Mechanism of formation of intermetallic coatings by the Cold Spray Technology

S P Kiselev, V P Kiselev, E A Maximovsky, T A Vidyuk, A V Ukhina and V S Shikalov

1 Khristianovich Institute of Theoretical and Applied Mechanics SB RAS, 4/1 Institutskaya Street, Novosibirsk 630090, Russia
2 Nikolaev Institute of Inorganic Chemistry SB RAS, 3 Acad. Lavrentyev Ave., Novosibirsk 630090, Russia
3 Institute of Solid State Chemistry and Mechanochemistry SB RAS, 18 Acad. Kutateladze Street, Novosibirsk 630128, Russia

E-mail: kiselev@itat.nsc.ru, kiselevvp@itat.nsc.ru, eugene@niic.nsc.ru, vidyuk@itat.nsc.ru, auhina181@gmail.ru, v.shikalov@gmail.com

Abstract. In the present paper, results of a study of a Ti₃Al₃ intermetallic coating obtained on the surface of titanium (Ti) by the method of Cold Gas Spraying (CGS) and heating to a temperature above the melting point of aluminum (Al) are reported. It is shown that the structure of the resultant coating depends on the heating temperature. At temperature \( T = 930 \, \text{K} \) the coating consists of a TiAl₃ intermetallic layer. At temperature \( T = 1270 \, \text{K} \) a layered coating is formed. In this coating, a TiAl₃ intermetallic layer, adjacent to the Ti surface, is followed by a second intermetallic layer consisting of Ti₃Al and Ti₂Al sublayers. The microhardness of the Ti₃Al/Ti₂Al double-layer coating proves to be three times higher than that of Ti. A qualitative explanation to the mechanism of formation of the layered coating is proposed.

1. Introduction
Currently, the cold spray (CS) method is widely used for creating metal coatings [1]. In this method, microparticles of the sprayed material are accelerated in a supersonic gas flow and, as they impinge onto an obstacle, they form a durable coating. However, the kinetic energy of microparticles is not sufficient for creating intermetallic coatings. In this case, it is necessary to use an additive method in which the coating obtained by the CS method is additionally subjected to high temperature. In this way, a coating formed by intermetallic compounds Ni-Al [2] and Fe-Al [3] and a coating formed by intermetallic compound Ti-Al were obtained in [4]. In publications [5] and [6], it was shown that a coating formed on the surface of titanium has a layered structure. In this coating, the first layer of intermetallic compound TiAl₃ borders on the Ti surface, and the second intermetallic layer, consisting of Ti₃Al and Ti₂Al sublayers, borders on the first layer. In the present paper, results of the study of the layered coating are reported.

2. Problem statement
A coating formed by aluminum (Al) microparticles was sprayed by cold gas spraying onto a titanium (Ti) plate (thickness of 1 mm, length of 10 mm, and width of 10 mm). In the experiments, ASD-1 Al 99.2 grade aluminum powder was used. The mean diameter \( d \) of Al microparticles in the powder was equal to about 25 \( \mu \text{m} \). Two grades of titanium alloy, OT4-1 (Ti-95%, Al-2%, Mn-1.4%) and VT20 (Ti-
92%, Al-5.5%, Zr-1.5%, V-1%) were used as the substrate. The aluminum coating was deposited onto the titanium plate using the CS facility of the Institute of Theoretical and Applied Mechanics SB RAS (ITAM SB RAS) equipped with a KUKA KR 16-2 six-axis robot for controlling the nozzle (KUKA Roboter GmbH, Germany). The obtained composition, consisting of a Ti plate and an aluminum coating with thickness \( h \approx 300 \, \mu m \), was subjected to uniaxial hot pressing in protective argon ambient using a compact laboratory press under a pressure of 5 MPa. The Ti plate coated with aluminum was heated to some temperature \( T \) for 15 minutes to be then held at this temperature for a time \( \Delta t \), and then it was cooled to temperature \( T = 300K \) during 15 minutes. The synthesis of the intermetallic compounds proceeded for some time that varied in various experiments from 90 to 15 minutes. The effect of temperature on the synthesis of intermetallic compounds was examined; to this end, a series of experiments was carried out at temperatures of 820, 930, 1270, and 1620 K. The elemental composition of the Ti\(_n\)Al\(_m\) intermetallic coatings was studied using a SEM EVO MA 15 scanning electron microscope (Carl Zeiss, Germany) equipped with an X-Max 80 mm\(^2\) EDS detector (Oxford instruments). Samples for analysis were prepared using an Ilion+ ion etching facility (Gatan). The analysis of the diffraction spectrum of backscattered electrons was performed using an SEM electron microscope equipped with a detector for backscattered electrons and a software package. The phase composition was analyzed by means of X-ray diffractometry on a D8 Advance diffractometer (Bruker). The microhardness of Ti and that of the intermetallic coating was measured by the Vickers method on cross-sectional cuts along the surface of the plate with a 5-mm step using an EMCO - TEST DuraScan 50 microhardness meter.

3. Discussion

A photo illustrating the cross-sectional structure of the coating obtained on a plate of titanium alloy OT4-1 using the electron microscope SEM EVO MA 15 equipped with the EDS detector is shown in Fig. 1.

![Figure 1](image_url)

\( T = 830K \), \( T = 930K \), \( T = 1270K \), \( T = 1620K \).

**Figure 1.** SEM images of cross-sectional cuts of Ti\(_n\)Al\(_m\) intermetallic compounds synthesized during 90 min at various temperatures (a – \( T = 830K \), b – \( T = 930K \), c – \( T = 1270K \), d – \( T = 1620K \)).
A cross-sectional cut of the sample that is annealed at a temperature $T = 830K$ is shown in Fig. 1(a). The areas occupied by Ti and Al are shown as light and dark regions, respectively. It is seen that at temperatures below the melting point of Al no synthesis of the intermetallic compound occur during 90 minutes. A cross section of the sample annealed at $T = 930K$ is shown in Fig. 1(b). The areas occupied by Ti and intermetallic TiAl$_3$ are shown as light and dark regions, respectively. Evidently, at the melting point of Al an intermetallic compound is synthesized on the Ti surface. At $T = 1270K$ a layered coating formed (see Fig. 1(c)). Here, an intermetallic saturated with aluminum was adjacent to the Ti surface (the region occupied by Ti is located below and shown in light color). An analysis performed using the EDS detector demonstrated that, here, TiAl$_3$ intermetallic compound formed. The second intermetallic layer supersaturated with Ti is located above. In the selected rectangular region, the concentration of Al is 21%, and the concentration of Ti is 79%. A more detailed analysis of the layered coating obtained at temperature $T = 1270K$ will be presented below. The cross-sectional cut of the sample annealed at temperature $T = 1620K$ is shown in Fig. 1(d). In this case, the reaction yielding the intermetallic compounds proceeds throughout the entire volume of titanium. A large volume in the intermetallic sample is occupied by the shrinkage pores arising during the cooling and crystallization of the intermetallic compound. An analysis performed using the EDS detector shows that all the possible phases, Ti$_3$Al, Ti$_3$Al$_5$, Ti$_2$Al$_5$, TiAl, TiAl$_3$, and TiAl$_5$, are distributed uniformly in the sample. From the performed analysis, it follows that the temperature at which the synthesis of the intermetallic compound proceeds on the Ti surface has a profound effect on the composition of the intermetallic coating. The formation of an intermetallic coating begins at a temperature close to the melting point of Al. The molten Al dissolves the solid Ti, and Ti atoms diffuse into the Al melt. Since the formation of the TiAl$_3$ intermetallic compound requires the least Gibbs free energy $\Delta G$, in the latter case TiAl$_3$ intermetallic compound appears upon cooling. As the temperature rises, other phases with a higher Gibbs energy $\Delta G$ could arise; therefore, upon cooling, a layered coating consisting of several phases forms. Paradoxical is the layered structure obtained at temperature $T = 1270K$. In this case, an intermetallic phase with a concentration of Ti lower than that farther from the Ti boundary borders on the Ti surface. Let us consider this case in more detail.

The cross-sectional structure of the intermetallic coating obtained at temperature $T = 1270K$ on a VT20 titanium alloy plate is shown in Fig. 2. The photographs are taken using the SEM EVO MA 15 electron microscope equipped with the EDS detector.
Figure 2. Cross-sectional cut of Ti covered with a layered intermetallic coating synthesized for 15 minutes at temperature $T = 1270K$: (a) – SEM image; (b-d) – the distribution of the elements Ti, Al, and O in section (a).

From Fig. 2 (a), (b), it is seen that the first layer of the intermetallic compound with a low Ti content and a high Al content (see Fig. 2 (c)) was adjacent to the Ti surface (the light layer below in Fig. 2 (a), (b)). An analysis of the elemental composition shows that this intermetallic compound was TiAl$_3$. The second intermetallic layer was supersaturated with Ti and depleted of Al, being a mixture of the Ti$_3$Al and Ti$_2$Al intermetallic phases. A narrow layer of alumina Al$_2$O$_3$ was located at the interface between the first and second intermetallic layers (see Fig. 2 (c), (d)). From Fig. 2(a), it follows that the first intermetallic layer had a heterogeneous structure consisting of TiAl$_3$ intermetallic microparticles ranging in size from 10 to 20 μm. In between the microparticles, Ti was located (light regions in Fig. 2(a)). A similar structure of the TiAl$_3$ intermetallic layer was previously observed in [7], where the growth of the intermetallic compound under similar conditions at temperature and pressure was studied. In [7], it was shown that after the destruction of the oxide film at the Ti-Al interface, a TiAl$_3$ melt film began to form on the Ti surface. Under the action of surface tension, this film coagulated into spherical droplets with the size of 10 μm. Then, the droplets underwent solidification and detached into the aluminum melt.

Let us consider now a possible mechanism underlying the formation of the layered coating shown in Fig. 2. In this case, at temperature $T = 1270K$, along with TiAl$_3$, a Ti$_3$Al phase can also arise. However, since the Gibbs free energy $\Delta G$ of TiAl$_3$ formation is lower than that of Ti$_3$Al [8], TiAl$_3$ microparticles appear on the Ti surface. Ti atoms, which participated in the formation of the intermetallic compounds, form due to their interaction with the Al atoms, incoming from the melt to the solid surface of Ti. Provided that one Ti atom appears per each Al atom leaving the melt, then after the formation of one TiAl$_3$ intermetallic molecule, three Al atoms and one Ti atom leave the melt. As a result, an excess of Ti atoms forms in the melt near the solid surface of Ti. The excess Ti atoms diffuse upward to the region where there is a lack of Al atoms (see Fig. 3). In this region, Ti$_3$Al and Ti$_2$Al intermetallics of Ti and Al atoms are formed in the melt, from which the solid Ti$_3$Al and Ti$_2$Al intermetallics precipitate upon cooling. One of the indirect arguments in favor of this mechanism is the homogeneous structure of the second Ti$_3$Al/Ti$_2$Al intermetallic layer (see Fig. 2(a)). The first and second intermetallic layers are separated by a layer formed by oxide films. Apparently, following the spraying of an aluminum coating onto the Ti surface by the CS method, the oxide films of titanium and alumina are destroyed. The resultant fragments of the oxide films do not participate in the reaction of formation of intermetallic compounds, and they coagulate at the interface between the first and second intermetallic layers.
Figure 3. A picture illustrating the formation of the layered structure of the intermetallic coating on a Ti surface.

Microindentation is used to measure the microhardness of the layered coating obtained at temperature \( T = 1270 \text{K} \). The distribution of the microhardness value over the cross section of the intermetallic coating along the surface of the sample is shown in Fig. 4.

Figure 4. Photograph of a cross-sectional cut of the Ti\(_n\)Al\(_m\) intermetallic compound synthesized at temperature \( T = 1270 \text{K} \); with indentation imprints – (a); distribution of the Vickers microhardness along the sample surface in the first intermetallic layer (TiAl\(_3\)) and in the second intermetallic layer (Ti\(_3\)Al and Ti\(_2\)Al) – (b).

From Fig. 3, it is seen that the microhardness of the first intermetallic layer (TiAl\(_3\)) was 30% higher than the microhardness of Ti, and the microhardness of the second intermetallic layer (Ti\(_3\)Al/Ti\(_2\)Al) exceeded the microhardness of Ti three-fold.

Conclusion
In the present paper, results of an experimental study of the structure of the Ti\(_n\)Al\(_m\) intermetallic coating obtained by the additive method on the surface of a Ti plate have been reported. First, an aluminum coating was sprayed onto the titanium surface using the cold spraying technique. The resultant titanium/coating composition was heated to a temperature above the melting point of aluminum. As a result of the heating, an intermetallic coating appeared on the surface of the titanium plate. The structure of the intermetallic coating substantially depended on the temperature to which the titanium/coating system was heated. At temperature \( T = 1270 \text{K} \) a layered coating formed. In this coating, a TiAl\(_3\) layer bordered on the titanium surface, this layer being followed by a layer consisting of Ti\(_3\)Al and Ti\(_2\)Al. A qualitative explanation to the formation of the layered structure of the intermetallic coating has been proposed. The microhardness of the Ti\(_3\)Al and Ti\(_2\)Al intermetallic layer is shown to exceed the microhardness of Ti three times.
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