Structure Formation Mechanisms during Solid Ti with Molten Al Interaction

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Abstract. The study discusses advantages and disadvantages of previously proposed mechanisms of the formation of structure between solid Ti and molten Al and presents a new mechanism based on the reviewed and experimental data. The previously proposed mechanisms were classified into three groups: mechanisms of precipitation, mechanisms of destruction and mechanisms of chemical interaction between intermetallics and melt. The reviewed mechanisms did not explain the formation of heterogeneous interlayer with globular aluminide particles and thin layers of pure Al, while the present study reveals variation in the solid Ti/molten Al reaction kinetics during various phases of laminated metal-intermetallic composite formation. The proposed mechanism considers formed during composite fabrication thin oxide interlayers between Ti and Al evolution and its impact on the intermetallic compound formation and explains the initial slow rate of intermetallic interlayer formation and its subsequent acceleration when the oxide foils are ruptured.

1. Introduction

One of the main problems of Ti/Al laminated metal composites with intermetallic interlayers (or just metal intermetallic laminates - MILs) production is the demand to obtain layers with proper thickness ratio.

The upper boundary of temperature range, where solid state diffusion in Ti/Al composites results in the formation of aluminides is only 100°C. The growth rate of aluminides is relatively small. The required thickness of intermetallic compound in Al/Ti MILs for possible applications is usually 50-100 µm. The time necessary to obtain intermetallic interlayer of the required width in Ti-Al composite exceeds tens of hours. Thus the efficiency of MIL production is significantly reduced by mentioned above factors.

Investigations on the possibility of intensification of diffusion between Ti and Al melts revealed the kinetics and the steps of diffusion processes [1-3]. However the mechanism of heterogeneous interlayer with globular aluminide particles and thin layers of pure Al formation remains unclear. The aim of the present study was to analyze the disadvantages of existing hypothesis for the mechanisms of interaction between Al melt and solid Ti and to propose a new explanation which corresponds with experimental data.

2. Materials and Experiments

In order to investigate the evolution of intermetallic formation at the interface of laminated Ti/Al composites, Ti/Al sheet was fabricated via explosion welding and subsequently heat treated.
Figure 1. Optical image of the explosion welded Ti/Al composite after heat treatment at 700°C for a) 10 min; b) 20 min; c) 30 min; d) 60 min; e) 90 min; f) 120 min; g) 150 min; h) 180 min; i) 210 min; j) 240 min.
The explosion welding parameters were chosen to avoid molten zone formation. Heat treatment was performed at 675°C, 700°C and 750°C for the range of times between 10 minutes and 4 hours.

The obtained specimens were studied by means of optical microscopy (optical microscope Olympus BX-61) and X-Ray diffraction patterns (diffractometer Dron-3).

The microstructures of the Ti/Al interface after explosion welding and subsequent annealing at 700°C is shown in figure 1. Microstructural changes, presented in figure 1 are similar to those obtained during heat treatments at 675°C and 750°C. The heat treated Ti/Al specimens diffraction patterns analysis identified the presence only of TiAl$_3$ intermetallic compound in the whole range of investigated temperatures and times.

As shown in figure 2 the initial formation rate of the uniform intermetallic layer is rather slow for all investigated heat treatment temperatures. The slow intermetallic formation process is followed by the acceleration of the intermetallic growth rate. The acceleration is achieved by the growth of the interlayer composed of spherical particles (figure 1 c-f).

![Figure 2](image)

**Figure 2.** The evolution of the total thickness of intermetallic layers (a) and total thickness of the Ti (b), involved into the reaction during heat treatment at 1 – 675°C, 2 – 700°C, 3 – 750°C

In order to explain the observed feature of the initial slow intermetallic growth rate with its subsequent acceleration, the consideration of solid Ti molten Al interaction mechanism is required.

### 3. Solid Ti/Molten Al interaction mechanism

The formation of two-phase interlayer with high content of aluminides between Al melt and solid Ti was previously observed during Ti brazing with Al solder. The proposed mechanisms of aluminide formation can be divided into three groups: mechanisms of precipitation, mechanisms of destruction and mechanisms of chemical interaction between intermetallics and melt.

Mackowiak J. and Shreir L. L. [4] proposed the three stage mechanism of precipitation, which included:

- the formation of saturated solution as a result of dissolution of Ti in Al;
- precipitation of the porous TiAl$_3$ layer, which is permeable for molten aluminum;
- the destruction of the continuous interaction layer as a result of tensile stress.

Subsequent investigations on the interaction between solid Ti and, surrounding it Al melt, have brought authors to reconstruct their theory. The stage of formation of saturated solution as a result of dissolution of Ti in Al was excluded, while new stages were proposed [5].
The four-stage mechanism of precipitation was proposed instead of the previous theory. The four stages were:

1. chemical reaction between solid Ti and Al melt, which resulted in the formation of thin molten aluminum previous layer;
2. the repulsion of precipitated aluminides from Ti boundary, caused by tensile stress in the reaction layer. The tensile stress occurred due to volume differences of TiAl₃ layer and saturated Ti;
3. the continuous interaction layer rupture. The rupture occurred in the corners of subjected in melt cylindrical Ti specimen and was caused by tensile stress exceeding TiAl₃ strength (figure 3);
4. concurrent precipitation and breakdown leading to the production of a cruciform pattern.

Slama G. and Vignes A. [6], based on the studies of microstructures of reaction layers, formed during the interaction between solid Ti and Nb with Al melt, proposed that the formation of two-phase layer, which contained crystallized Al and the reaction products of Al, can be explained by the rupture of continuous Al layer on the solid Ti boundary. The rupture is caused by tensile stress, which occurs due to volume differences in reacted Ti (Nb) and intermetallic.

The fact that solid Nb - molten Al system has a critical temperature below which the two-phase interaction layer is formed, while above which only the continuous intermetallic layer on solid Nb is formed, acknowledges the hypothesis of Slama G. and Vignes A. The authors proposed the emergence
of stress exceeding the yield point of Nb on the interface between materials above the critical
temperature. The stress leads to the deformation and hardening of Nb.

However due to recrystallization of Nb the hardening does not result in the Nb to achieve the strength
higher than of aluminide and thus does not lead to the rupture of the aluminide. The complex relation
of continuous aluminide thickness on the temperature of melt on the surface of Nb (figure 4) was
explained by coexistence of two features:
1. the increase in the speed of reaction between solid Nb and Al melt. The stress value increased
during the reaction which contributed to aluminide rupture.
2. the decrease in the yield point of Nb and acceleration of recrystallization processes, which
contributed to stress relaxation.

The authors did not observe critical temperature in solid Ti - Al melt system even at 1200-1300°C
above which the constant growth of continuous intermetallic layer could occur. The microhardness
tests and SEM identified the emergence of solid solutions of Al in Ti in front of the TiAl3-Ti interface
under the studied temperatures. The microhardness of the solutions was 2.7-5.2 GPa. High hardness
value of the emerged Ti(Al) blocked the evolution of plastic deformation and thus decreased the stress
value in the formed aluminide layer.

Subsequent studies attempted to complement the proposed by Slama G. and Vignes A. mechanism.
Thus Sujata. M., Bhargava S. and Sanga S. [7] agree with the statement that TiAl3 layer, formed on
solid Ti, experiences elaborate stress state due to high difference between density value of Ti and
TiAl3 and the stress value increases with the growth of aluminide thickness or with the acceleration of
aluminide growth rate.

Due to the limited plasticity of TiAl3, the layer can undergo crack and fracture if the critical thickness
is achieved due to the critical stress. Fragments separated from the solid Ti layer uncover the surface
on which the chemical reaction between the solid Ti and molten Al resumes.
The evolution of temperature of Ti-Al compacts of various chemical compositions during powder agglomeration a) – at 700°C b) – at 800°C; 1 – 5 at. % Ti; 2 – 10 at. % Ti; 3 – 12.5 at. % Ti; 4 – 15 at. % Ti; 5 – 20 at. % Ti; 6 – temperature of the dilatometer tube [8]

The figure 5 demonstrates the interaction layer microstructure evolution at various temperatures and reaction times. In order to explain the evolution of the interaction layer, Sujata, M. et al. [7] assumed the produced in the interaction layer heat leads to the convective heat flux in the melt occurring. The heat is produced as a result of exothermal reaction of TiAl₃ formation and leads to the temperature growth of reaction products and adjacent Al melt. The flow of molten Al, caused by thermal gradient, carry separated TiAl₃ fragments away from the reaction layer. Cracks in the separated particles contribute to their subsequent fragmentation during thermal flow transportation.

The results of Ti-Al liquid phase heat treatment dilatometric investigations [8] contribute to the importance of thermal effects role. Short-term temperature growth of Ti-Al compacts subjected to
temperatures higher than 770°C was observed due to exothermal process of aluminide formation. The temperature of compacts was 400°C higher than the furnace temperature (figure 6).

The proposed mechanisms cannot explain observed in this study modification in the kinetics of 2-phase layer formation. As seen in figure 2, during this modification the uniform intermetallic layer growth in the bond between Ti and Al stops and the continuous interlayer with spherical intermetallic inclusions starts growing.

Harach D. J. and Vecchio K. S. [9] proposed the third group of mechanisms of reaction layer with spherical TiAl3 inclusions formation. The mechanisms are based on the idea of molten intermetallic compounds formation. As shown in figure 7 the reaction starts at the interface of Al/Ti.

The surface tension dominates the gravitational forces and the reactions products are in the form of spheres. The reduction in contact area between Ti and Al leads to the decline of the reaction rate which results in the spherical particles solidification. Additional intermetallic nucleuses occur and grow along the Ti/Al interface during the solidification process.

Due to the spherical particles are constrained in space, the process of solidification leads to the emergence of loads, which extrude the first spherical particle into the liquid and uncover hidden interphase area.

Such process is apparently possible only at temperatures above 800°C when, due to significant exothermal effects, the temperature in specific areas can exceed the TiAl3 melting point (1395°C). However two phase layer was observed in the range of heat treatment temperatures between 675°C and 750°C (figure 1). In this temperature range the two phase layer formation reaction rate is rather low and temperature increases very slightly.

4. The new solid Ti/molten Al interaction mechanism idea

Taking previous studies and experimentally obtained results into consideration the new mechanism of the aluminide formation processes can be proposed. Ti and Al have a high affinity for oxygen. As a result of hot rolling or explosion welding the Ti-Al interface has oxygen layers with highly defective structure. Such oxygen layer discontinuities can occur during the deformation caused by the difference in plasticity values of oxygen layers and metals. Subsequent heat treatments of the bimetal can also lead to oxygen layers rupture due to the difference in thermal expansion coefficient values.

When the bimetal is treated above Al melting point, the Ti/Al interface represents a multilayer system: molten Al; solid Al oxide Al2O3; solid Ti dioxide TiO2 or monoxide TiO; solid Ti. Thus molten Al does not experience uniform contact with Ti, the solid Ti- molten Al contact is located only in some areas with fractured oxide layers [2].

The transfer of titanium and aluminum atoms through the oxide interlayers, caused by the difference in chemical potentials of Ti and Al, results in the formation of local areas with solid solutions of aluminum in titanium as well as the dissolution of diffused titanium atoms in the melt. The rate of diffusion processes of Ti and Al atoms is decreased by oxygen layers. Thus the atomic transition is carried out mainly by diffusion through isolated channels in the areas with ruptured oxygen layers and leads to the formation of local regions of supersaturated solid solution Ti(Al). The intermetallic nucleuses of various compositions stochastically form in the local regions. The most thermodynamically possible composition TiAl3 has the smallest size of nucleus.
When the size of the formed nuclei exceeds the critical value (figure 8), the possibility of their growth is increasing. The ratio of intermetallic growth along the TiO$_2$ solid - Ti solid interface is the highest among all directions. This contributes to the diffusion in the direction with injections of Al atoms.

**Figure 8.** Mechanisms of Ti-Al structure transformation during heat treatment at temperatures higher than Al melting point: a) – Al nucleus formation, b, c, d) – transversal growth of thin interlayer parts, e, f) – formation and accelerated growth of intermetallic phase nucleus in the channels between oxide layer parts, g, h) – intermetallic fragmentation, i, j) – uniform intermetallic layer formation, the layer is covered with molten Al.
The growth of aluminide fragments ends up with the formation of the uniform layer at the interface. Ti atoms, which penetrated through oxide layer ruptures dissolve in the Al melt until the solubility limit of Ti in Al (0.2-1.3% at 670-750°C) is reached. The subsequent Ti atoms supply results in the formation of arbitrarily located crystals of TiAl₃ phase, which is driven away to grain boundaries by expanding nucleus during the solidification and crystallization processes.

Uniform distribution of the intermetallics across the volume of the melt can be explained by higher speed of transportation processes in the melt compared to the diffusion of Ti through the oxide layers. The growth of aluminide layer volume causes the oxide layer fragmentation, which leads to the increase in the contact area between Ti intermetallic and Al melt. The formation and growth of intermetallic phase nucleus takes place in the regions of Al melt - Ti intermetallic contact. The kinetics of the process was previously described by Kolmogorov [10]:

$$X(t) = 1 - \exp \left[ - \int_0^t I(t') V(t', t) dt' \right],$$  

(1)

where $X(t)$ – the forming phase volume fraction, $I(t)$ – the rate of new phase centers formation, $V(t', t)$ – volume at time $t$ of the nucleus, formed at $t'$.

$$V(t', t) = g R^D \left( t', t \right), \quad R(t', t) = \int_{t'}^t u(t) dt,$$

(2)

where $u(t)$ – nucleus growth ratio, $R(t', t)$ – nucleus radius, $D$ – the dimension of space, $g$ – geometrical multiplicator: $g=2\pi,4\pi,4\pi/3$ for $D=1,2,3$ respectfully.

The formation of intermetallic compound in regions constrained by reacted Ti causes the subsequent oxide layer between Ti and Al melt rupture. This leads to the increase in internal stress and contributes to the fragmentation of intermetallic layer. The emerged intermetallic fragments are then pressed out of reaction volume.

The Rehbinder effect [11] contributes to the fragmentation of the formed intermetallic layer. The effect consists in the adsorption reduction in strength, strain relief and decrease in strength in solids.

The intermetallic TiAl₃ has ionic bond; the liquid Al melt wetting of the intermetallic is lower than pure Al and Ti wetting. However TiAl₃ contact angle is significantly lower than 90° due to its metallic properties. The more the crystal area is covered by Al melt, the less surface energy the crystal has. Such feature facilitates the diffusion of Al melt across the surface of the forming intermetallic crystal. The micro cracks expansion is contributed by the melt which diffuses across the juvenile surfaces with active centers. The surfaces occur at the beginning of small cracks. The oxide layer rupture, as well as fragmentation of intermetallic compound, accompanied by emerged capillaries, significantly facilitates the Al melt transport to the reaction surface, which contributes to the acceleration of local intermetallic growth and consequently uniform interlayer covered with melt formation.

The rupture of the diffusion barrier (oxide foil) and fragmentation of the intermetallic layer between Ti and Al melt contributes to the increase in thickness value of the two-phase reaction products (aluminum spherical particles, covered with Al melt) layer. The reaction products are constantly separating from the intermetallic layer of critical thickness value. The separated spherical particles are driven away from the interaction layer by newly formed particles. The increase in temperature results in the decrease of viscosity of the melt and contributes to the acceleration of intermetallic formation reaction and thus leads to thermal gradient growth. Heat flows transport Al spherical particles which results in their number reduction in the two-phase interaction products layer.
The proposed mechanism explains the initial slow formation of the uniform intermetallic layer on the Ti/Al interface with subsequent acceleration of the intermetallic growth and formation interaction during the growth of interlayer composed of spherical particles.

5. Conclusion

1. Based on the comparison between mechanisms of precipitation, destruction and chemical interaction between intermetallics and melt, and analysis of the evolution of the microstructure of Ti/Al bimetal treated above the Al melting point, the new explanation of the bond area processes was proposed. The explanation considers the oxide layers at the Ti/Al interface.
2. The explanation for the conversion of the intermetallic growth rate from slow to high has been proposed. The impact of the Rehbinder effect and the oxide layer rupture was considered.

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