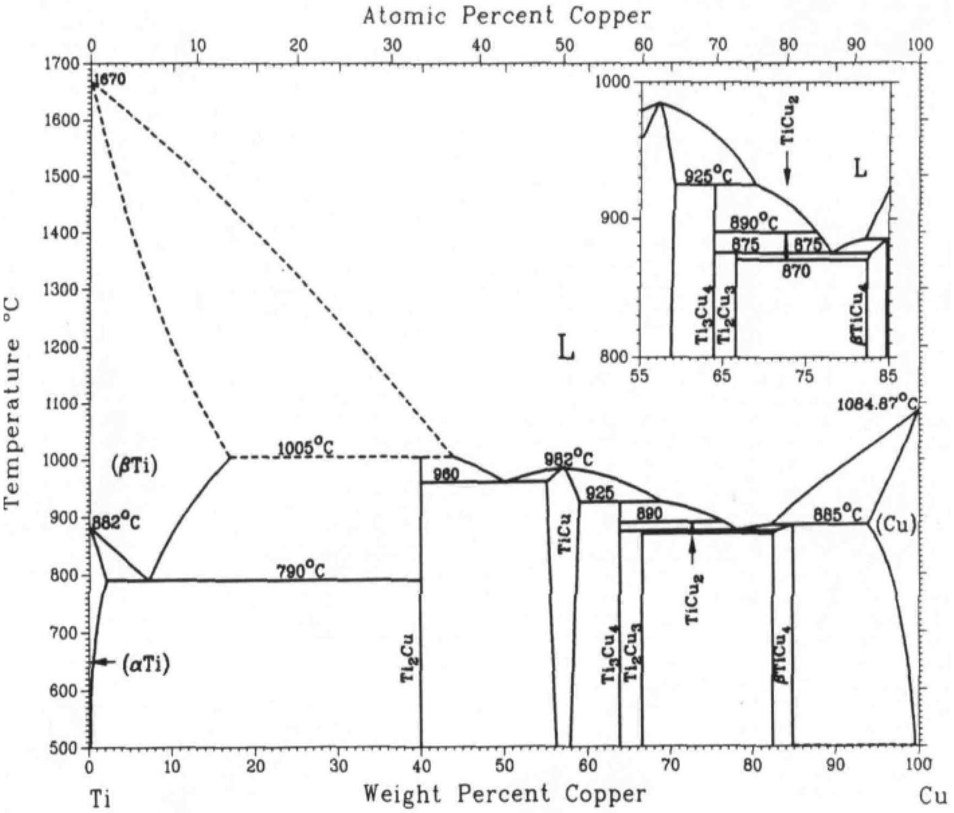

Fig. 7. Cu-Ti binary phase diagram [13].

gion passing from a liquid state to a solid state. So, growth of the $Cu_4Ti + Cu_4Ti_3$ structure seems to be the factor responsible for the progress of the process and development of the interfacial zone. Since the structure resulting from solidification of locally melted reaction zone contains phases rich in Cu, melting consumed more Cu than Ti. For this reason, the boundary between the intermetallic layer and the copper migrates toward the copper side.

It is very important for the high electrical conductivity of Cu-intermetallic phases composite to maintain a low concentration of titanium in the copper layers of the composite. The plot of the concentration of Ti and Cu across the layer of intermetallics into the adjacent layer of copper, as obtained by X-ray diffraction, is presented in Fig. 9. The results of the Ti concentration measurements are listed in Table 1. The concentration profile shows that the penetration of Ti atoms across

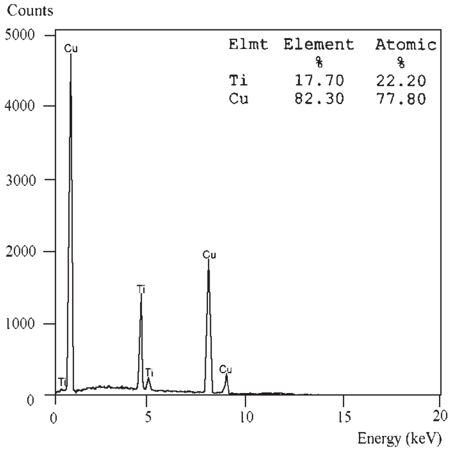

Fig. 8. X-ray spectrum for A-marked area of structure depicted in Fig. 5.

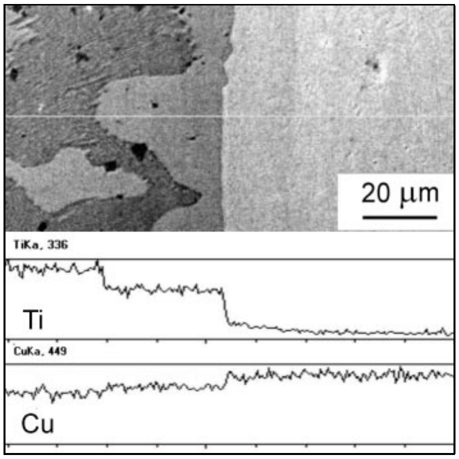

Fig. 9. Microstructure and concentration of Cu and Ti profiles across the interface intermetallic phases-copper.

the intermetallics-copper boundary is very limited. Structural transformations that occur with the liquid phase contribution are passing too fast to cause an increase of Ti concentration in the copper layer, excluding the vicinity of the intermetallic phases-copper interface.

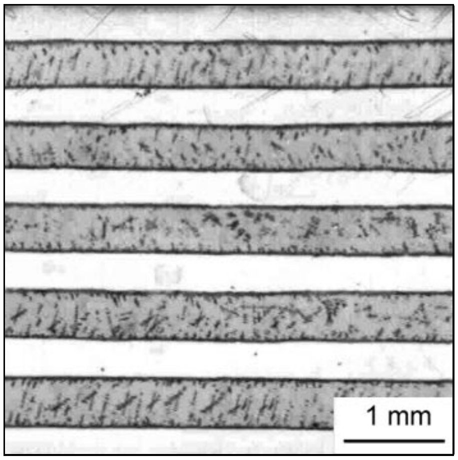

Fig. 10. Microstructure of the Cu-intermetallic phases layered composite formed at temperature of 890 °C.

The structural phenomena that are taking place at the copper-titanium interface allow the proposition of an easy and economical method of producing a layered composite. Copper and titanium sheets are formed alternately into a packet and heated to form intermetallic layers. It is obvious that all the titanium must be fully consumed and transformed together with part of the copper sheets into intermetallic compounds. Any ratio of Cu layers to intermetallic layers in the composite can be obtained by choosing the thickness ratio of starting Cu and Ti sheets. So, the electrical and mechanical properties of the composite can be designed. An example of the Cu-intermetallic phases

Table 1. Titanium segregation in copper at the copper-intermetallic phases boundary.

Distance from intermetallic phases zone [μm]	Titanium concentration [at.%]
5	4.14
10	2.60
15	0.23

composite structure formed at a temperature of 890 ℃ is presented in Fig. 10. Observed at low magnification, the structure of a Cu-intermetallic phases composite is similar to the composites produced on a base of Ni, Fe and Ti with coupled metals by self-propagating high temperature reactions [7–9].

4. Conclusions

The principal results of this study can be summarised as follows:

1. In a consequence of a reaction occurring between copper and titanium at a temperature of 890 ℃, an inhomogeneous structure is formed at the interface of Cu--Ti couple. It was found using microprobe analysis that the reaction zone contains intermetallic compounds, most probably: Cu_4Ti, Cu_4Ti_3, CuTi and $CuTi_2$.

2. The reaction zone growth is controlled by an increase in the dendritic structure.

3. The predominant part of the structure formed in the reaction zone is the $Cu_4Ti + Cu_4Ti_3$ intermetallic mixture.

4. Since the main part of the reaction products are phases rich in copper, a front of the Cu-Ti reaction migrates into the copper.

5. The concentration of titanium in the copper elemental layer, measured across the intermetallics-copper boundary, strongly decreases with increasing distance from this boundary.

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