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Processing and structure of laminated iron-intermetallics composites

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Abstract

Using Fe sheets and Cu and Ti foils, Fe-intermetallic phases laminated composites have been fabricated through reactive sintering at 900^{o}C for 15, 30 and 120 minutes in vacuum. After 15 minutes at 900^{o}C all titanium layers were fully consumed but there were thin (about 40 μm) unreacted layers of copper. What was important, the copper layers could still block the diffusion of Ti to Fe. With increasing annealing time up to 30 minutes at 900^{o}C the layers of Cu disappeared completely forming intermetallic phases. Thus, the final microstructure consisted of alternating layers of intermetallic phases and unreacted Fe metal. The microstructure was revealed in optical and scanning electron microscopy (SEM). The study exhibited the presence of different reaction products in the diffusion zone and their chemical compositions were determined by energy dispersive spectroscopy (EDS). The occurrence of different intermetallic compounds such as Ti_2Cu, TiCu, Ti_3Cu_4, TiFe, $TiFe_2$, T_1 ($Ti_{33}Cu_{67-x}Fe_x$; 1<x<2,5), T_2 ($Ti_{40}Cu_{60-x}Fe_x$; 5<x<17) and T_3 ($Ti_{43}Cu_{57-x}Fe_x$; 21<x<24) was predicted from the ternary phase diagram Fe-Cu-Ti. The study revealed that titanium could migrate to iron through copper layers when a treating time at 900 ^{o}C was longer than 15 minutes, hence, copper layers could not effectively hinder the formation of brittle Ti-Fe base intermetallics.

Keywords: Innovative materials, Laminated composite, Iron, Intermetallic phase

1. Introduction

Laminated structures are being intensively studied for a number of potential applications: structural components, armour, electronic devices, etc. Metal-metal [1, 2], metal-ceramic [3, 4], metal-ceramic-intermetallic [5] and metal-polymer [6] systems have shown desirable properties. Since two decades there is a great interest in metal-intermetallic laminated (MIL) composites. The intermetallic phases, as a distinct class of materials, have unique properties: high resistance to oxidation and corrosion, high melting point, relatively low density and give high hardness and stiffness to the laminated composites. Unreacted metal provides the necessary high strength, toughness and ductility for the system to concurrently be flexible. Methods for the production of MIL composites include: diffusion bonding [7], magnetron sputtering [8], electron beam evaporation [9], vacuum plasma spraying [10] and synthesis reactions between dissimilar elemental metal foils. Reaction synthesis using foils has some advantages over some other methods. The obvious economic benefit lies in the ease of processing. To obtain a composite foils of one metal are placed alternately with thicker foils 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 is fully consumed in the course of reaction. Because the products of the synthesis are growing into a layer, finally a metal-intermetallic laminated composite is obtained. The multilayered structure of the composite allows for variations in the layer thickness and phase volume fractions of the components simply through the selection of initial foil thickness, which consequently allows for the optimisation of mechanical properties for practical applications. Also the size and the number of layers of the component that can be produced is not limited. 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. Earlier researches reveal that MIL composites can be produced by reaction synthesis that occurs at the interface of Ni and Al [11, 12], Mg and Al [13], Nb and Al [14, 15], Fe and Al [16], Ti and Al [17, 18] or Cu and Ti [19-23] foils. In the present study, a reaction process was developed to fabricate laminated Fe-intermetallic composites using Fe sheets and Cu and Ti foils. Copper does not form any intermetallic with iron and form intermetallics with titanium. The melting point of Cu is lower with respect to Fe end Ti, so, increase in the flow-ability of the copper at higher temperature should encourage a good contact between the faying surfaces. It has been reported by Ghosh et al. [24] and Kato et al. [25] that direct bonding of iron to titanium promotes the formation of different brittle intermetallic phases like $TiFe_2$, TiFe and Fe_2Ti_4O. Unfortunately, all these brittle intermetallic compounds impair the mechanical properties. The main aim of using copper interlayer was to improve the joint quality by reducing brittle Ti-Fe-base intermetallics. This paper summarises the processing and structure investigations of laminated iron - Ti-Cu-Fe-base intermetallics composites.

2. Experimental procedure

The rectangular samples with the dimensions of 50 mm length and 10 mm width of 0.6 mm thick sheets of iron, 0.1 mm thick foils of copper and 0.1 mm thick foils of titanium were used to fabricate a laminated Fe-intermetallic composite. The chemical compositions of the base materials are given in Table 1.

Table 1.
Chemical compositions of the base materials

Material	Chemical composition (at. %)
Fe99,9 (armco)	Fe: 99.89, C: 0.02, S: 0.02, P: 0.02, Al: 0.02, Si: 0.02, Mn: 0.01, O: 0.01, N: 0.01
Cu99,99	Cu: 99.99, Fe: 0.001, Ni: 0.001, Zn: 0.001, Sn: 0.001, Pb: 0.001, Sb: 0.001, As: 0.001, S: 0.001
Ti99	Ti: 99.02, Fe: 0.09, C: 0.02, Al: 0.27, V: 0.09, Cr: 0.05, Mo: 0.01, O: 0.44, N: 0.01

The joining surfaces of the samples were prepared by conventional grinding techniques using 800-grit abrasive paper. As it was necessary to remove oxide layers, the iron sheets and copper foils were cleaned in an aqueous HNO_3 solution (5%), while the titanium foils in HF solution (2%). Rinsed first with water and then with ethanol and dried rapidly, the foils were placed alternately to form multilayer sandwiches of iron/copper/titanium/copper/iron (5 Fe, 8 Cu and 4 Ti layers), which were then treated in a vacuum furnace under vacuum of 10^{-2}Pa. An external load of 5 MPa was applied at room temperature to ensure good contact between the foils. The temperature was initially raised to 850 ^{0}C and then the pressure was released to avoid an expulsion of liquid phases. It has been earlier found [19] that a temperature of 890 ^{0}C is sufficient for the liquid phase to appear at the copper-titanium interface. Subsequently, the temperature was increased to 900 ^{0}C, which was necessary for the initiation and rapid development of the structural processes at the interfaces of iron, copper and titanium. The samples were held at a temperature of 900 ^{0}C for 15, 30 and 120 minutes. After that they were furnace-cooled in vacuum till room temperature. A pressure of 5 MPa was applied during cooling at 850 ^{0}C to avoid a possible porosity (Figure 1).

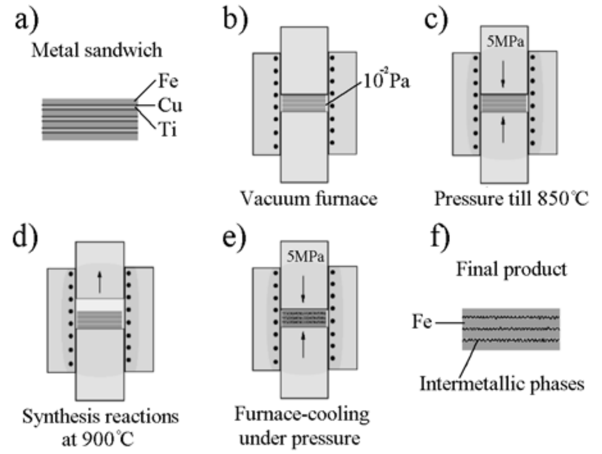

Fig. 1. A schematic diagram of Fe-intermetallic composite fabrication

After fabrication, the specimens were cut, mounted in a cold setting resin, mechanically ground initially with a grade 800 abrasive paper and finally polished on 1 µm diamond suspension using Struers polishing machine. Microstructural observations were performed using a JEOL JMS 5400 scanning electron microscope and a Carl Zeiss NEOPHOT 2 optical microscope. Before the samples were examined with the optical microscope they had been etched using an aqueous HNO_3 solution (5%) and HF solution (2%) to reveal any iron grain boundaries and the structure of the intermetallic layers. The chemical composition of the phases was determined in atomic percent using an Oxford Instruments ISIS 300 system.

3. Results and discussion

At the beginning of the structural investigations a microstructure developed due to solid state diffusion was studied. Figure 2 shows the microstructure of the diffusion-bonded joints Fe-Cu and Cu-Ti formed in the sample after holding for 15 minutes at 850 ^{0}C.

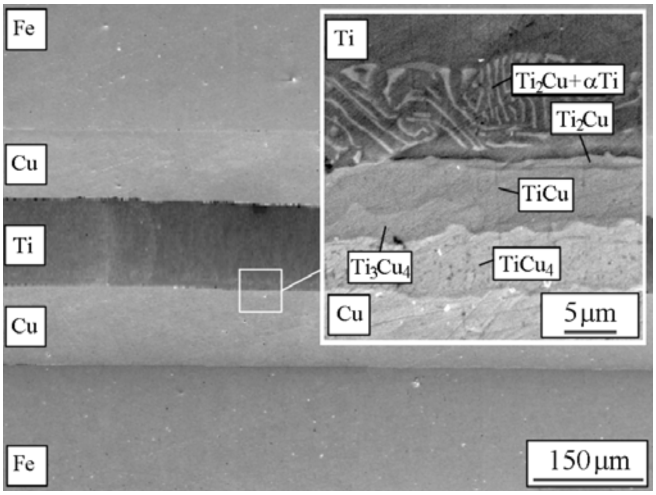

Fig. 2. Scanning electron micrographs showing the diffusion joints developed for Fe-Cu and Cu-Ti couples annealed at 850 ^{0}C for 10 minutes

Diffusion occurred between the copper interlayer and two substrates Fe and Ti. The Fe-Cu bonding interface was planar in nature and only a thin diffusion layer of solid solution was revealed. In Cu-Ti diffusion zone five distinct reaction layers were observed (Fig. 2). The analysis of the microstructure was based on the Ti-Cu binary phase diagram [26] using X-ray spectroscope. Adjacent to titanium the eutectoid mixture containing Ti_2Cu and αTi (solid solution of copper in titanium) was identified. This double-phase layer was followed by thin single-phase layers: Ti_2Cu, TiCu, Ti_3Cu_4 and $TiCu_4$. In the Ti-Cu diagram the liquid phase appears at 875 ^{0}C as a product of the eutectic reaction between Ti_3Cu_4 and $TiCu_4$, so it is obvious that at 900 ^{0}C reactions are much faster. Figure 3 shows the microstructure of the intermetallics layer formed after heat treatment at 900 ^{0}C for 15 minutes. The reactions with liquid transformed intermetallics to mushy stage, leading to this type of microstructure.

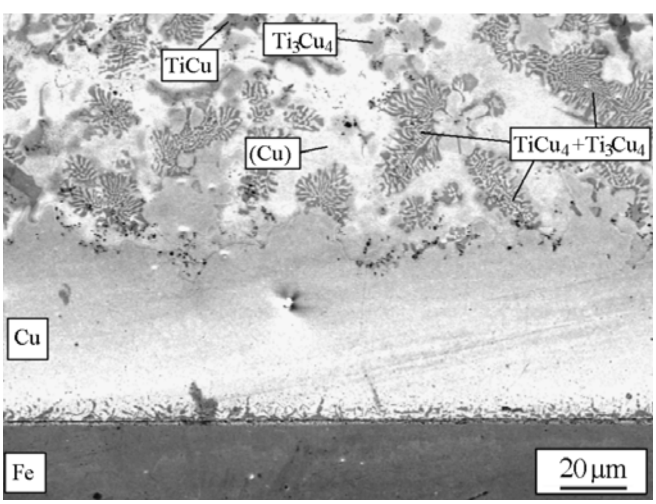

Fig. 3. Microstructure of the reaction zone formed after heat treatment at 900 ^{0}C for 15 minutes

In the temperature interval 882-900 ^{0}C, iron and titanium both have bcc structure. Owing to more open crystallography of bcc matrix, copper atoms can travel longer distance in titanium lattice than vice-versa [27], so after 15 minutes at 900 ^{0}C all titanium was fully consumed but there were thin (about 40 μm) unreacted layers of copper (Fig. 3). What is important, the copper layers could still block the diffusion of Ti to Fe. With increasing annealing time up to 30 minutes at 900 ^{0}C the layers of Cu disappeared completely (Fig. 4).

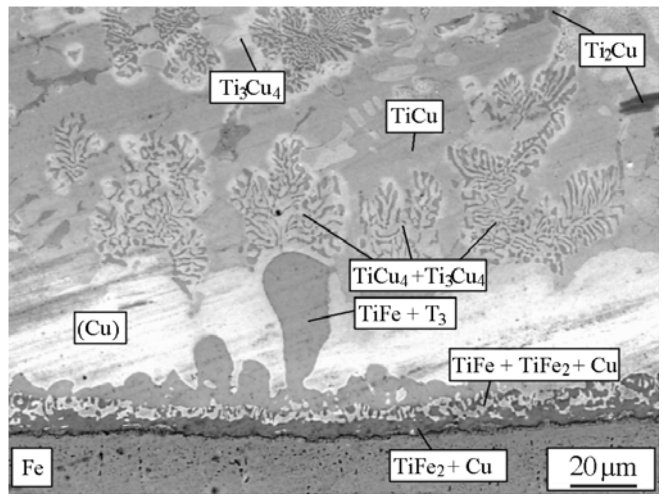

Fig. 4. Microstructure of the reaction zone formed after heat treatment at 900 ^{0}C for 30 minutes

A study of the above structure was based on the Fe-Cu-Ti ternary phase diagram constructed by Beck et al. [28] that is depicted in Figure 5.

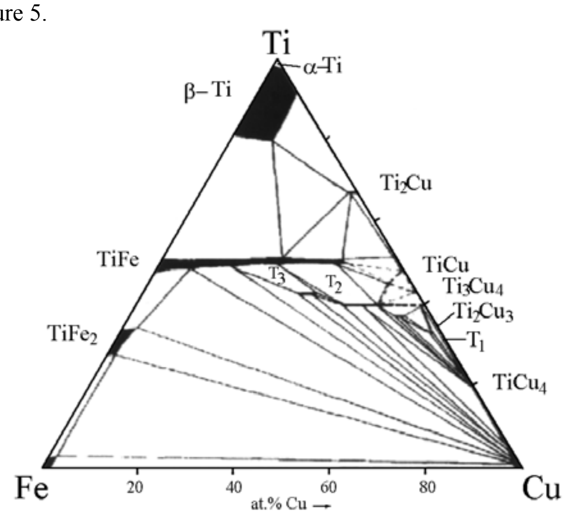

Fig. 5. Isothermal cross-section through the ternary phase diagram Fe-Cu-Ti at 850 ^{0}C [28]

Intermetallic compounds of the binary Ti-Cu system (Ti_2Cu, TiCu, Ti_3Cu_4, $TiCu_4$) with very low iron content (less than 0.5 at. %) were found in the reaction zone of the sample (Fig. 6).

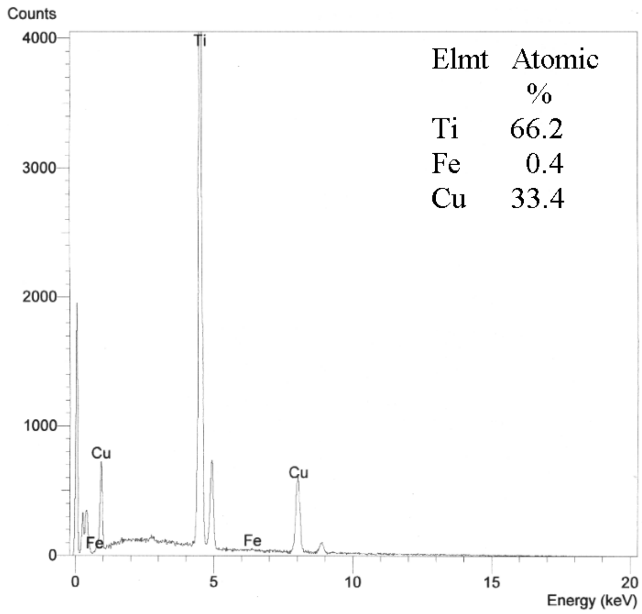

Fig. 6. The energy spectrum for emitted X rays for Ti_2Cu

Also a layer of the copper-based solid solution (Cu) was still detected. Besides that, the continuous layer of the mixture $TiFe_2$ and Cu and the fragmented layer of another mixture TiFe and ternary phase designated T_3 ($Ti_{43}Cu_{57-x}Fe_x$; 21<x<24) were presumably observed. Figure 7 shows an example of X-ray energy spectrum for TiFe+T_3 region of the structure depicted in Figure 4.

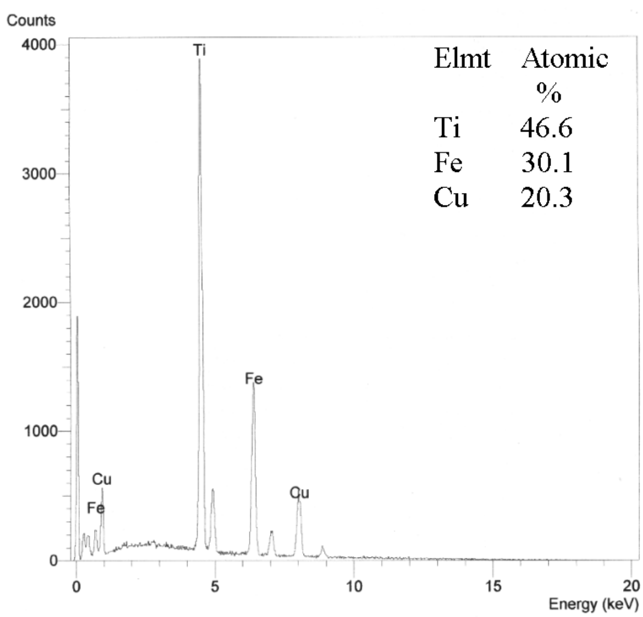

Fig. 7. The energy spectrum for emitted X rays for TiFe+T_3 region in Figure 4

It is evident from metallographical examinations that the predominant part of intermetallics synthesised at 900 ^{0}C for 30 minutes was synthesised in the region passing from a liquid state to a solid state. The temperature of 900 ^{0}C promotes mass transfer of the alloying elements across the interface, which is responsible for the increase in volume fraction of the reaction products. Diffusion of chemical elements becomes easier, i.e. after 30 minutes of treating Ti can migrate through Cu to Fe, hence, copper layer cannot hinder the formation of brittle Ti-Fe-base intermetallics. With increasing annealing time up to 120 minutes at 900 ^{0}C the structure of intermetallics was formed due to solid state transformations (Fig. 8).

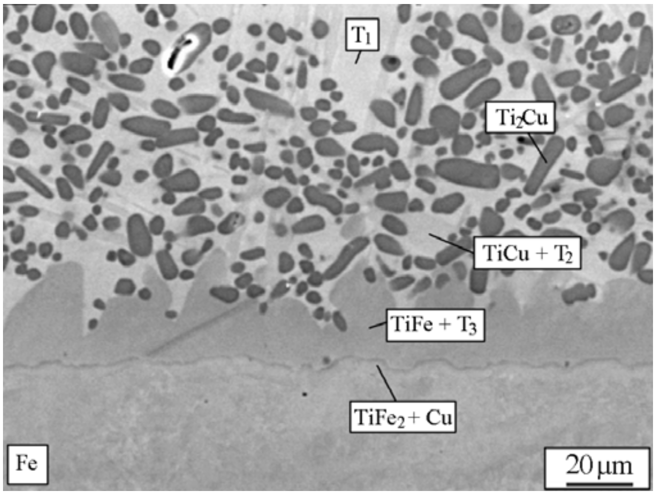

Fig. 8. Microstructure of the intermetallic layer formed after heat treatment at 900 ^{0}C for 120 minutes

Using X-ray microanalysis, it was found that the thin area containing Ti (29.8 at. %), Fe (59.5 at. %) and Cu (10.7 at. %) was presumably the phase mixture of $TiFe_2$ + Cu. Adjacent to $TiFe_2$ + Cu, the deeply shaded area, consisted of Ti (49.6 at. %), Fe (30.1 at. %) and Cu (20.3 at. %), perhaps was a phase mixture of TiFe + T_3. T_3 is $Ti_{43}Cu_{57-x}Fe_x$; 21<x<24 having structure closely related to Ti_3Cu_4 [29]. It was also reported by van Beck et al. [28] that nearly 38 at. % Cu could be dissolved in FeTi. A lightly shaded region consisting of Ti (41.5 at. %), Fe (5.9 at. %) and Cu (52.6 at. %) perhaps was a phase mixture of TiCu + T_2. T_2 phase is $Ti_{40}Cu_{60-x}Fe_x$; 5<x<17 with structure resembled to the Ti_2Cu_3 intermetallic compound [28]. A bright areas contained Ti (33 at. %), Fe (1.5 at. %) and Cu (65.5 at. %), hence, the ternary phase T_1 ($Ti_{33}Cu_{67-x}Fe_x$; 1<x<2,5) might be present. An intermetallic compound of the binary Ti-Cu system with very low iron content was presumably found in the dark shaded islands with composition of Ti (66.3 at. %), Fe (0.4 at. %), Cu (33.3 at. %). It perhaps was Ti_2Cu. After processing, the composite microstructure consisted of alternating, well-bonded Fe and intermetallics layers (Fig. 9).

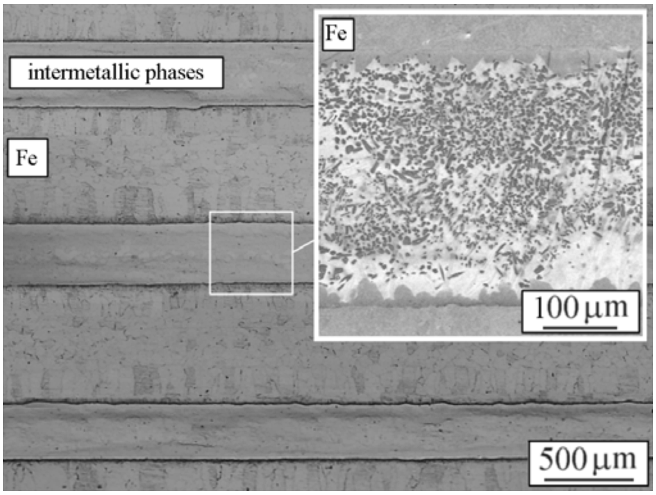

Fig. 9. Optical and scanning electron micrographs showing a typical microstructure of the laminated composite produced from Fe, Cu and Ti foils at 900 ^{0}C after treating for 120 minutes

4. Conclusions

In a consequence of a reaction occurring between iron sheets and copper and titanium foils in vacuum at a temperature of 900 ^{0}C, a laminated Fe-intermetallics composite is formed. It is evident from metallographical examinations that the predominant part of intermetallics is synthesised in the region passing from a liquid state to a solid state. The inhomogeneous reaction zone contains intermetallic compounds, presumably: Ti_2Cu, TiCu, Ti_3Cu_4, TiFe, $TiFe_2$, T_1 ($Ti_{33}Cu_{67-x}Fe_x$; 1<x<2,5), T_2 ($Ti_{40}Cu_{60-x}Fe_x$; 5<x<17) and T_3 ($Ti_{43}Cu_{57-x}Fe_x$; 21<x<24). The study reveals that titanium can migrate to iron through copper layer when a treating time at 900 ^{0}C is longer than 15 minutes, hence, copper layer cannot effectively hinder the formation of brittle Ti-Fe base intermetallics.

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