

EFFECT OF NICKEL AND COBALT ADDITIONS ON INFILTRATION BEHAVIOR, MICROSTRUCTURE AND HARDNESS OF W-AG COMPOSITES

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Abstract: In this research, infiltration behavior of W-Ag composite compacts with Nickel and Cobalt as additives has been investigated. Nickel and Cobalt were added to Tungsten powder by two distinct methods: mixing elementally and reduction of salt solution. The coated Tungsten powders were compacted under controlled pressures to make porous skeleton with 32-37 vol. % porosity. Infiltration process was carried out at 1100 °C under a reducing atmosphere for 1h. The effect of additives on infiltration of Ag and density were evaluated by SEM and Archimedes methods. Properties of the specimens were compared following two distinct processes namely: I) sintering simultaneously with infiltration process and II) sintering prior to infiltration (pre-sintering process). It was found that specimens which were pre-sintered and then infiltrated with molten silver represent higher hardness and finer microstructure than the specimens infiltrated simultaneously with sintering.

Keywords: Infiltration; W-Ag Composites; Powder Metallurgy; Mixing Elementally; Reduction of Salt Solution.

1. INTRODUCTION

Tungsten-silver and tungsten-copper composites are widely used in mechanical and electrical engineering. Typical applications of these composites are high, medium, and low-voltage circuit breakers, resistance welding electrodes, electrode materials for electrical discharge machining, and heat sink materials for microelectronic packaging. More recently, these composites have been tested as heat flux components in experimental fusion reactors [1] and as materials in MHD (magneto hydrodynamics) power generation systems [2]. They combine the high hardness, hot strength, and wear resistance of tungsten with the outstanding electrical and conductivity of silver and copper. Furthermore, tungsten increases the resistance of the materials against spark and arc erosion (burn-off) and decreases the sticking and welding tendency, which are both important criteria for heavy-duty electrical contacts [3]. Under arcing conditions, the contacts are cooled through the melting and evaporation of silver or copper ("transpiration" cooling), an effect which was earlier used for rocket nozzle throat liners (e.g. water-launched ballistic missiles) made of W-Ag [4]. W-Ag and W-Cu composites are not

classified as alloys, because the mutual solubility of the components is practically zero, therefore they are called "pseudo alloys". Powder metallurgy is the only viable way to produce such composites of high quality. The method of production depends on the composition ratio. Materials with 20 to 50 wt% silver or 10-40 wt% copper are commonly produced by infiltration, while at higher silver or copper contents the powders are blended, pressed, and subsequently solid-state sintered [5, 6].

2. EXPERIMENTAL PROCEDURES

Tungsten powder with average particle size of 10.6µm and purity of more than 99.9% was used as raw material. Fig. 1 shows representative SEM micrograph taken from tungsten powder which exhibits the morphology of particles. Cobalt and nickel were added to tungsten powder as additives by two distinct metallurgical methods. In mixing elementally a double cone mixer was used for 15 h. The milling was performed for 10 h under rotation speed of 300 rpm. On the other hand, in reduction of salt solution method, NiCl₂. 6H₂O and CoCl₂. 6H₂O (with 97% purity, Merck Germany) were mixed with tungsten powder. The mixture was heated at 130 °C for 12 min to

remove H_2O and methanol. In the next step, the mixture was held at $600\text{ }^{\circ}\text{C}$ for 90 min in hydrogen atmosphere. During this process, nickel and cobalt particles were deposited on tungsten particles. The weight of additives was selected to obtain 0.4 % wt of additives in the powder mixture. Considering the average porosity of specimens 35 vol. % and volume of compacted specimens 1.65 cm^3 , it could be possible to calculate the amount of silver for infiltration process. The powder was uniaxially compacted with a single action press to obtain a porous skeleton. The powder was pressed with diameter 16 mm and thickness 8 mm to obtain a desire porosity of 32-37 vol. %. A tube furnace with controlled atmosphere was used for sintering and infiltration process. Hydrogen with 99.99 % purity was entered to oven after preheating at $300\text{ }^{\circ}\text{C}$. Two methods were applied for sintering and infiltration of compacted specimens. In sintering simultaneously with infiltration process, sintering and infiltration were done at the same time. For this purpose, a sheet made from silver was put on the porous specimens in the oven. Heating rate was $25\text{ }^{\circ}\text{C}/\text{min}$ and flowing rate of hydrogen was 3.5 lit/min. Specimens were held at $1100\text{ }^{\circ}\text{C}$ for 1 h. The specimens were then cooled in argon atmosphere with flowing rate of 4 lit/min.

In pre-sintering process, sintering was done prior to infiltration. Specimens were compacted to 420 MPa and sintered at $1100\text{ }^{\circ}\text{C}$ for 25-50 minutes under Hydrogen atmosphere. The amount of porosity in all samples was approximately 35% in the sintered condition. After infiltration, the specimens were cooled in argon atmosphere with argon flowing rate of 3.5 lit/min.

The density of pressed composites was determined by Archimedes technique. The specimens were initially polished with silicon carbide paper up to 1200 grit paper. Final polishing was done on an automatic polisher with diamond paste. The polished surfaces of specimens were etched for 10-15 seconds using Murakami etchant containing of 1 g KOH + 4 g $K_3Fe(CN)_6$ + 95 ml H_2O . The microstructure of composites was observed by scanning electron microscopy (PHILIPS-XL30). Hardness was measured using a Rockwell hardness tester

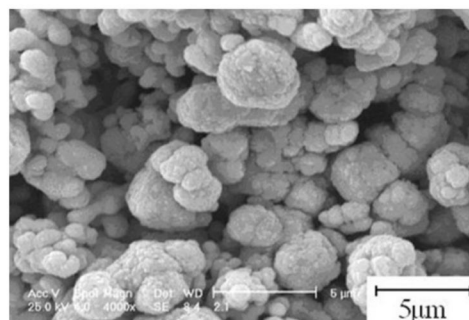


Fig. 1. SEM image of tungsten powder.

according to ASTM B227 [7] and five indentation were done in each sample to obtain average value.

3. RESULTS AND DISCUSSION

3. 1. Microstructural Assessment

The dispersion of nickel and cobalt particles as additives in tungsten powder by two different methods is shown in Fig. 2(a-d). As can be seen, samples prepared by reduction of salt solution method have better dispersion of nickel and cobalt than mixing elementary method due to creation of a salt solution. In mixing elementary method the nickel and cobalt particles can be clearly distinguished. The powders were investigated by X-ray mapping of the elements. Normally the W-Ni specimens are sintered at $1300\text{ }^{\circ}\text{C}$ in the blended condition. However, preliminary investigations, demonstrated that coated powders could be sintered at $1100\text{ }^{\circ}\text{C}$ successfully, that may be due to higher activity at W/Ni or W/Co interfaces.

In sintering simultaneously with infiltration process the dispersion and continuity of silver in reducing salt solution specimens are better than mixing elementally specimens. Silver dispersion in boundaries is also more uniform in specimens containing cobalt due to higher diffusion and uniform grain growth. In the specimens containing cobalt as an additive, because of higher penetration, grain growth is more rapid and it could be a suitable parameter for diffusion of molten silver in porous skeleton of tungsten.

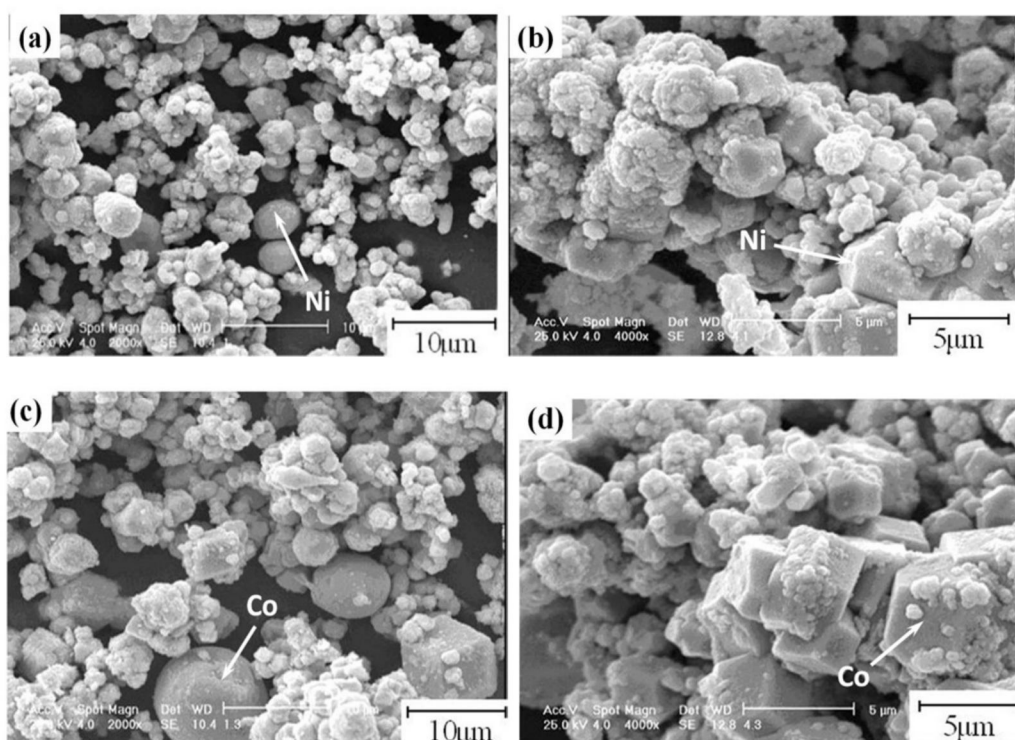


Fig. 2. SEM micrographs of silver-tungsten (a) with nickel by mixing elementary method (b) with nickel by reduction of salt solution method (c) with cobalt by mixing elementary method (d) with cobalt by salt reduction of solution method

Specimens containing cobalt have coarser grains than specimens containing nickel. In fact, in specimens containing cobalt and in sintering simultaneously with infiltration process, in addition to a rearrangement of particles, existence of an inter-metallic phase of cobalt causes coarser grain size and a more contiguity among grains as it is indicated in Fig. 3.a and b. Bright regions in Fig. 3.a are related to silver and dark regions are related to tungsten. In Fig. 3.b

the bright regions are related to solution of silver and nickel and the dark regions are related to tungsten.

3. 2. Hardness

Microstructure has a direct effect on hardness. In fact, hardness is related to the volume fraction of hard phase [8]. A schematic of the hardness of different specimens is shown in Fig. 4. As can be

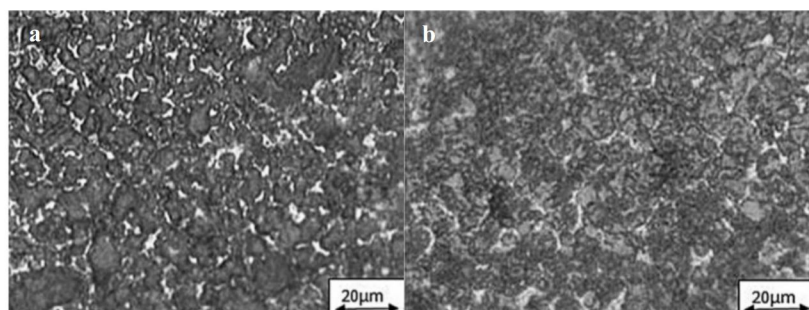


Fig. 3. a. the microstructure of specimen containing cobalt added by reducing salt solution in sintering simultaneously with infiltration process **b.** the microstructure of specimen containing nickel added by reducing salt solution in sintering simultaneously with infiltration process.

seen clearly, using pre-sintering process leads to higher hardness values due to bond strengthening which it is the dominant mechanism in pre-sintering process. Finer grains of specimens in pre-sintering conditions were obtained. Specimens containing cobalt have high strength bonds due to higher sintering rate in solid state phase. On the other hand, in sintering simultaneously with infiltration process, specimens containing cobalt have higher hardness values because of existing cobalt in grain boundaries and immiscibility of cobalt in molten silver and higher sintering rate.

4. CONCLUSIONS

Reduction of salt solution as compared with mixing elementally exhibits a better effect on dispersion and infiltration of the liquid phase.

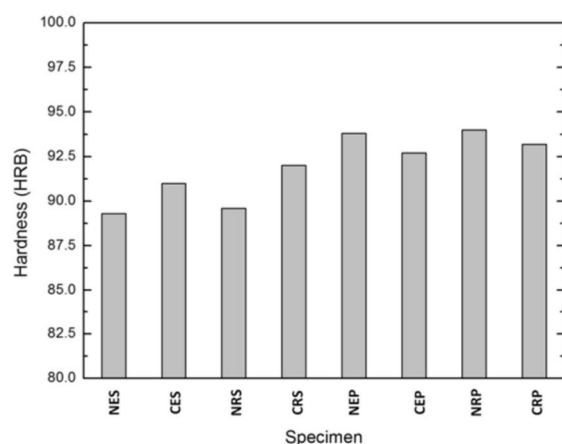


Fig. 4. Schematic of the hardness of different specimens

- NES: Nickel added by mixing elementally in sintering simultaneously with infiltration process.
 CES: Cobalt added by mixing elementally in sintering simultaneously with infiltration process.
 NRS: Nickel added by reduction of salt solution sintering simultaneously with infiltration process.
 CRS: Cobalt added by reduction of salt solution in sintering simultaneously with infiltration process.
 NEP: Nickel added by mixing elementally in pre-sintering process.
 CEP: Cobalt added by mixing elementally in pre-sintering process.
 NRP: Nickel added by reduction of salt solution in pre-sintering process.
 CRP: Cobalt added by reduction of salt solution in pre-sintering process.

Pre-sintered specimens achieved higher hardness (4%), compared with sintering simultaneously with infiltration.

In sintering simultaneously with infiltration process the dispersion and continuity of silver in reducing salt solution specimens are better than mixing elementally specimens.

In the specimens containing cobalt as the additive, because of higher penetration, grain growth is more rapid.

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THE FORMATION OF $TiAl_3$ DURING HEAT TREATMENT IN EXPLOSIVELY WELDED Ti-Al MULTILAYERS

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Abstract: Metallic-intermetallic laminate (MIL) composites are promising materials for structural applications especially in the aerospace industry. One of the interesting laminate composites is the Ti-TiAl₃ multilayer. In this work, commercially pure sheets of aluminum and titanium with almost equal thickness of around 0.5 mm were explosively joined. The achieved multilayers were annealed at 630 °C in different times so that an intermetallic layer was formed at the Ti/Al interface. The resulting microstructure was studied by optical and scanning electron microscopy and Energy Dispersive Spectroscopy (EDS). TiAl₃ was the only intermetallic phase that was observed in all annealing times. The kinetics of the formation of TiAl₃ was investigated and compared to previous research studies performed on Ti-Al multilayers which were fabricated using methods other than explosive welding.

Keywords: Intermetallic; Laminate Composites; TiAl₃; Intermetallic Formation Kinetics.

1. INTRODUCTION

Materials that maintain their mechanical properties at high temperatures are in demand for high-temperature structural applications in which high values of strength-to-weight and stiffness-to-weight ratios are essential [1]. Intermetallics such as Ti₃Al and Ni₃Al maintain their strength and even develop reasonable ductility at elevated temperatures. According to a simple definition, intermetallics are compounds of metals whose crystal structures are different from those of the constituent metals, and thus develop properties different from the constituting metals [2,3]. Titanium aluminide intermetallic compounds offer an attractive combination of low density and good oxidation and ignition resistance with unique mechanical properties such as high strength and elastic stiffness as well as excellent high temperature retention. Thus, these compounds belong to the few classes of emerging materials that have the potential to be used in demanding high-temperature structural applications whenever specific strength and stiffness are of major concern [4]. Five main intermetallics, i.e. Ti₃Al, TiAl, Ti₂Al₃, TiAl₂ and TiAl₃ can be seen in the Ti-Al phase diagram [5].

Among the titanium trialuminide based composites, the multilayer "metallic-

intermetallic laminate" (MIL) composites should be emphasized. This composite possesses a unique set of mechanical properties. An important advantage of the multilayer composites is the possibility of combining the properties of both the hard and refractory intermetallics and the ductile matrix [6]. Metallic-Intermetallic composites have many application such as damping elements or blast energy absorber [6]. Reactive foil sintering is one way for producing these composites; however, the necessity to apply high pressures to prevent oxidation during sintering of the foils makes this process expensive for the production of this group of materials.

Explosive welding or bonding followed by annealing can be utilized as a non-expensive method to produce these types of materials. Explosive welding is the process of forming a bond by explosively impacting two metallic plates onto each other under controlled conditions. The explosive welding process yields excellent bonding of similar or dissimilar metals with different hardness, melting points, thermal-expansion characteristics and electrode potentials. Furthermore, the process can be applied to a broad range of thicknesses and area dimensions due to the ability to distribute the high energy of explosion over the entire welding

area [7]. Applications of explosive welding are therefore numerous, from the production of "sandwich" plates for coinage to the more sophisticated use of titanium-to-stainless-steel transition joints in spacecraft [7]. The high strength and fracture toughness of explosively welded materials are due to the particular structural state of the welds formed by the dynamic interaction of work pieces [8-12].

Unlike the pressure-applying methods such as reactive foil sintering, explosive welding provides a very good contact between layers before heat treatment of layers without the need to apply high pressures. The kinetics of intermetallic formation in Ti-Al multilayers have been studied by several investigators [13-15]; however, there is a lack of information about kinetics of the formation of intermetallics during the heat treatment of explosively welded Al-Ti multilayers. Therefore, the present work is undertaken to study the kinetics of the formation of intermetallics during annealing of explosively welded Al-Ti multilayers.

2. EXPERIMENTAL

2.1. Materials and Explosive Welding

Six alternative sheets of aluminum and CP-titanium were explosively welded together. The initial thickness of aluminum and titanium sheets was almost 0.5 mm. The chemical composition of

Table 1. Chemical composition of initial materials for explosive welding.

Material	Composition wt. %			
Ti Plates	Ti=99.93	Al=0.03	C=0.04	
Al Plates	Al=99.55	Fe=0.32	Mg=0.03	Ti=0.05

initial materials is presented in Table 1. As shown in 0 1, parallel set-up for explosive welding was used. Ammonium nitrate mixed with TNT and fuel oil was used as explosive. The welding assembly was placed on a wooden plate placed on a sand bed.

2.2. Microstructural Studies

The cross section of samples were ground and polished to 0.3 μm finish. Microstructural investigation and analysis of the samples were conducted using an optical and scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS).

2.3. Heat Treatment

After studying the interface of initial as-welded samples, the multilayer samples were annealed between 1 and 70 hours at 630°C in

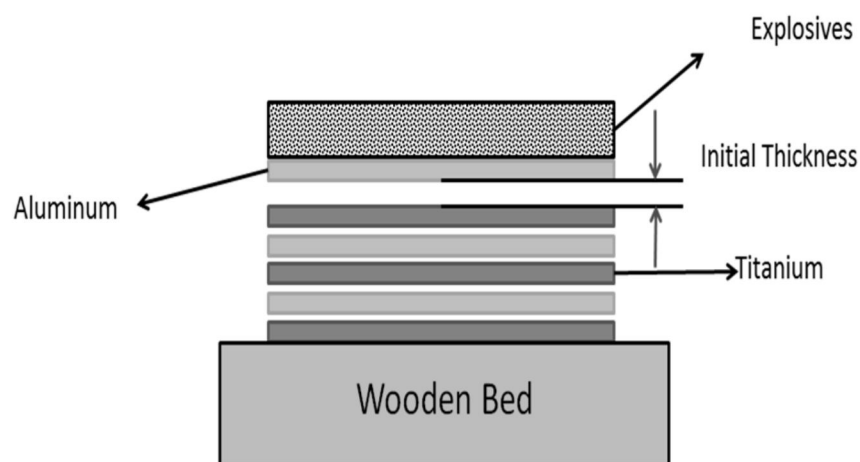


Fig. 1. Schematic presentation of parallel setup used for Ti-Al multilayer explosive welding.

ambient atmosphere using a resistance furnace. Intermetallic thickness was measured using optical and scanning electron micrograph images. Since the intermetallic phase could be readily distinguished, no etchant was used.

3. RESULTS AND DISCUSSION

3. 1. Structural Studies of Ti-Al Composite After Explosive Welding

Scanning electron micrograph of the initial multilayer sample (after explosive welding and rolling) is shown in Fig. 2(a). As can be seen in this figure, there is a smooth interface between aluminum and titanium layers, and no vortex zones are formed. The vortex zones are microvolumes which are sometimes formed by

explosive welding and can have different shapes, depending upon the welding conditions and the properties of the joined materials [8]. In the specimens prepared for the study no vortex was detected between layers. However, intermetallics were formed at different locations of the interfaces (Fig. 2b)), although the formation was not uniform. EDS analysis of these intermetallics is shown in Fig. 2(c). These analyses show that the initial intermetallic was TiAl_3 . The formation of TiAl_3 is favorable from both thermodynamic and kinetic points of view. Based on the optical images of sample (Fig. 3), average thickness of the intermetallic formed before heat treatment was $9.54 \pm 2.84 \mu\text{m}$.

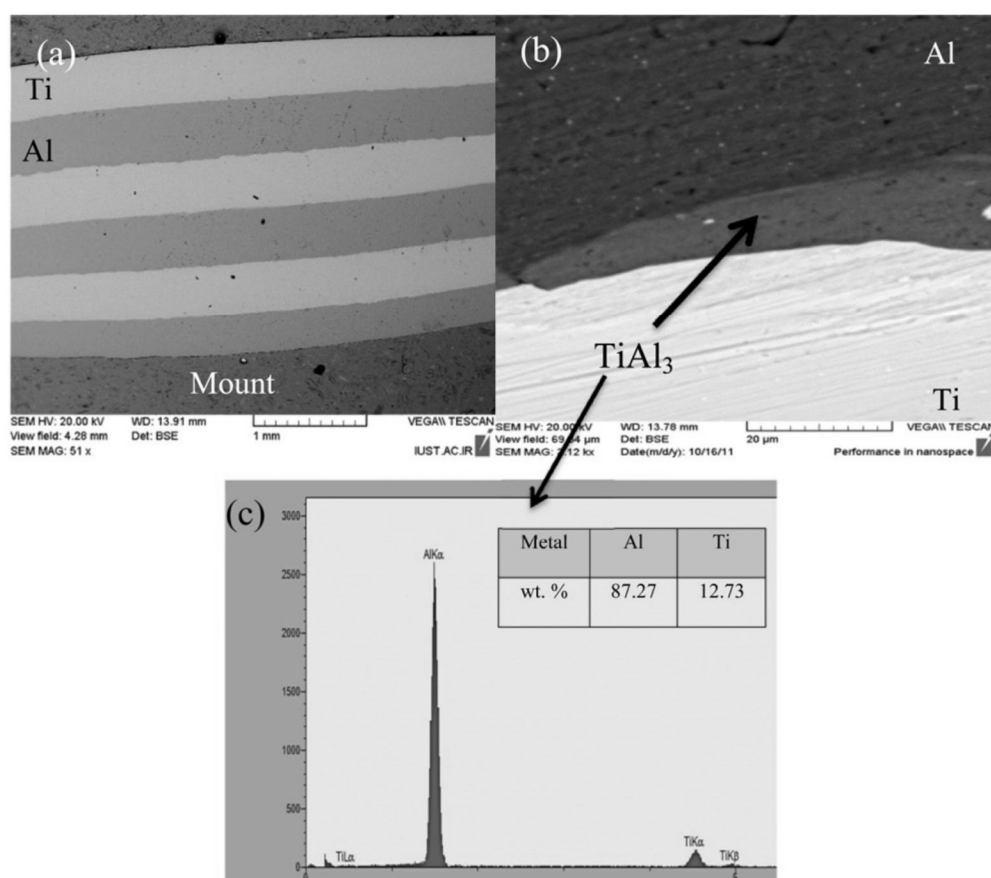


Fig. 2. SEM micrographs of as-welded sample, (a) the Ti/Al multilayer, (b) the intermetallics formed at the interface (c) EDS analysis of the intermetallic phase.

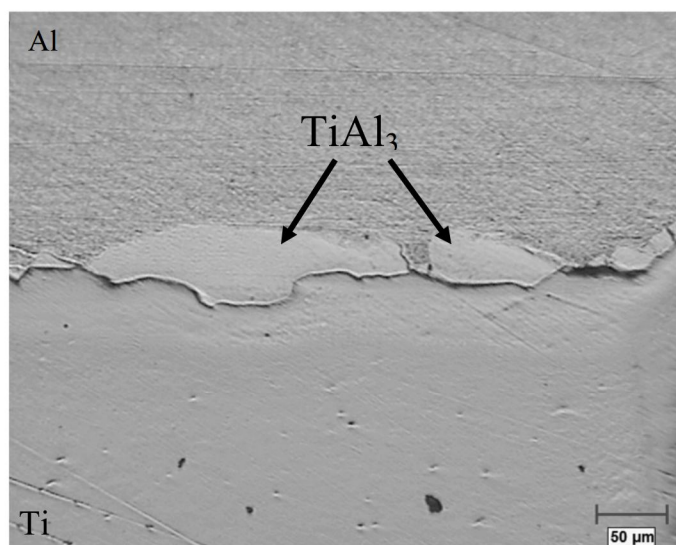


Fig. 3. Optical micrograph showing the non-uniform formation of TiAl_3 at Ti/Al interface in the as-welded sample.

3. 2. Microstructural Studies of Annealed Samples

During annealing at 630 °C, the intermetallic layer grows at the interface between titanium and aluminum. TiAl_3 is the only intermetallic formed independent of the annealing time. Aluminum, titanium and TiAl_3 thickness variations during heat treatment were measured. Intermetallic thickness variation vs. time is shown in Fig. 4. As

can be seen in this figure, the intermetallic growth takes place through two different mechanisms. The first part of the growth (until 10 hours), shows a linear behavior between thickness and time, this stage is reaction-controlled [16]. After 10 hours of annealing, on the other hand, a parabolic relationship between thickness and time can be seen, which is indicative of diffusion controlled behavior.

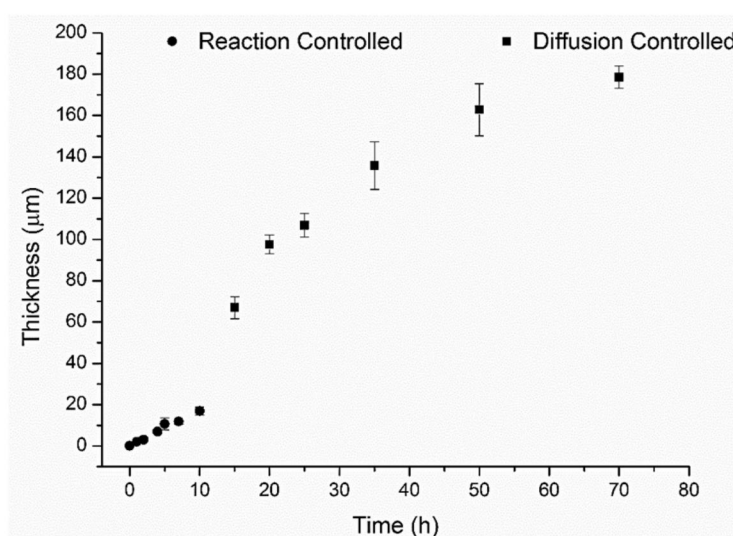


Fig. 4. Dependence of the average thickness of intermetallic layer on the annealing time

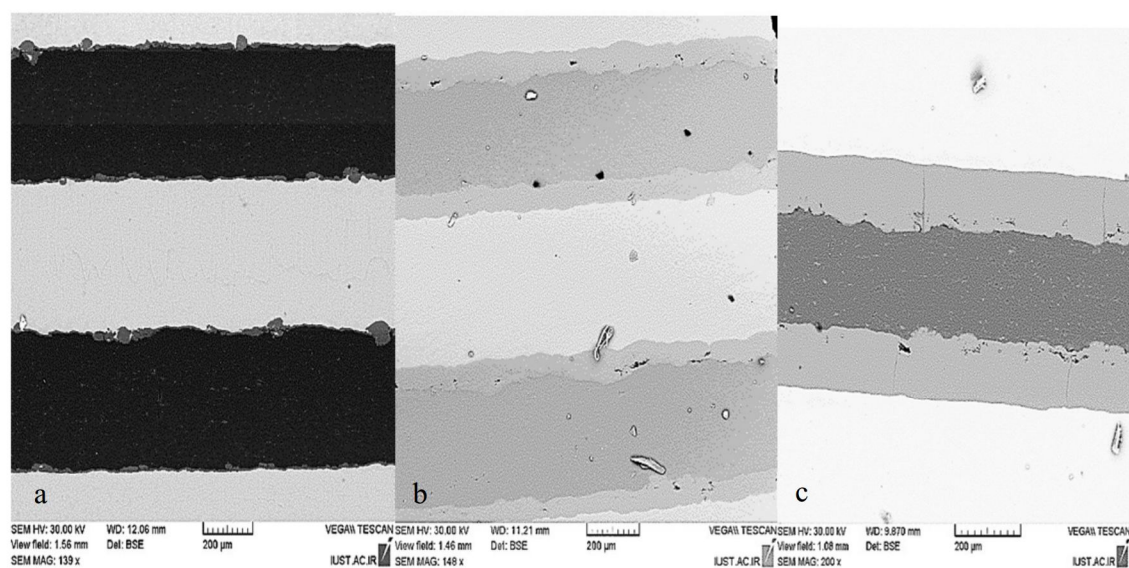


Fig. 5. Aluminum and titanium layers thickness decrease during annealing of layers at 630 for (a) 5h, (b) 15h and (c) 35h.

By passing of time and growth of intermetallic layer, the thicknesses of aluminum and titanium layers were reduced. The decrease in thickness can be seen in Fig. 5. As shown in this figure, the thickness of aluminum decreases more rapidly than titanium. Aluminum and titanium thickness reduction as a function of heat treatment time is shown in Fig. 6. By heat treatment at longer

TiAl₃ multilayers will form. Ti-TiAl₃ is a laminate composite with a very good compressive strength and low density and high Young's modulus [17].

The experimental results for measurement of TiAl₃ thickness which was already demonstrated in Fig. 4, is re-plotted as a function of time in logarithmic scale in Fig. 7. To express the

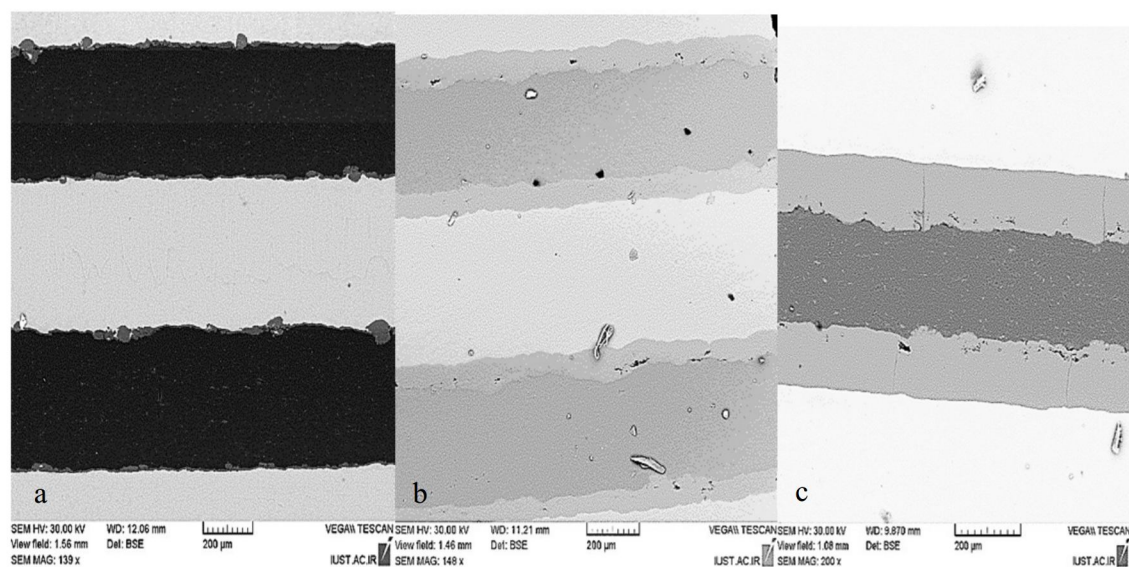


Fig. 6. Aluminum and titanium thickness reduction as a function of annealing time.

times, aluminum will totally be consumed and Ti- intermetallic thickness variation (x) as a function

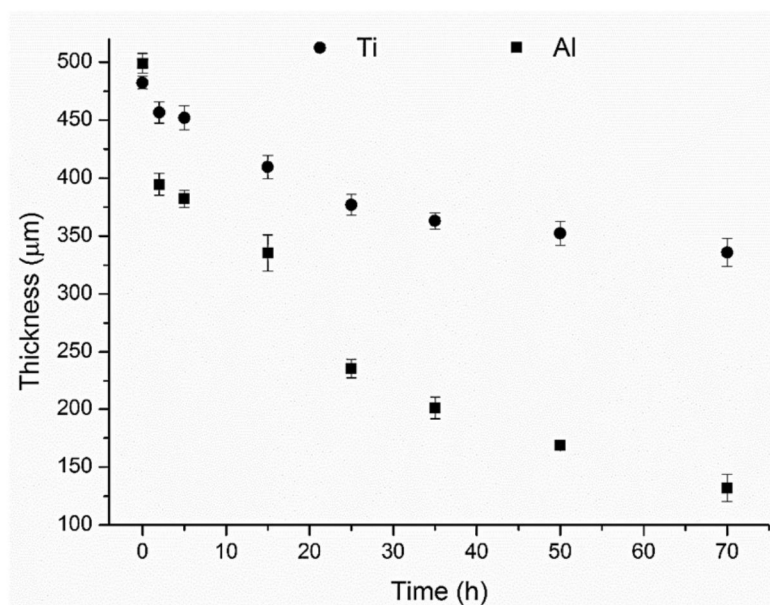


Fig. 6. Aluminum and titanium thickness reduction as a function of annealing time.

of annealing time (t), Eq. (1) can be assumed. Since there is a delay before the formation of intermetallic layer as well as the activation of the second mechanism, an initial time (t_0) was accounted for in Eq. (1), which changes it to the form of Eq. (2):

$$x = kt^n \quad (1)$$

$$x = k(t - t_0)^n \quad (2)$$

where n is the growth exponent and k is the

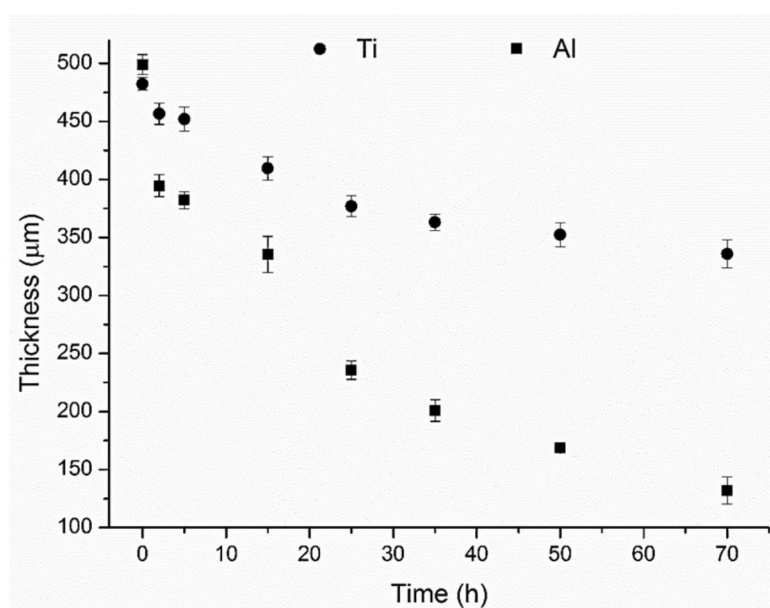


Fig. 7. Plot of thickness vs. time as fitted to Eq. (2) for both diffusion-controlled and chemical-controlled mechanisms.

growth rate constant. For first and second stages, theoretically, n should be 1 and 0.5, respectively. Using Eq. (2) and fitting it separately for two different steps in Fig. 7, " n " and " k " were calculated separately for both mechanisms. It can be seen that for reaction controlled mechanism, n and k are 0.96 and $1.86 \mu\text{m}/\text{sn}$, respectively, while for diffusion controlled mechanism n and k are 0.31 and $50.96 \mu\text{m}/\text{sn}$, respectively. Thus, the kinetic of the intermetallic formation at 630°C can be expressed in the form of Eqs. (3) and (4):

For reaction controlled mechanism:

$$x = 1.86 \times t^n \quad (3)$$

For diffusion controlled mechanism:

$$x = 50.96 \times (t-t_0)^{0.31} \quad (4)$$

CONCLUSION

MIL composites can be produced in several ways, e.g. reactive foil sintering, but most of these methods need quite expensive equipment. Combination of explosive welding and annealing is an inexpensive and effective way to produce these kind of composites. In this work, 6 alternative layers of Al and Ti were explosively welded together and then annealed at 630°C from 1 to 70 hours to produce intermetallic layer. In the as-welded sample, intermetallic were already formed nonuniformly. EDS analysis showed that TiAl_3 is the only intermetallic compound formed in the interface. The thicknesses of intermetallic, aluminum and titanium layers were measured. It was shown that aluminum is consumed faster than titanium. Growth exponent of TiAl_3 in explosively welded titanium and aluminum at the annealing temperature of 630°C is about 1.3.

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