FORMATION OF DIFFERENT TITANIUM ALUMINIDES BY ELECTROSPARK DEPOSITION

Pyachin S.A., Burkov A.A.
Institute for Materials Science, Khabarovsk Scientific Center, Far East Branch, Russian Academy of Sciences, e-mail: pyachin@mail.ru

Coatings containing Ti–Al intermetallics are fabricated by the electrospark deposition of titanium on aluminum and aluminum on titanium. The microstructure and composition of the grown coatings is studied by scanning electron microscopy, X–ray diffraction, and S–ray microanalysis. It is found that the surface layer formed in argon mostly contains the α–$TiAl_3$ intermetallic independent of the duration and frequency of discharge pulses. The γ–TiAl and α_2–Ti_3Al phases can be obtained by aluminum deposition on titanium followed by the subsequent deposition of a second titanium layer. Aluminum oxide and titanium nitride are additionally formed during the deposition of electrospark coatings in air.

1. INTRODUCTION

There is the modern tendency to use titanium aluminides to develop protective and wear–resistant coatings. A TiAl layer deposited onto a pseudo-α-titanium alloy makes it high-temperature oxidation resistant while retaining its protective properties when stretching the titanium substrate [1]. The Ti_3Al-containing coating on a titanium surface has excellent wear resistance due to its increased hardness. A similar coating based on a $TiAl_3$+TiAl mixture exhibits high oxidation resistance [2]. Thus, phase modifications of Ti-Al compounds make it possible to control the properties of intermetallic coatings, which are achieved in practice by choosing the methods and conditions of their deposition. In this study, we fabricated coatings based on titanium aluminides using the electrospark alloying based on metal transfer from anode to cathode during multiply repeated electric discharges. This technology has some advantages that as the technological simplicity of metal deposition in a gas medium at atmospheric pressure, the homogeneous composition of the surface layer due to molten-state mixing of the materials used as electrodes, and high coating-substrate adhesion [3]. The objective of this study is to determine the main features of the formation of electrospark coatings based on titanium aluminides with tailored stoichiometric ratios. To solve the posed problem, the effect of the total deposition time, frequency, discharge-pulse length, and gas atmosphere on the phase composition of the intermetallic coatings is studied.

2. EXPERIMENTAL

Pure titanium and aluminum cylindrical rods 3.5 mm in diameter were used as anodes. Aluminum (AK8 alloy) plates 1×1×0.5 cm in size and titanium (VT20 alloy) cylinders 11 mm in diameter and 5 mm in height were used as cathodes. During the experiments, the pulse repetition rate f was from 0.1 to 1 kHz. The discharge time τ was 80–400 μs. The current pulse amplitude was 110±10 A; the interelectrode voltage was 30±5 V. The coatings were grown by the electrospark deposition of aluminum onto titanium and titanium onto an aluminum substrate in argon or in air. In some cases, Ti and Al were alternately deposited on the same sample. The coating microstructure was studied using a MIM-10 optical microscope and an EVO 40HV scanning electron microscope in the phase contrast mode. Microprobe elemental analysis was performed using an INCA ENERGY 350 energy-dispersive spectrometer incorporated into the electron microscope. The phase composition of the metal surface layers was studied using a DRON-7 X-ray diffractometer in Cu$K\alpha$ radiation. The coating thickness was measured using a CALLTEST abrasive wear device.

3. RESULTS

3.1. Titanium Deposition onto Aluminum

The study of electrospark-produced titanium coatings on an aluminum substrate showed that the gas atmosphere during deposition has an effect on the microstructure and phase composition of the formed layers. The surface layer differs in the structure from the substrate and consists of a mixture of phases of different densities. Comparing the concentrations of detected elements, it was found that the average ratio of Ti and Al atomic concentrations in most areas of the surface layers is ~ 1:3.48 which is close to the ratio of elements in the α–$TiAl_3$ intermetallic. In the coatings grown in argon, areas with higher titanium content are observed, in which the atomic concentration ratio Al:Ti is in the range of 1.5–2.5, i.e., close to the stoichiometry of the $TiAl_2$ intermetallic. With distance from the sample surfaces to the substrate, the titanium content insignificantly decreases, while the aluminum concentration increases.

The formation of $TiAl_3$ as the basic intermetallic in electrospark-produced titanium coatings on aluminum independent of deposition conditions was confirmed by X-ray diffraction studies (Fig. 1). The deposition of a titanium coating in air is accompanied by its oxidation, which is caused by the interaction of electrode materials with the components of air. Additional Al_2O_3 and TiN peaks appear in the X-ray diffraction patterns of such coatings. As the deposition time increases, the reflection intensities in the TiN and Al_2O_3 X-ray diffraction patterns increase to 16 min and then decrease. This is caused by the intense destruction of the surface layer due to defect accumulation. The effect of the discharge-pulse length on the phase composition of the coatings deposited in air is as follows: as τ increases from 80 to 400 μs, the Al_2O_3 and TiN content becomes larger in comparison with α-$TiAl_3$ (Fig. 2). As the discharge frequency increases from 100 to 500 Hz, the aluminum-oxide content becomes higher relative to titanium nitride and α-$TiAl_3$. Titanium aluminides of other stoichiometric compositions than $TiAl_3$ were not detected.

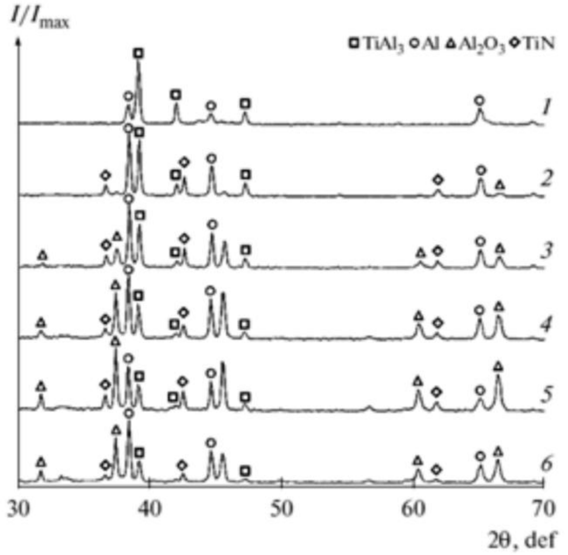

Fig. 1. X-ray diffraction patterns of the titanium coatings deposited onto aluminum in various media in (1) 4 min, argon; (2) 2 min, air; (3) 6 min, air; (4) 10 min, air; (5) 16 min, air; (6) 20 min, air; $\tau = 200$ μs, $f = 500$ Hz.

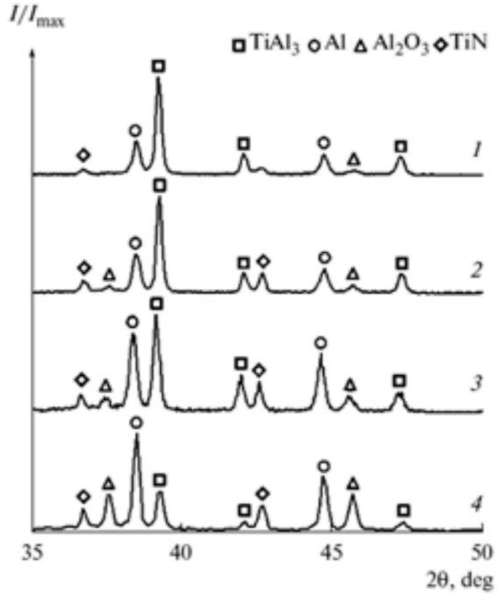

Fig. 2. X-ray diffraction patterns of titanium coatings on aluminum, deposited in air at discharge times of (1) 80, (2) 160, (3) 280, and (4) 400 μs; $f = 250$ Hz, $t = 4$ min.

3.2. Aluminum Deposition onto Titanium

The aluminum coating on titanium, deposited in argon, is more homogeneous, and it contains a smaller number of cracks and pores in comparison with the titanium coating on aluminum. Observed inclusions smaller than 1 μm in diameter and of higher density than the basic coating material are observed. According to the X-ray microanalysis data, the ratio of atomic concentrations in these regions is close to unity, i.e., they are γ-TiAl intermetallic cluster regions. The titanium and aluminum concentrations differ at various depths. The ratio of the concentrations of these elements in the upper layers of the coating is close to that of the $TiAl_3$ intermetallic; in deeper layers, it is close to that of the TiAl intermetallic. X-ray diffraction analysis of the upper layers of the aluminum coatings on titanium, grown at short (less than 2 min) deposition times in argon, showed that they consist of a set of phases, Al, Ti, and $TiAl_3$ (Fig. 3). As the total deposition time increases, content of the α-$TiAl_3$ phase rises. Similar coatings grown in air contained aluminum oxide whose content increased with the deposition time.

3.3. Aluminum Deposition onto Titanium with Additional Titanium Deposition

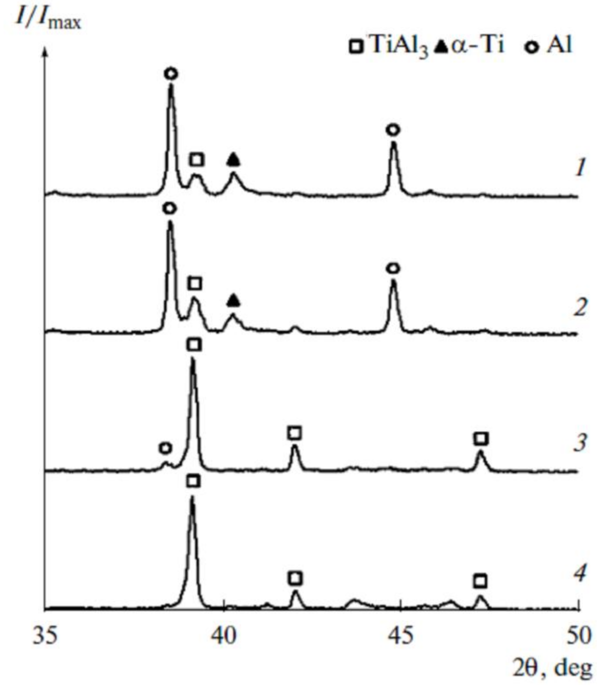

Fig. 3. X-ray diffraction patterns of the aluminum coatings deposited onto titanium in argon in (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 4 min; $f = 1000$ Hz, $\tau = 300$ μs.

To obtain the Ti_3Al compound, we proposed the growth of combined coatings by the sequential deposition of aluminum and titanium. The first aluminum layer was deposited onto titanium in various times from 1 to 4 min; the second titanium layer was deposited in 1–3 min. Despite the two-stage deposition of the metals, combined coatings did not exhibit a pronounced layered structure. X-ray diffraction spectra of the combined coatings are shown in Fig. 4. The coating composition is characterized by the presence of three main phases: Ti, $TiAl_3$, Ti_3Al, and TiAl. As the deposition time of the first aluminum layer increases from 1 to 4 min, the titanium content decreases, and the TiAl and $TiAl_3$ intermetallic content remains approximately at the same level. As the deposition time of the second titanium layer increases, Ti_3Al becomes a major phase. However, during 3-min Ti deposition, the α-titanium content appreciably increases, while intermetallic concentrations decrease (Fig. 5). X-ray microanalysis showed that as the deposition time of the first Al layer was increased to 4 min, the Al content in the coating increased; the Al:Ti concentration ratio shifted toward aluminum and reached 2.3, which indicated the dominance of γ-TiAl and α_2-Ti_3Al. In the case of 3-min aluminum deposition and 3-min titanium deposition, the ratio was close to unity.

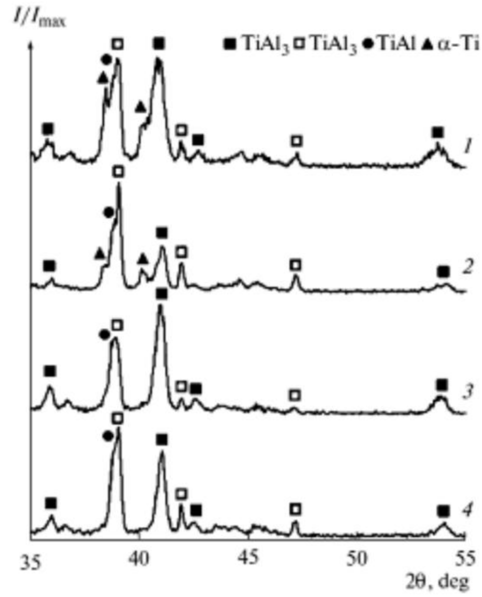

Fig. 4. X-ray diffraction patterns of the combined aluminum and titanium coatings on the titanium substrate. The deposition time of the first aluminum layer: (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 4 min. The deposition time of the second titanium layer is 1 min. Argon atmosphere; f – 1000 Hz, τ – 300 μs.

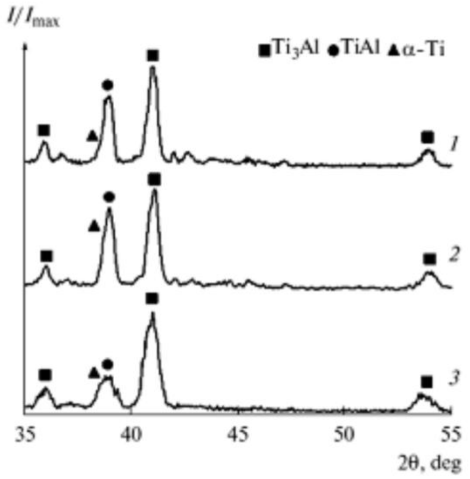

Fig. 5. X-ray diffraction patterns of the combined aluminum and titanium coatings on the titanium substrate. The deposition time of the first aluminum layer is 3 min. The deposition time of the second titanium layer is (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 4 min. Argon atmosphere; f = 1000 Hz, τ = 300 μs.

4. CONCLUSIONS

The formation of titanium aluminides in coatings deposited by the electrospark alloying method was studied. It was shown that α-$TiAl_3$ is as a rule formed during titanium deposition onto aluminum and aluminum deposition onto titanium in argon. In the case of alloying in air, titanium nitride and aluminum oxide are additionally formed. The discharge duration and frequency affect the quantitative ratios of phases. Composite coatings with a dominant concentration of one of the intermetallics of the “titanium–aluminum” system can be grown by varying the electrospark deposition time of the first aluminum layer and the second titanium layer.

References

1. C. Leyens, M. Peters, and W. A. Kaysser, Surf. Coat. Technol. **94–95**, 34 (1997).
2. A. Hirose, T. Ueda, and K. F. Kobayashi, Mater. Sci.Eng. A **160**, 143 (1993).
3. A. D. Verkhoturov, *Formation of a Surface Layer of Metals in Spark Alloying* (Dal’nauka, Vladivostok, 1995) [in Russian].