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MICROSTRUCTURE EVOLUTION AT THE Cu-Ti INTERFACE DURING HIGH TEMPERATURE SYNTHESIS OF COPPER-INTERMETALLIC PHASES LAYERED COMPOSITE

EWOLUCJA MIKROSTRUKTURY NA GRANICY Cu-Ti PODCZAS WYSOKOTEMPERATUROWEJ SYNTEZY KOMPOZYTU WARSTWOWEGO MIEDŹ-FAZY MIĘDZYMETALICZNE

Structural transformations connected with a new processing technique used for fabrication of the copper-intermetallic phases layered composites from copper and titanium sheets were investigated. Formation and growth of intermetallic phases produced at elevated temperatures at the copper-titanium interface were examined for both polyphase diffusion and for process occurring in the liquid phase presence. Since no exothermic peak has been dedected during differential thermal analysis for the Cu-Ti couple, it is suggested that the process of intermetallic phases synthesis is not of the SHS type. Results of the microscope observations and electron probe microanalysis allowed, on the basis of the Cu-Ti equilibrium diagram, to recognize a row of intermetallic compounds that were synthesised in the layer form at the Cu-Ti interface. The measurements have shown that for intermetallics synthesis with the liquid phase contribution the rate of the layer growth exceeds many times the layer growth rate due to polyphase diffusion. It was demonstrated that in the way of high temperature synthesis of intermetallic phases with the liquid phase presence the copper-intermetallic phases layered composite can be processed from copper sheet and titanium foil, stocked alternatively into a packet. As-synthesised composite layers containing intermetallic phases are metallurgically bonded with the copper layers.

Keywords: intermetallic phases, layered composite, copper

Badano przemiany strukturalne związane z nową techniką uzyskiwania z blach miedzi i tytanu kompozytów warstwowych miedź-fazy międzymetaliczne. Analizowano wysokotemperaturowy proces formowania i wzrostu warstwy faz międzymetalicznych na granicy między miedzią a tytanem, który może przebiegać zarówno na drodze dyfuzji reaktywnej, jak i z udziałem fazy ciekłej. Termiczna analiza różnicowa przeprowadzona na próbce-parze dyfuzyjnej Cu-Ti nie ujawniła pików egzotermicznych mogących świadczyć, że reakcje tworzenia faz międzymetalicznych są typu SHS. Obserwacje mikroskopowe oraz mikroanaliza rentgenowska pozwoliły, w oparciu o układ równowagi fazowej miedź-tytan, rozpoznać szereg związków międzymetalicznych tworzących warstwę na granicy między miedzią a tytanem. Z pomiarów wynika, że gdy proces syntezy faz międzymetalicznych zachodzi z udziałem fazy ciekłej wzrost warstwy faz międzymetalicznych jest wielokrotnie szybszy niż w przypadku przemian strukturalnych zachodzących w wyniku dyfuzji reaktywnej. Pokazano, że z blachy miedzianej i folii tytanu ułożonych naprzemiennie w pakiet uzyskać można, na drodze wysokotemperaturowej syntezy faz międzymetalicznych z udziałem fazy ciekłej, kompozyt miedź-fazy międzymetaliczne. Utworzone w wyniku syntezy warstwy kompozytu zawierające fazy międzymetaliczne połączone są metalurgicznie z warstwami miedzi.

1. Introduction

In the last years a new technique for fabrication of metal-intermetallic phases layered composites has been proposed. The method is based on high temperature synthesis of intermetallics at the interface between two elemental metals. To obtain a composite thin sheets of one metal are placed alternately with thicker sheets of

another metal into a packet. The packet is heated to a temperature that starts the reaction between the metals. The process is continued till one of the metals (thinner sheets) is fully consumed in the course of reaction. Because the products of the synthesis are growing into a layer, we finally obtain a metal-intermetallics layered composite. In the way of the intermetallic phases synthesis a Ni-intermetallics [1-4], Fe-intermetallics [2],

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Ti-intermetallics [2, 3, 5] and Ti₃Al_{2.5}V-intermetallics [6] layered composites have been processed.

This procedure was adopted to produce the copper-intermetallic phases layered composite from copper and titanium elemental metals. The process of intermetallic compounds synthesis proceeds via liquid phase that appears at the copper-titanium interface. The presence of the liquid phase remarkably accelerates transformation of all the titanium together with part of the copper sheets into a structure containing intermetallic phases. As it is seen, the principal problem connected with the composite formation is the synthesis of intermetallic phases at the copper-titanium interface. The paper deals with the in situ growth of the intermetallics layer between copper-titanium sheets and contains also the analysis of the final microstructure of the copper-intermetallic phases composite.

2. Experimental procedure

The process of intermetallic phases synthesis was examined using Cu-Ti couple. The square 10 x 10 mm specimens were cut from 2.5 mm thick copper of 99.9 % purity and 2.0 mm thick titanium sheets of 99.6 % purity. The joining surfaces were polished on 600 grade abrasive paper just before bonding, and a Cu-Ti couple was placed in a vacuum furnace. The liquid phase appeared at the copper titanium interface at 890 °C. Heating till the temperature of 810 °C was performed under a pressure of 5 MPa to obtain initial diffusion bonding between the metals. The bonded Cu-Ti couples were then used to investigate the rate of growth of the intermetallics layer thickness for the passing via liquid phase reaction. Also the structure development in the copper-titanium reaction zone was examined. To study the growth of the intermetallics layer the samples were kept at 890 °C for varying time periods and then air-cooled. The increase of the intermetallics layer thickness was determined using optical microscopy on mechanically polished and etched specimens. To identify the structure forming at the copper-titanium interface the Cu-Ti couple was held at the temperature of 890 °C for 10 minutes

and furnace-cooled to room temperature. The structural observations of a mechanically polished specimen were performed on an electron scanning JMS 500 microscope. The chemical composition of the phases was determined by electron microprobe analysis using ISIS 300 Oxford Instruments. The same experimental procedure was used for structural examination of the Cu-Ti interface after annealing of the Cu-Ti couple at 870 °C for 10 minutes. The thermal effects of the copper-titanium interaction were studied by differential thermal analysis (DTA) using a Setsys 16/18 (Setaram, France) thermal analyzer. Cu-Ti couple-specimens in the form of a pallet (4 mm dia.) were heated in an open ceramic crucible between 30-1000 °C in flowing argon atmosphere (volume flow rate $v = 0.8 \text{ dm}^3 \text{ h}^{-1}$) with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. Next, the samples were cooled at the same experimental conditions. The DTA curves of the heating and cooling processes were registered.

On the basis of experiments described above a multi-layered copper-intermetallics composite was formed. The copper sheet 0.7 mm thick was alternatively stacked between titanium foil of 0.1 mm thickness. A packet nearly 10 mm thick was heated in a vacuum-furnace to temperature of 890 °C, held for 10 minutes and cooled till room temperature. Up to the temperature of 810 °C the packet was heated under the pressure of the 5 MPa. Using the same procedure as previously the microstructure of the as synthesised composite layers was examined. The synthesised structure was reexamined after prolonged to 1 hour maintenance of the composite at the temperature of 890 °C.

3. Results and discussion

Figure 1 shows a layer formed in a Cu-Ti sample, which was held at the temperature of 890 °C for 10 minutes. The dendritic structure indicates the presence of a liquid phase at the copper-titanium interface. The measurements of the thickness of the reaction products show that the reaction zone is increasing progressively with the copper-titanium reaction time (Fig. 2).

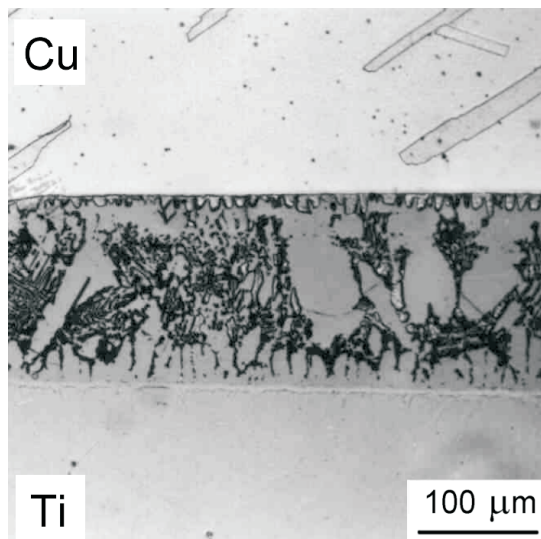


Fig. 1. Reaction zone formed after holding a Cu-Ti couple at 890 C for 10 minutes

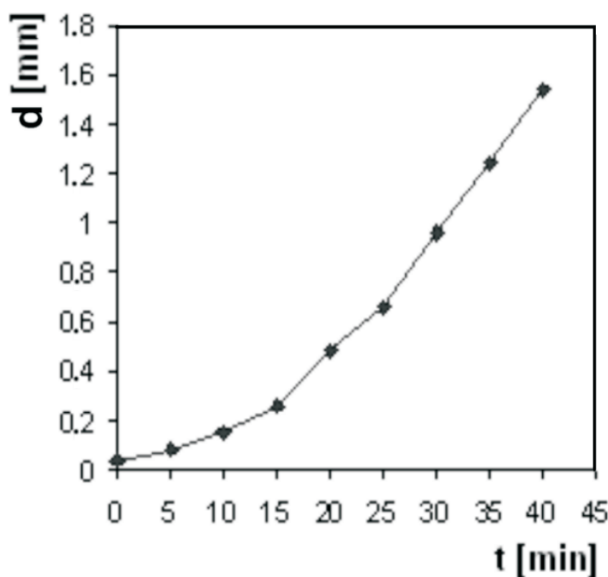


Fig. 2. Thickness of the intermetallic phase layer d vs time of holding t of Cu-Ti couple at the temperature of 890°C

On the basis of measurements a simple relationship between the thickness (expressed in mm) of the intermetallics layer d and the holding time t (expressed in min) at the temperature of 890 °C was derived (1)

$$d = 0.001 t^2 \quad (1)$$

The above dependence can be expressed by the generally accepted equation (2)

$$d = At^n, \quad (2)$$

where: d – thickness of the layer,
 t – holding time,
 n – time exponent,
 A – constant.

As distinct from the solid state diffusion the time exponent value ($n=2$) considerably exceeds n value characteristic of solid state diffusion [7-12]. Thus, the rate of

synthesised layer growth with the liquid phase contribution strongly exceeds the parabolic growth of intermetallic phases due to interdiffusion in the solid state.

A structural examination of the layer growth with the liquid phase contribution that was performed by a scanning electron microscope equipped with a system for microprobe analysis allowed to find a number of intermetallic compounds synthesised from the elemental metals. Figures 3, 4 and 5 show the scanning electron micrographs of the copper-titanium reaction zone shown previously in Fig. 1. The prevailing part of the heterogeneous structure was formed during solidification. We can distinguish the single phase A, C, D and E regions, and the two-phase structure: region marked B and region marked F (on the titanium side). The analysis of the above microstructure was based on the Cu-Ti binary phase diagram presented in Fig. 6.

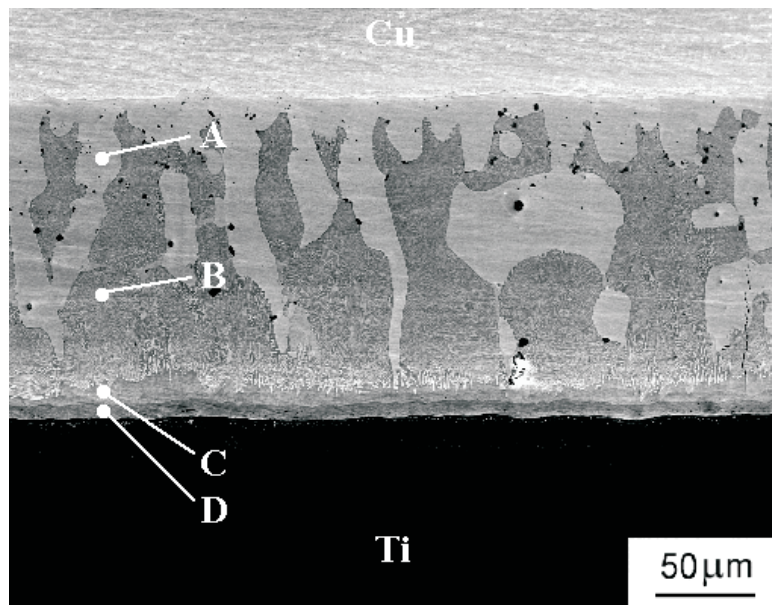


Fig. 3. Scanning electron micrographs showing the layers developed for Cu-Ti couple annealed at 890 °C for 10 minutes

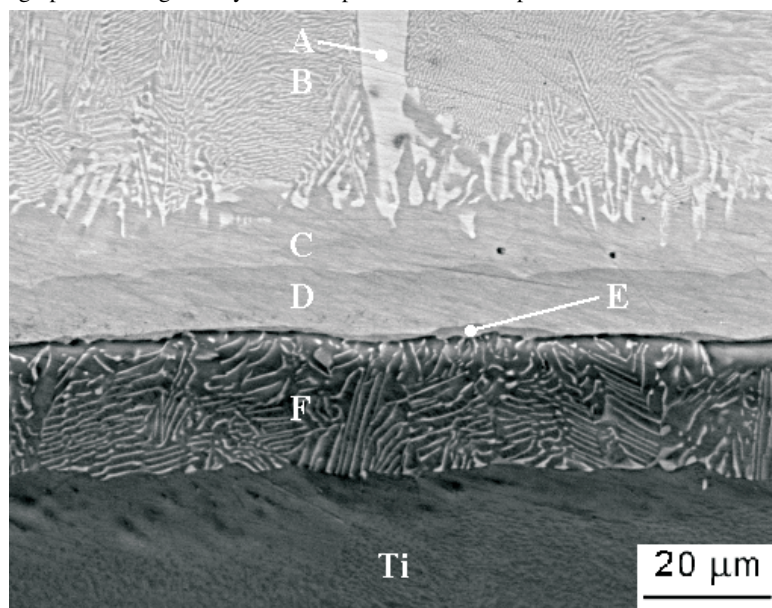


Fig. 4. Scanning electron micrographs showing the layers developed for Cu-Ti couple annealed at 890 °C for 10 minutes. Microstructure observed on the titanium side

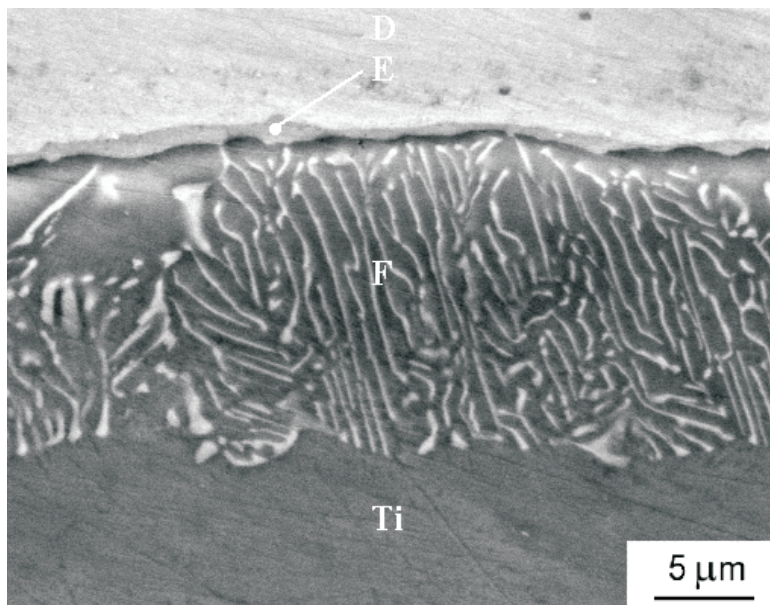


Fig. 5. Scanning electron micrographs showing the layers developed for Cu-Ti couple annealed at 890 °C for 10 minutes. Microstructure observed on the titanium side

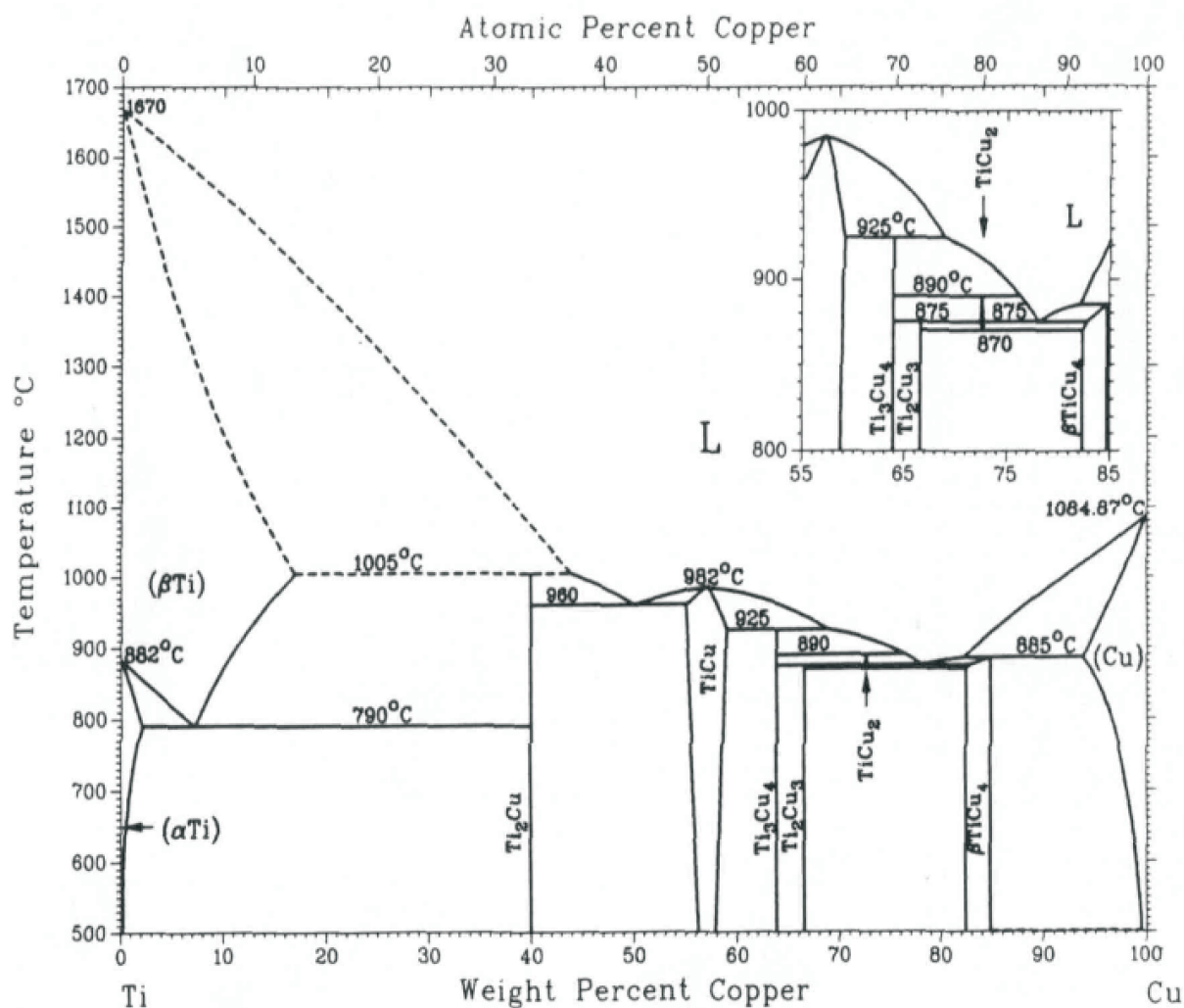


Fig. 6. Cu-Ti binary phase diagram [13]

The EDS spectra for homogeneous A, C, D and E regions of the reaction zone are presented in Fig. 7. The Cu : Ti ratio, about 4 : 1 for single-phase A-area, suggests a Cu_4Ti intermetallic compound. X-ray microanalysis of the other single-phase areas allows to find the intermetallic compounds: Cu_4Ti_3 for the sublayer marked C, CuTi for the sublayer mared D and CuTi_2 for the sublayer marked E. On the basis of the Cu-Ti diagram and mi-

croanalysis of the B marked area we are suggesting that the heterogeneous structure that was formed during solidification (region marked B) is the Cu_4Ti and Cu_4Ti_3 mixture. In the same way a two-phase structure observed in the neighborhood of titanium (area F in Fig. 4 and Fig. 5) was identified as a eutectoid mixture of the two phases: CuTi_2 and solid solution of copper in titanium.

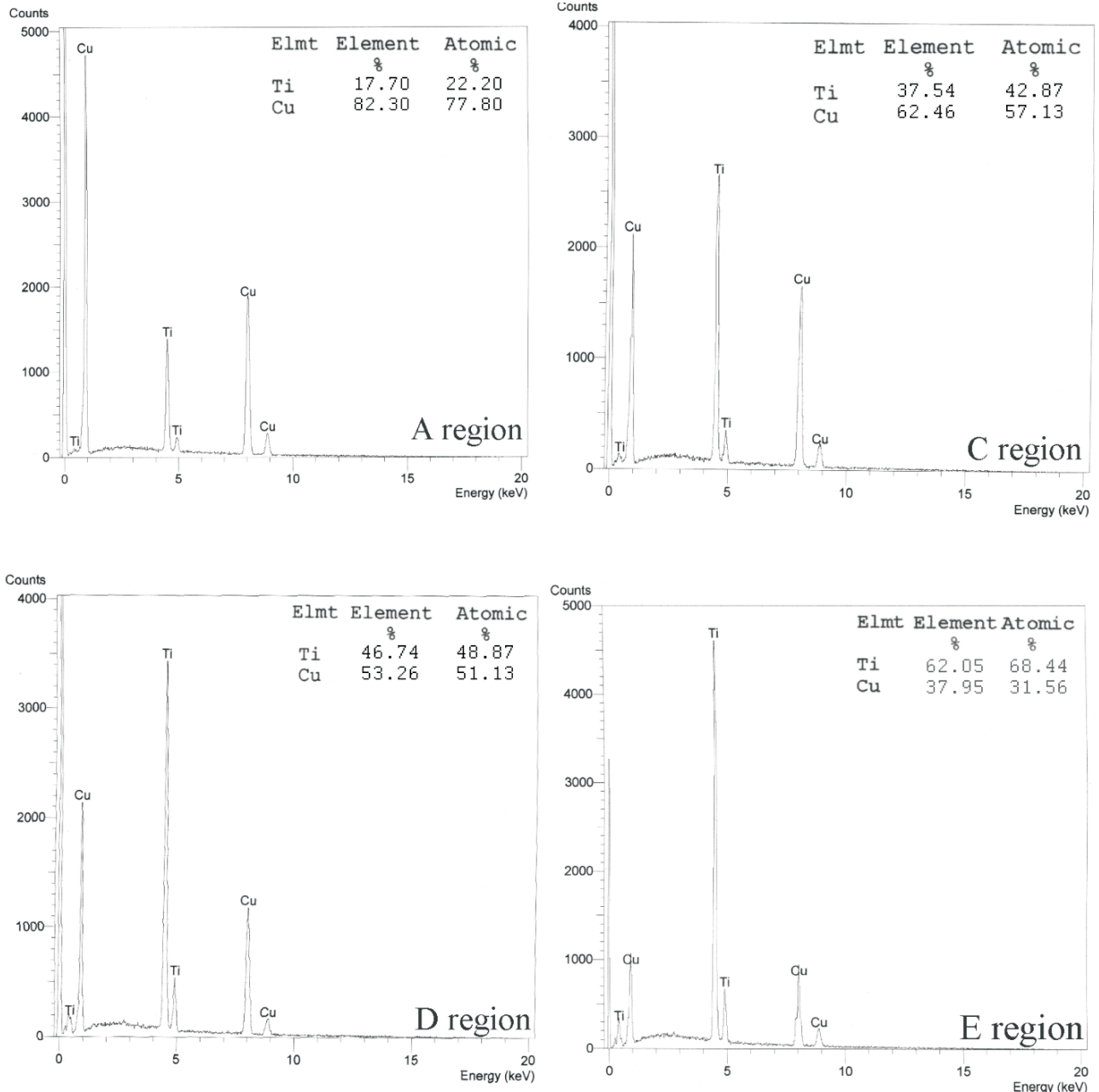


Fig. 7. X-ray spectrum for homogeneous regions of the reaction zone marked A, C, D and E in Fig. 3-5

For comparison a microstructure developed due to solid state diffusion was studied. Figure 8 shows the microstructure of the reaction zone formed in Cu-Ti sample

after keeping the specimen for 10 minutes at the temperature of 870 °C.

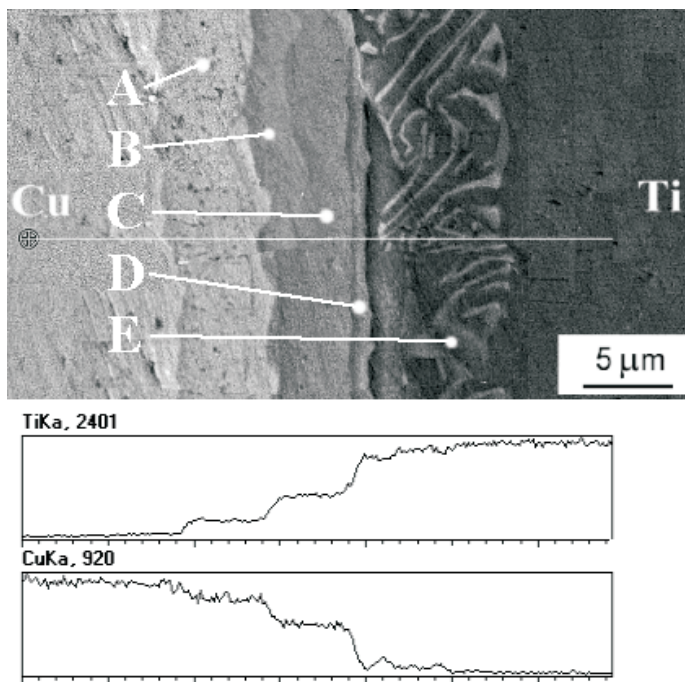


Fig. 8. Scanning electron micrographs showing the diffusion layer developed for Cu-Ti couple annealed at 870 °C for 10 minutes together with concentration of Ti and Cu profiles across the copper-titanium interface

The eutectoid mixture containing CuTi_2 and solid solution of copper in titanium (region E from the titanium side) was, as formerly, followed by the CuTi_2 thin single-phase sublayer (region D) and subsequently by thicker the CuTi sublayer (region C). The X-ray spectrum obtained in the remaining, next layer in the neighbourhood of titanium (region B) is shown in Fig. 9. The Cu : Ti ratio slightly differs from 4: 3 ratio that was found previously for a next to CuTi layer synthesised with the

liquid phase contribution. According to Cu – Ti binary phase diagram the result may correspond to Cu_4Ti_3 compound as well as to Cu_3Ti_2 compound. Unfortunately, it is impossible to determine the definite atomic ratio of the investigated phase by the experimental procedure used in this work. Finally, a sublayer formed from the copper side, labeled in Fig. 8 as the region A, was examined. The X-ray diffraction indicates the Cu_4Ti intermetallic compound.

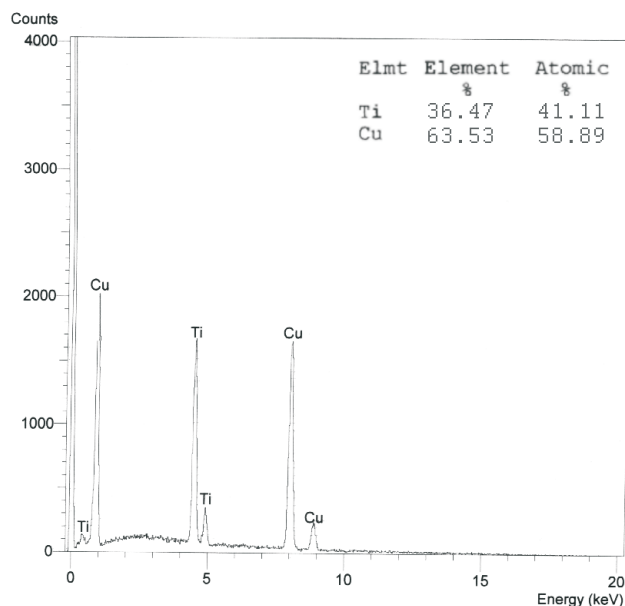


Fig. 9. X-ray spectrum for homogeneous regions of the reaction zone marked B in Fig. 8

Propagation of the intermetallics synthesis front may be accompanied by a strong exothermic effect. The highly exothermic process that produces intermetallics phases is known as self-propagating high temperature synthesis (SHS) [14 - 16]. This means that the SHS reaction once initiated is self-sustaining – can develop without external heating. Alman, Rawers and Hawk [2], who formed Ni-intermetallics, Ti-intermetallics and Fe-intermetallics layered composite, maintain on the basis of an earlier work [17] that the process of the intermetallic phases synthesis proceeds via SHS reaction between aluminium and elemental Ni, Ti and Fe metals. To detect the thermal effects associated with the structural transformation at a copper-titanium interface, differential thermal analysis (DTA) was performed for Cu-Ti couple

heated to 1000 °C. Figure 10 shows a DTA plot as received from the experiment. One must realize, before analysis of the DTA curve, that the specimen (Cu-Ti couple) consists of elemental copper and titanium metals and a thin layer between them containing products of solid-state diffusion at the Cu-Ti interface. The first endothermic peak at the temperature of 793 °C indicates (according to the Cu-Ti binary phase diagram and the structure observation) the transformation of Ti_2Cu intermetallic compound together with solid solution of copper in the alpha titanium (α) into solid solution of copper in the beta titanium (β):

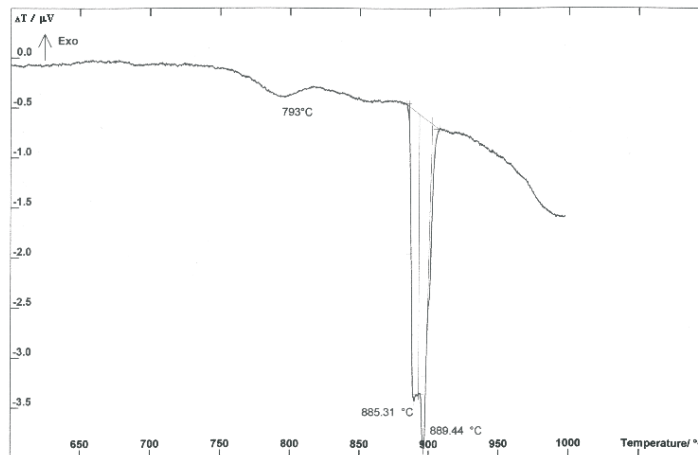
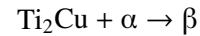


Fig. 10. DTA curve for Cu-Ti couple heated to the temperature of 1000 °C

The second endothermic peak with the onset at the temperature of about 880 °C and minimum at 889 °C corresponds to allotropic change from α Ti to β Ti (at 885 °C) and to melting of the solid phases at the Cu-Ti

interface. No other peaks were observed up to 1000 °C. The exothermic peak that was found at the temperature of 876 °C during cooling corresponds to solidification of the melted specimen (see Fig. 11).

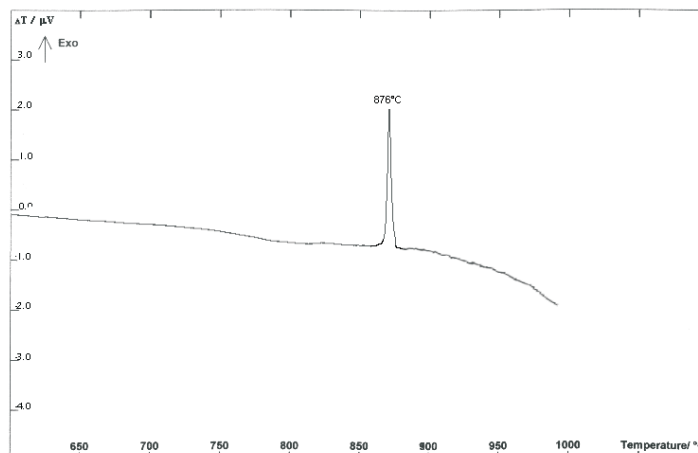


Fig. 11. DTA curve for specimen cooled from 1000 °C to 600 °C

The result of the DTA analysis shows that the process of intermetallic phases synthesis at the interface of copper and titanium sheets is not of the SHS type. For example, the exothermic peaks were found for the synthesis of NiAl compound with reaction enthalpy of -58.8 kJ/mol [18] and for synthesis of TiAl_3 and TiAl compounds with the enthalpy of -146 kJ/mol and -75 kJ/mol, respectively [19]. Evidence of the SHS reaction is also reported for formation from elemental powders of Ti_5Si_3 compound with the enthalpy -579.8 kJ/mol and for synthesis of NiSi compound with the enthalpy of -89.6 kJ/mol [20]. It should be noticed that high thermal conductivity of copper does not favor the self propagating process of intermetallic phases synthesis because of easy heat transport from the Cu-Ti reaction zone.

The presented structural transformations that are taking place at the Cu-Ti interface allow to produce a copper-intermetallic phases layered composite. In such case the reaction between alternately placed copper sheets and titanium foils must lead to complete consumption of titanium. Therefore titanium foils with a part of the copper sheets were fully transformed into layers of intermetallics. Figure 12 shows the micrograph of a composite processed from copper sheet 0.7 mm thick and titanium foil of 0.1 mm thickness that were formed into a packet and held at the temperature of 890°C for 10 minutes. Figure 13 shows details of the microstructure of the composite layer synthesised from copper and titanium elemental metals with the liquid phase contribution.

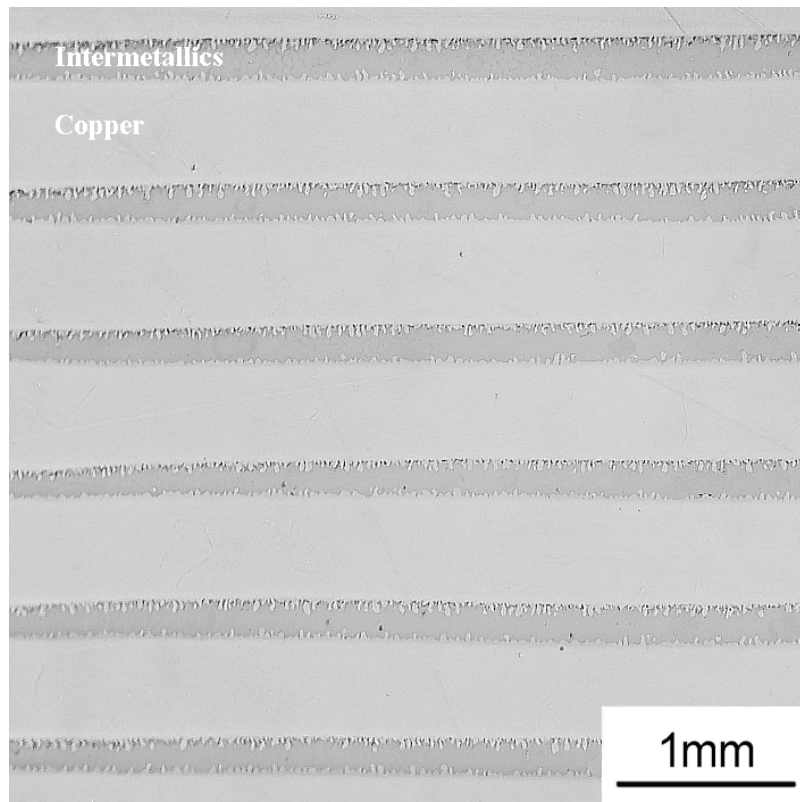


Fig. 12. Light microscopy micrograph of a copper-intermetallic phases composite

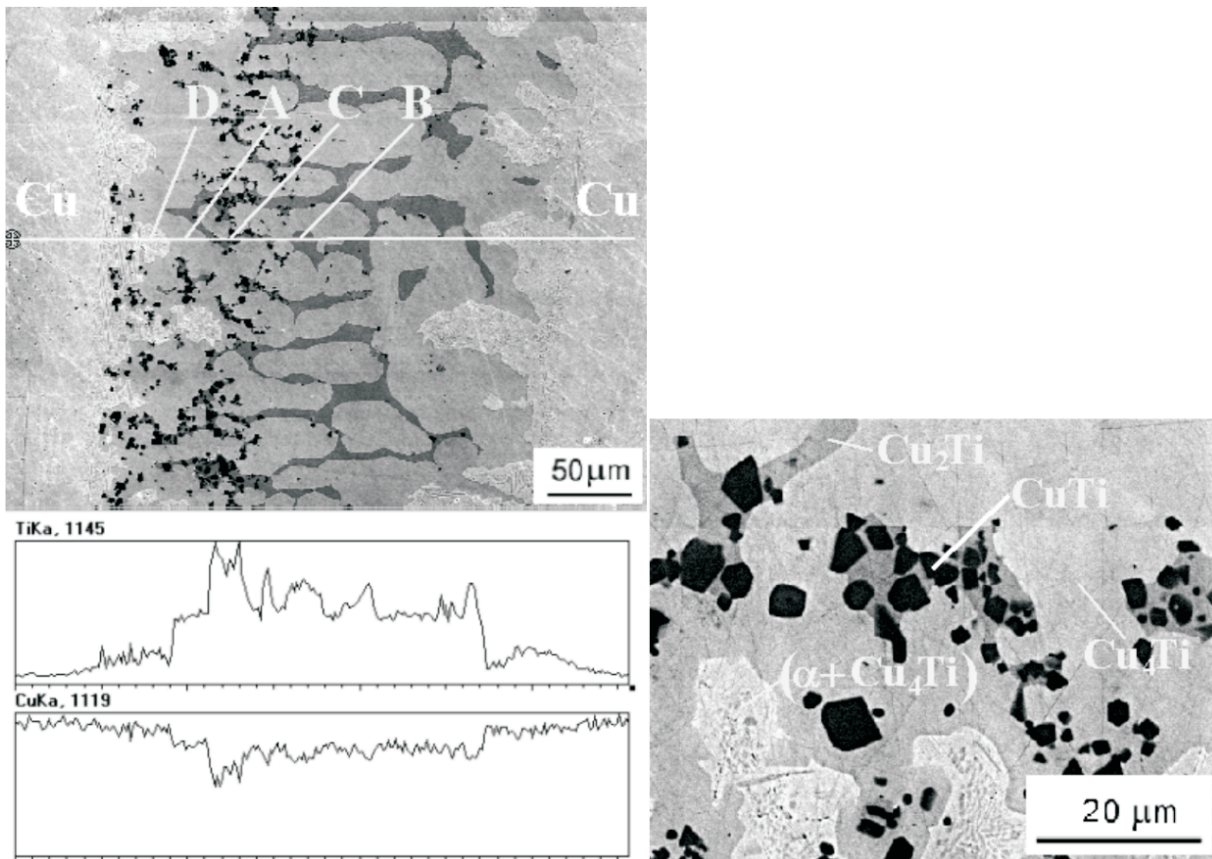


Fig. 13. Scanning electron micrographs showing morphology of the composite layer containing intermetallic phases

X-ray diffraction spectra for homogeneous A, B and C regions of the synthesised composite layer are presented in Figure 14. The result for single-phase marked A: 22% at. Ti and 77.8% at. Cu suggests the Cu_4Ti compound. The remaining phases identified from the B and C homogeneous areas are Cu_2Ti and CuTi , respectively (see patterns of the X-ray diffraction in Fig. 14 B and Fig. 14 C). It must be noticed here that according to Cu - Ti diagram the Cu_2Ti phase can exist only in a narrow range of elevated temperatures. But the evidence of the single phase in the B area together with the nearly perfect Cu : Ti ratio that was 2 : 1 allow us to suggest that the Cu_2Ti phase was undercooled till room temperature. Adjacent to copper, the heterogeneous area marked D in Figure 13 contains, according to X-ray microanalysis, 9% at. Ti and 90.3% at. Cu. Taking into account the copper layer vicinity we are suggesting, on the basis of the Cu - Ti diagram a two phase structure containing Cu_4Ti intermetallic compound and a solid solution of titanium in copper.

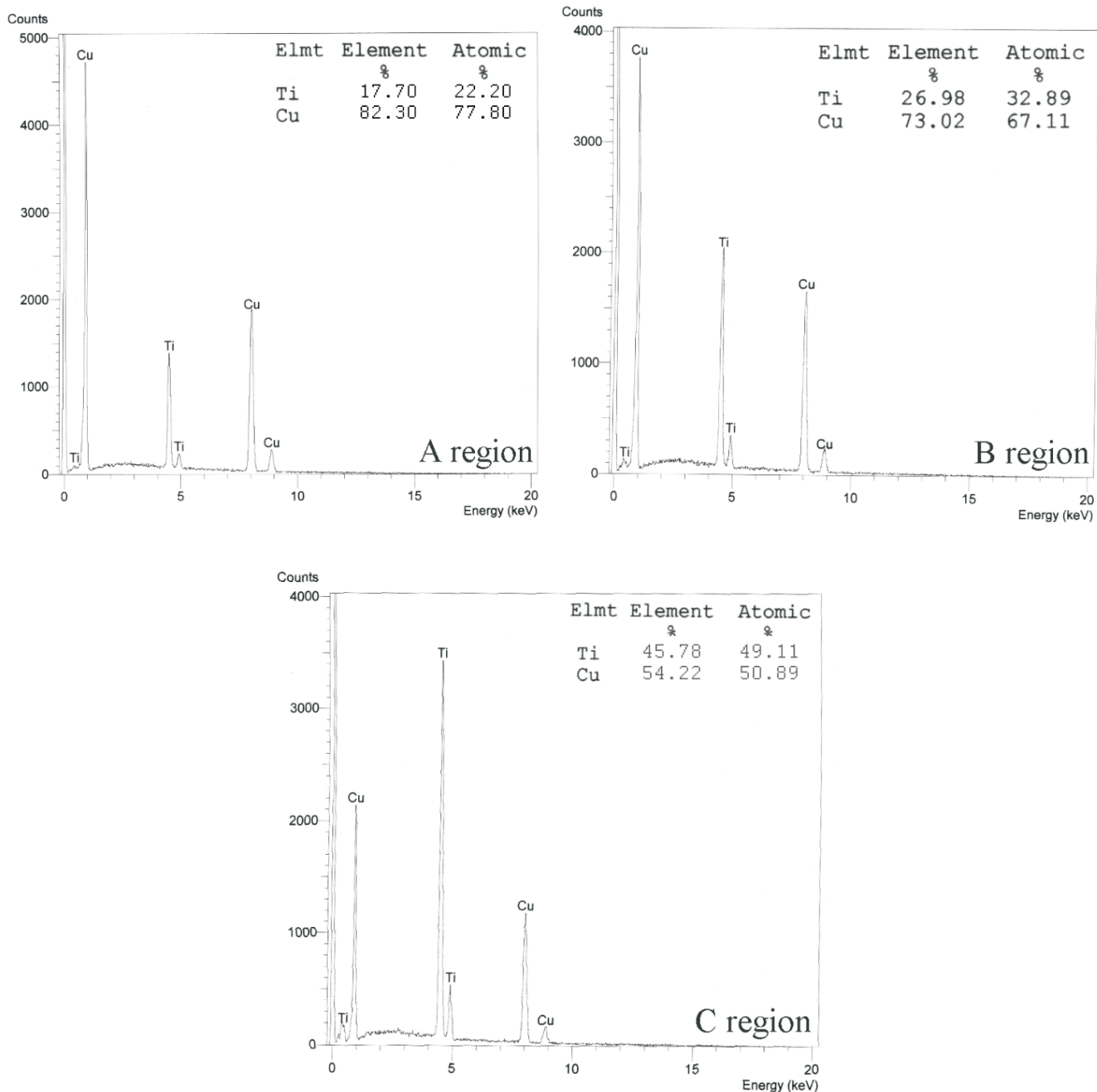


Fig. 14. X-ray spectrum for regions of the composite layer marked A, B and C in Fig. 13

The same phases were observed in the microstructure of the synthesized composite layers after prolonged to 1 hour maintenance of the composite at the temperature of 890 °C.

4. Conclusions

1. Due to solid state diffusion at the temperature of 870 °C a thin layer of intermetallic compounds is formed at the Cu-Ti interface. The electron microprobe analysis indicated from the copper substrate side a sub-
2. layer of Cu_4Ti intermetallic compound. Next to the Cu_4Ti a sublayer containing a single phase probably of Cu_3Ti_2 or Cu_4Ti_3 was observed and in turn, a single phase of the CuTi and the CuTi_2 sublayers. The two-phase structure nearest to the titanium-substrate was interpreted on the basis of X-ray spectrum and Cu-Ti binary phase diagram as an eutectoid mixture of CuTi_2 and a solid solution of copper in titanium.

3. The result of the electron microprobe analysis together with the analysis of the Cu-Ti phase diagram allow to find that the prevailing part of the structure resulting from the in-situ reaction at the Cu-Ti interface with the liquid phase contribution is the Cu_4Ti and Cu_4Ti_3 intermetallic mixture. Nearer to the titanium-substrate, a thin sublayer of the Cu_4Ti_3 single phase and next of the CuTi and CuTi_2 single phases sublayers were identified. In the neighbourhood of titanium an eutectoid mixture of CuTi_2 and solid solution of copper in titanium was formed.
4. The front of the Cu-Ti reaction migrates into copper, since phases rich in copper are the dominating fraction of the structure synthesised with the liquid phase contribution.
5. The process of intermetallic phases synthesis from the copper and titanium sheets is not of the SHS type as no exothermic peak was observed on the differential thermal analysis curve for Cu-Ti couple heated to 1000 °C.
6. The structural transformation that takes place with the liquid phase contribution between the copper and titanium sheets provides the opportunity to produce a copper-intermetallic phases layered composite. As-synthesised microstructure of the composite layers contains rich in copper phases: of the Cu_4Ti , Cu_2Ti and the CuTi intermetallic compounds. The heterogeneous microstructure in the neighbourhood of the copper layers corresponds to the mixture of Cu_4Ti intermetallic compound and solid solution of titanium in copper.

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