DOI: 10.21062/mft.2022.069 http://www.journalmt.com

Microstructure and Phase Composition of thin Protective Layers of Titanium Aluminides Prepared by Self-Propagating High-Temperature Synthesis (SHS) for Ti-6Al-4V Alloy

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Titanium aluminides were prepared using self-propagating high-temperature synthesis (SHS) from powder aluminium and compact Ti-6Al-4V alloy at 800 °C. The resulting material was subsequently annealed at the same temperature for 3 hours. The coating was successfully bonded to the matrix using SHS while forming intermetallic phases of cubic $TiAl_3$ in areas of powdered aluminium. The resulting coating was approximately 14 μm thick. Material annealing resulted in further reactions between the $TiAl_3$ coating and Ti-6Al-4V matrix, forming a thin layer of γ-TiAl. Using SEM, the different phase composition of annealed and unannealed material was clearly visible, however, clear determination of emerging phases was very difficult due to the small thickness of the intermetallic coating. Eventually, phases were determined by a combination of cross-section μ-XRD and various EDS analyses.

Keywords: self-propagating high-temperature synthesis (SHS), titanium aluminides, intermetallics, coatings

1 Introduction

Titanium aluminides are promising materials in aerospace due to their favorable ratio between density and strength combined with elevated oxidation resistance and creep resistance at high temperatures (up to 800 °C [1]) compared to commonly used aerospace materials such as aluminium alloys [2], titanium and Ti6Al4V [3]. Titanium and aluminium can form a variety of intermetallic phases including γ-TiAl, α_2-Ti_3Al, $TiAl_2$ and $TiAl_3$ of which γ-TiAl are the most industrially important for their high temperature properties and their relatively low brittleness [4]. It is very difficult to achieve a homogeneous structure in the production of TiAl intermetallics by conventional methods such as vacuum arc remelting and the production is expensive due to the high melting temperature of these aluminides. Big disadvantage is also the high content of interstitial impurities such as oxygen or nitrogen, as well as the porosity of the material which leads to a mechanical properties detoriation [5]. Therefore, new ways of producing these aluminides are being investigated. It was proven that titanium aluminides can be prepared by SHS [6, 7], additive manufacturing using selective laser melting (SLM) or electron beam melting (EBM) [8], hot isostatic pressing (HIP) [9], spark plasma sintering (SPS) [10] and other methods.

SHS is often used to prepare the desired compound, which is then crushed, and the resulting powder is suitable for another compactization method [11, 12]. This work presents a use of SHS for creating a thin TiAl-based coatings on Ti-6Al-4V alloy in one step.

2 Experimental/experiment

Aluminium powder was deposited on Ti-6Al-4V alloy, uniformly dispersed with ethanol, and fixed with a 10 nm layer of sputtered gold. The SHS process took place in an evacuated quartz ampoule placed in a furnace heated to 800 °C with duration of 15 min, schematically shown in Fig. 1. Obtained bulk sample was observed by SEM (TESCAN VEGA 3 LMU) with EDS detector, a relief of the sample surface was taken using a Keyence VHX-J250 microscope, phase composition was measured by μ-XRD (D8 Discover with VANTEC 2D detector) and the distribution of the individual phases was determined by EDS analysis. Subsequently, the sample was annealed for 3 hours under the same conditions and the same analyses were performed.

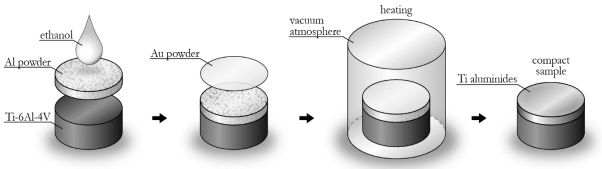

Fig. 1 *Schematic drawing of sample preparation*

3 Results and discussion

Fig. 2 shows an overview picture of compacted sample. Al powder wasn't applied to the entire matrix before SHS process but in places of deposition, we can observe the formation of intermetallic phases between Ti and Al. Part of the Au nanoparticles (small white dots) remained on the surface on the TiAl coating, but majority concentrated on the edges of the coating as you can see in Fig. 3. The coating has an average thickness of 13.8 ± 1.0 μm and is relatively uniformally distributed on the matrix, except around the edges, see Fig. 4. Using Keyence VHX-J250 microscope, the thickness fluctuation of the intermetallic coating was determined approximately as 3 μm which is more significant compared to Ti-6Al-4V matrix which varies within 1 μm.

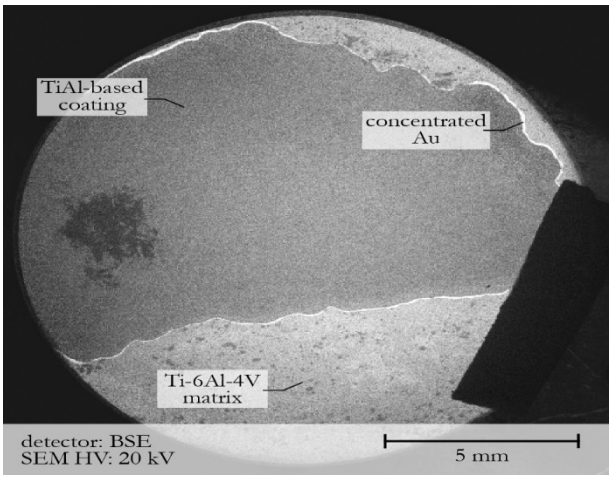

Fig. 2 *Sample after SHS*

As shown in Fig. 5 A, the surface of intermetallic coating oxidized creating mainly oxides of iron and aluminium (determined by EDS) after annealing even though the annealing took place in a vacuum - oxygen was probably deposited on the matrix before annealing. The presence of iron probably comes from contamination during cutting the material into cross-section. The most significant oxidation occurred on the edges of the coating. Although Au particles were also observed on the edges (Fig. 5 A), those on the whole surface were dissolved in the coating, see Fig. 5 B (no white particles can be seen on the surface in contrast with Fig. 3).

To determine chemical and phase composition in the bulk, a cross section was made and EDS and μ-XRD analysis were performed. As can be seen in Fig. 6 A/B, the coating porosity is independent of annealing. The annealed material (Fig. 6 B) shows an extended bonding layer between the coating and the Ti-6Al-4V matrix. The bonding layer of unannealed material reaches 2.8 ± 0.4 μm and is enlarged to 7.6 ± 0.6 μm towards the coating. During the annealing, another chemical reaction was taking place and according to EDS point analysis, see Tab. 1, γ-TiAl phases were formed in the places of this bonding layer (spectrum 4 in Fig. 6). However, the results of the EDS analysis are greatly influenced by the surrounding elements since the interaction volume of the electron beam with the material is comparable to the size of the observed phases. μ-XRD analysis was performed to confirm $TiAl_3$ and γ-TiAl phases determined based on the atomic weight ratio of the elements. As shown in Fig. 7, both diffractograms before and after annealing contain only one maximum of γ-TiAl or cubic $TiAl_3$ (at a position of 45.7°) and thus the phases cannot be clearly determined. The X-ray beam interfered with the bulk of the acrylic resin because it is impossible to target a specific spot on the material with sufficient accuracy (50 μm) and the acquired signal comes from an even larger area [13]. There are multiple maxima belonging to it in the diffractogram. Although the phases were not confirmed by μ-XRD analysis, the combination of μ-XRD and EDS suggests that the coating is formed by the intermetallic phases $TiAl_3$ and γ-TiAl.

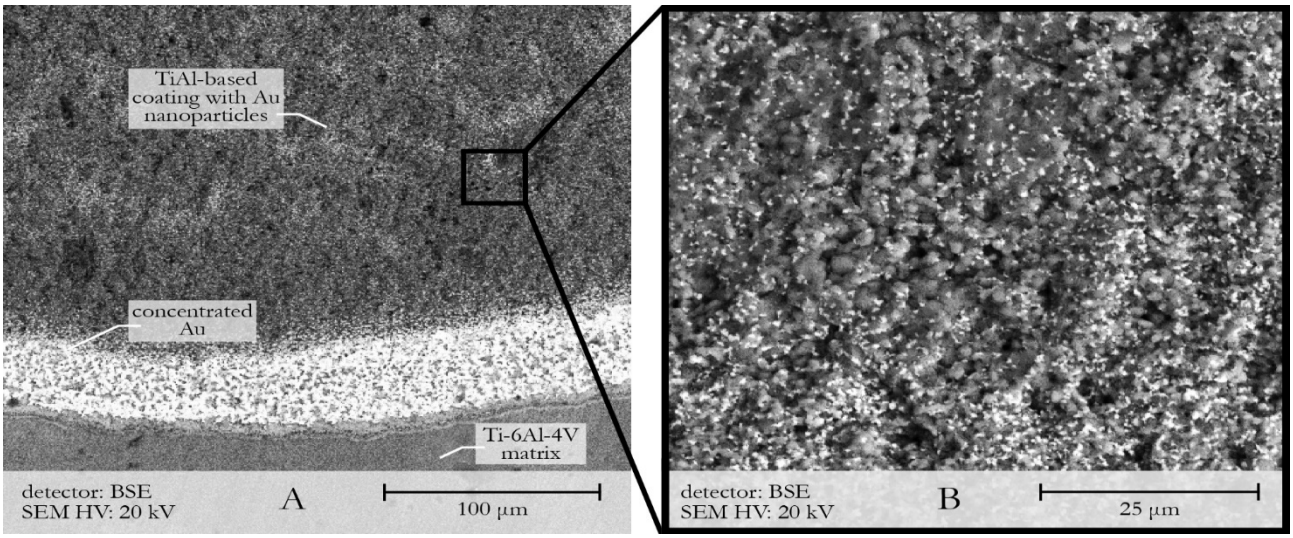

Fig. 3 *Microstructure of surface of the sample before annealing, A – magnification 500x, B – magnification 2000x*

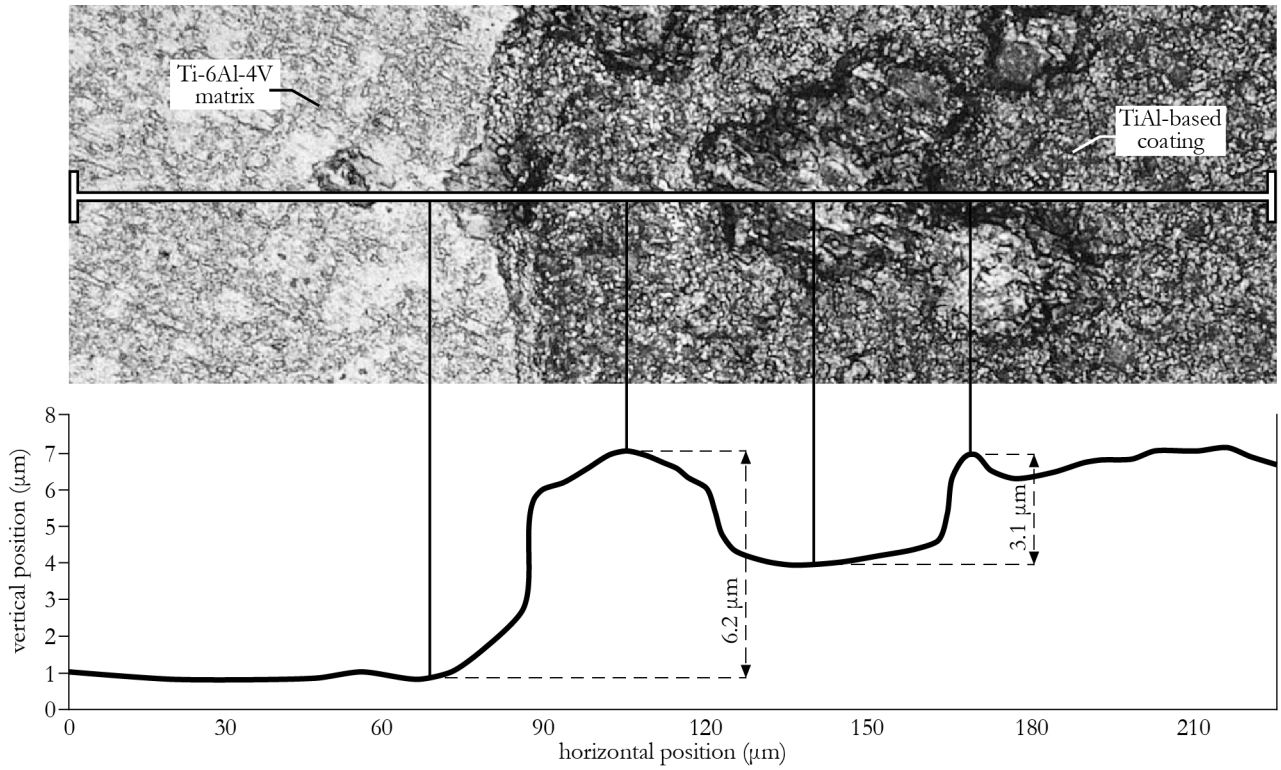

Fig. 4 *Height profile of the sample on the coating boundary*

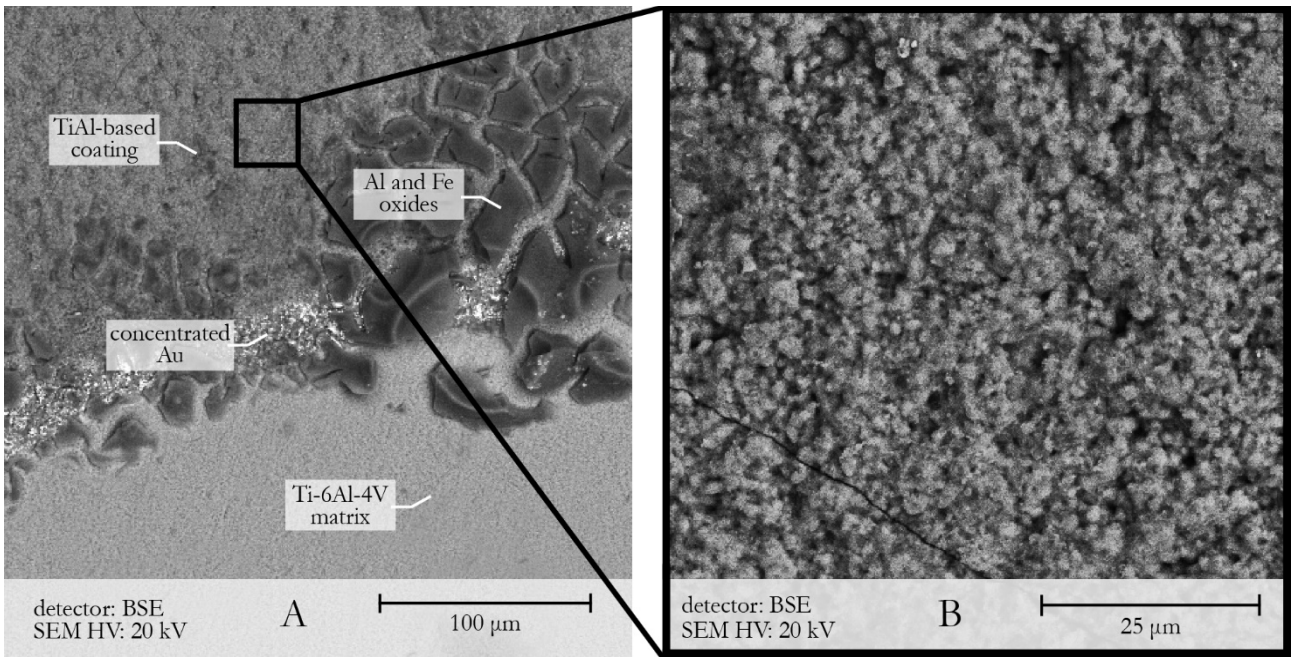

Fig. 5 *Microstructure of surface of the sample after annealing, A – magnification 500x, B – magnification 2000x*

Tab. 1 *Chemical composition in wt. % acquired using EDS point analysis of spectra 1-4 in Fig. 6 with phase composition evaluation*

sample	spectrum	phase	Ti (wt. %)	Al (wt. %)	Au (wt. %)	C (wt. %)	O (wt. %)	Si (wt. %)	V (wt. %)
before annealing	1	$TiAl_3$	35.4 ± 0.2	53.7 ± 0.3	4.7 ± 0.2	5.1 ± 0.4	0	0	1.1 ± 0.1
	2	$TiAl_3$	45.7 ± 0.2	43.2 ± 0.2	4.8 ± 0.2	5,1 ± 0,3	0	0	1.2 ± 0.1
after annealing	3	$TiAl_3$	33.6 ± 0.2	51.8 ± 0.2	6.2 ± 0.2	6.1 ± 0.3	0.9 ± 0.2	0	1.5 ± 0.1
	4	TiAl	57.2 ± 0.2	29.4 ± 0.1	5.6 ± 0.2	4.7 ± 0.2	0	0	3.1 ± 0.1

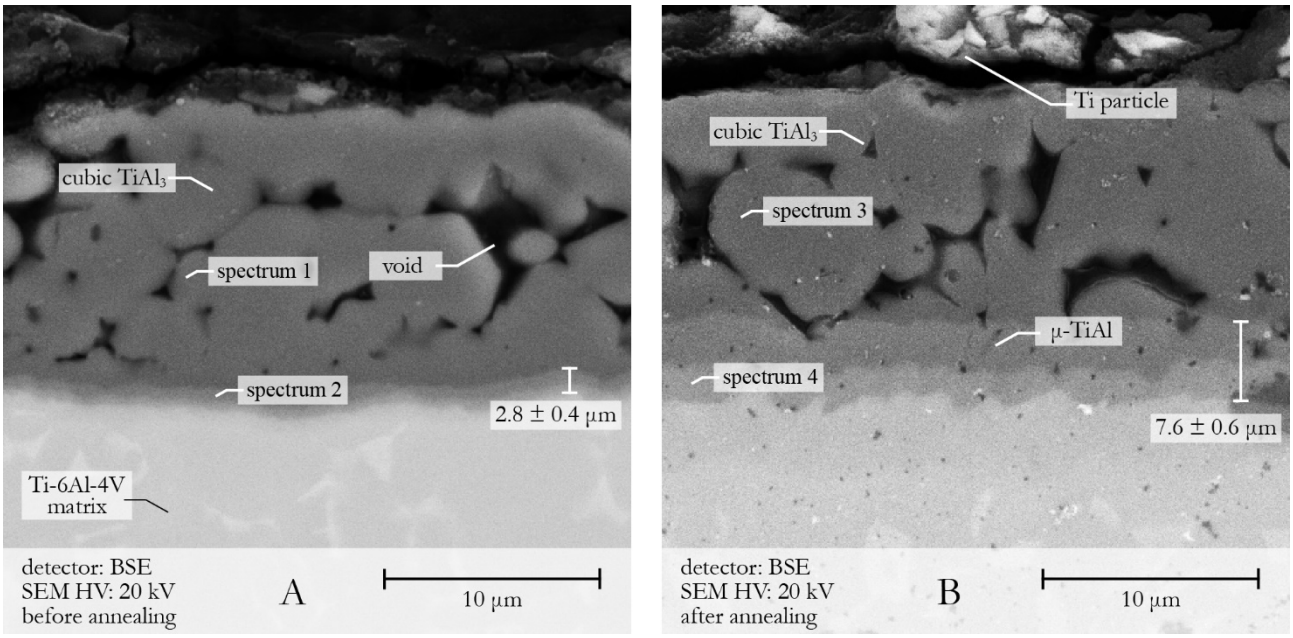

Fig. 6 *Microstructure in cross-section of the sample before (A) and after (B) annealing, magnification 5000x*

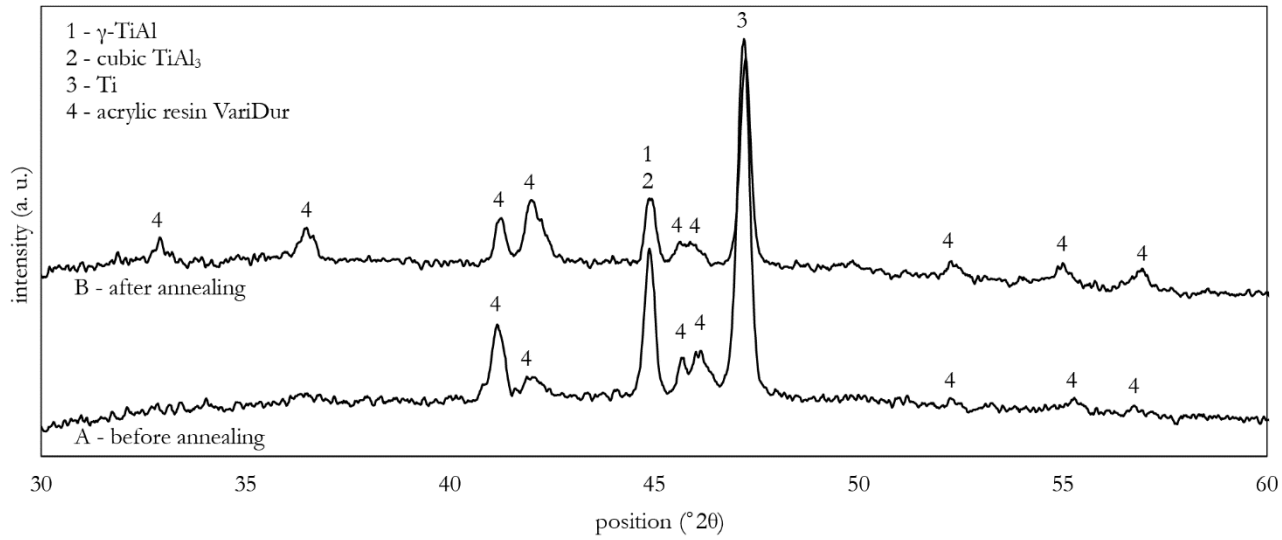

Fig. 7 *µ-XRD diffractograms before (A) and after (B) annealing*

4 Conclusion

In this paper was proven that titanium aluminides coating can be prepared in one step using SHS. The coating consisted most likely of $TiAl_3$ and γ-TiAl. For further phase composition specification, more precise analyses are required. For example, to observe the coating interface by TEM on a precisely localized lamella prepared by FIB-SEM. To achieve lower porosity of the coating it is possible to apply pressure on the sample before performing SHS. A higher proportion of the intended γ-TiAl could be achieved by increasing the annealing time.

Acknowledgement

This work was supported from the grant of Specific university research - grant No A1_FCHT_2022_007.

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