

Neutron diffraction of titanium aluminides formed by continuous electron-beam treatment

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Abstract. Ti-Al-based alloys were produced by hybrid electron-beam technologies. A composite Ti-Al film was deposited on a Ti substrate by electron-beam evaporation (EBE), followed by electron-beam treatment (EBT) by a continuously scanned electron beam. The speed of the specimens motion during the EBT were $V_1 = 1$ cm/sec and $V_2 = 5$ cm/sec, in order to realize two different alloying mechanisms – by surface melting and by electron-beam irradiation without melting the surface. The samples prepared were characterized by XRD and neutron diffraction to study the crystal structure on the surface and in depth. SEM/EDX analysis was conducted to explore the surface structure and analyze the chemical composition. Nanoindentation measurements were also carried out. No intermetallic phases were registered in the sample treated at velocity V_1 , while the sample treated at V_2 exhibited a $\text{Ti}_3\text{Al}/\text{TiAl}$ structure on the surface, transformed to Ti/TiAl in depth. The nanoindentation test demonstrated a significant negative hardness gradient from the surface to the depth of the sample.

1. Introduction

Ti-Al-based alloys combine attractive mechanical properties, light weight and excellent oxidation behavior at high temperatures. Titanium aluminides are widely used as a protective material, e.g., in the field of automotive and aircraft industry. Some aircraft engines manufacturers have successfully introduced γ -TiAl for turbine blades [1-3]. It has been found that the mechanical properties are greatly improved when the alloys consist of a mixture of γ -TiAl and α_2 - Ti_3Al phases, rather than the single phase structure of γ -TiAl [4]. Due to the very good oxidation behavior of aluminium, the presence of a TiAl_3 phase is capable of causing the formation of a thin oxide film, such as Al_2O_3 , on the surface, which acts as a protective barrier to organic environmental pollutants [5].

There exist several technologies for production of the alloys discussed above, including thin-films deposition [6], ion implantation [7], etc. It should be noted that many studies have been published describing the formation of Ti-Al alloys induced by pulsed electron-beam surface treatment, [8,9], but

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the formation of Ti-Al alloys by irradiation with continuous electron beams has been less well investigated.

In this study, a composite Ti-Al film was deposited on an α -Ti substrate by electron-beam evaporation followed by electron-beam treatment with a continuously scanned electron beam, thus realizing two different alloying mechanisms – by surface melting and by surface irradiation without melting. The crystal structure was determined by XRD on the surface and by neutron diffraction in depth. SEM/EDX analyses were carried out in order to explore the surface structure and to analyze the chemical composition; a nanoindentation test was also conducted to examine the mechanical properties.

2. Experimental part

A composite Ti-Al film with a thickness a 10 μm was deposited on an α -Ti substrate by electron-beam evaporation followed by electron-beam treatment with a continuously scanned electron beam. When applying this method, the accelerated electrons provoke interactions of the atoms from the deposited layer and the substrate, forming intermetallic alloys. The experiments were conducted on a Leybold Heraeus (EWS 300/ 15 - 60) installation with the following technological parameters: accelerating voltage $U = 55 - 60$ kV, beam current $I = 40$ mA, focusing lens current $I_f = 512$ mA. The alloying process was controlled by varying the speed of motion of the specimens. A low speed of specimen motion corresponds to a long interaction time of the electron beam and the treated area, increasing the temperature and, thus, melting the surface. In order to realize two different alloying mechanisms (by melting the surface, and by surface irradiation without melting), two different speeds were chosen: $V_1 = 1$ cm/sec and $V_2 = 5$ cm/sec.

The phase composition on the surface was characterized by X-ray diffraction. The experiments were performed on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and a LynxEye detector. The XRD patterns were registered within the range from 20° to 80° at 2θ scale with a step of 0.02° .

Scanning electron microscopy (SEM) analysis was carried out in order to explore the surface structure. The experiment was performed on a dual-beam scanning electron/focused system (SEM/FIB LYRA I XMU, TESCAN), equipped with an EDX detector (Quantax 200, Bruker). In this study, secondary electrons were used with high voltage $HV = 30$ kV and a work distance of 8.7 mm.

Neutron diffraction experiments were performed in order to study the phase composition in the volume of the samples. The measurements were conducted on a DN-2 diffractometer of the IBR-2 fast pulsed reactor at the Frank Laboratory of Neutron Physics (FLNP) JINR (Dubna, Russia). IBR-2 is a high-flux pulsed reactor with a peak thermal neutron flux of 10^{16} neutrons/cm² s at the moderator. The reactor operates in a time-of-flight mode, which implies time-dispersive measurements instead of the most common angle-dispersive diffraction. The initial velocity of each neutron is determined by the time of arrival of the neutron into the detector. Since the neutron flux is formed after passing through the moderator, it has a velocity (and hence, wavelength) distribution defined by the Maxwell thermal distribution and the resultant neutron spectra are a blend of this distribution and the sample diffraction pattern. The scattering angle and direction are fixed by the position of the detector during the experiment. Diffraction maxima in the scattered intensity appear when the Bragg conditions are fulfilled. The relation between the time of the flight and the interplanar distance d_{hkl} is as follows (modified Bragg law):

$$d = \frac{ht}{2mL \sin \theta}, \quad (1)$$

where d – interplanar distance; t – time of neutron flight; L – distance from the neutron source to the detector; θ – angle position of the detector; h – Plank constant; m – mass of the neutron.

Figure 1 represents schematically the DN-2 diffractometer. The neutrons are transported from the neutron source to the sample position in a bent neutron guide constructed from straight mirror sections with a length of 0.5 m. The guide together with the specially designed neutron moderator enables the

use of the long-wavelength neutrons in the range 1.2 – 20 Å. The time-of-flight neutron experiments were performed for 13.5 hours with an SNM17 neutron detector filled with ^3He . The detector was positioned at 63.8° and the neutron flight path from the moderator to the detector was 24.27 m. The neutron flux at the sample was $\sim 5 \times 10^6$.

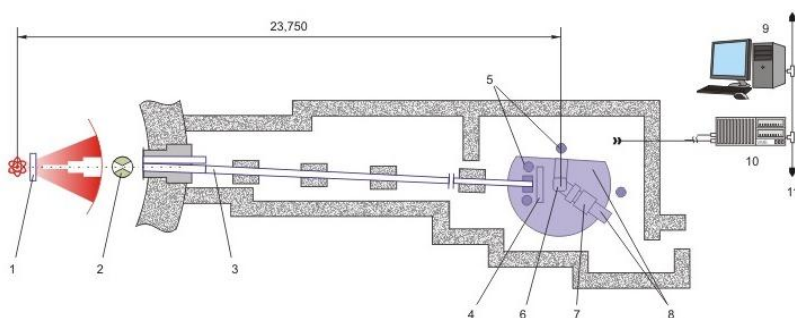


Figure 1. DN-2 diffractometer at the IBR-2 pulsed reactor.

In figure 1: 1 – moderator; 2 – background chopper; 3 – neutron guide tube; 4 – ring detector; 5 – ^3He detectors; 6 – goniometer; 7 – two-coordinate position-sensitive detector; 8 – mechanical part with a moveable arm; 9 – control and operative visualization/analysis; 10 – data acquisition; 11 – data transfer.

The nanoindentation test was performed to study the mechanical properties of the samples prepared. The experiment was conducted on a nanomechanical tester (Bruker, USA). Prior to the indentation, the surface of the samples was polished; the force applied was 200 mN.

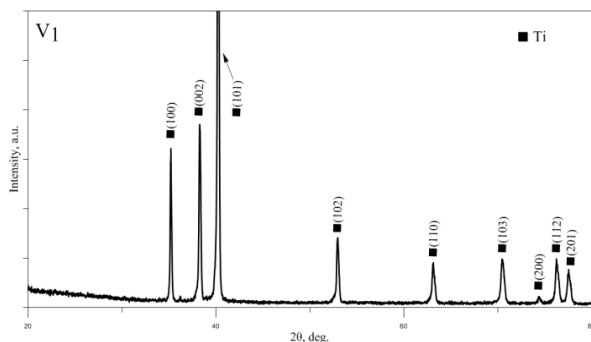


Figure 2. XRD pattern of the sample treated at V_1 speed of specimen motion.

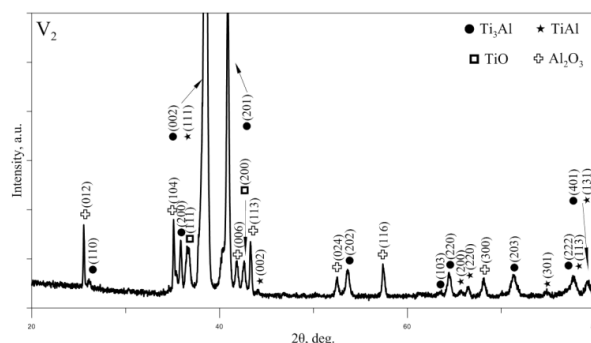


Figure 3. XRD pattern of the sample treated at V_2 speed of specimen motion.

3. Results and discussion

Figures 2 and 3 represent the XRD patterns of the samples. The diffractogram of the specimen treated at speed V_1 does not contain any peaks corresponding to intermetallic Ti-Al phases, while at speed V_2 , an intermetallic Ti-Al structure is visible with a main phase $\alpha_2\text{-Ti}_3\text{Al}$. In addition, the pattern exhibits several peaks corresponding to $\gamma\text{-TiAl}$ and some peaks of Al_2O_3 and TiO phases, because the sample was retrieved from the vacuum chamber directly after the EBT process. The latter phases demonstrate the good oxidation behavior of the sample.

A SEM image taken from the surface of the sample treated at speed V_2 is shown in figure 4. The EDX analysis showed that an intermetallic Ti-Al structure has been formed with a significant degree of oxidation. The mean ratio of Ti:Al was about 3:1, which corresponds to the main Ti_3Al phase, according to the XRD analysis. The dark precipitations, marked by asterisks, correspond to Al_2O_3 with a negligible amount of Ti ($\sim 4\%$). Thus, the SEM/EDX results confirmed the phase composition as evaluated by XRD.

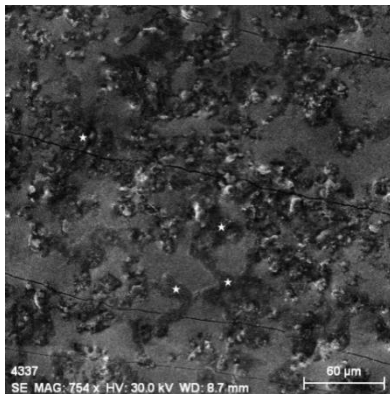


Figure 4. SEM image of the surface of a Ti-Al alloy.

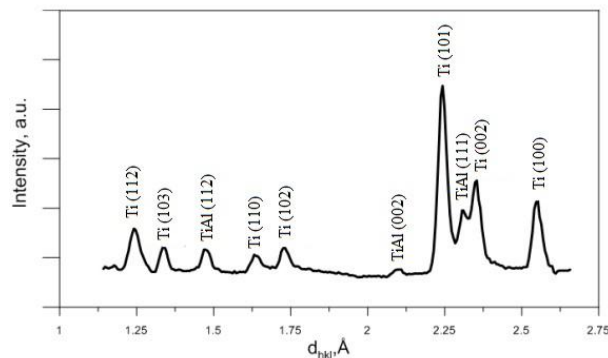


Figure 5. Time-of-flight neutron diffraction pattern of a TiAl alloy.

Figure 5 shows the time-of-flight neutron diffraction spectrum. It should be noted that, while for X-rays the penetration depth is limited by photo-electric absorption, the material is essentially transparent for neutrons [10]. Thus, neutron diffraction is an appropriate technique for in-depth crystal structure investigations. The pattern is presented by the interplanar distance distribution, contrary to the XRD spectra presented as an angle distribution. One can see several diffraction peaks corresponding to polycrystalline Ti, and some peaks of γ -TiAl. Thus, besides on the surface, an intermetallic Ti-Al structure has been formed in depth. The results obtained from neutron diffraction

Measurements showed that the $\text{Ti}_3\text{Al}/\text{TiAl}$ surface structure has been transformed to Ti/TiAl in the volume. It was thus shown that the combination of X-ray and neutron diffraction is an appropriate method of studying the in-depth phase composition distribution. Therefore, we can predict a transformation of the mechanical properties from the surface to the volume.

According to [4], the hardness on the surface should be much greater than in the volume of the sample produced. In order to study the mechanical properties, a nanoindentation test was carried out whose results are presented in figure 6, where a significant decrease from the surface to the volume is visible. The hardness measured at a depth of 0.7 μm was about 18.5 GPa, while at 1.5 μm it decreased to about 5 GPa.

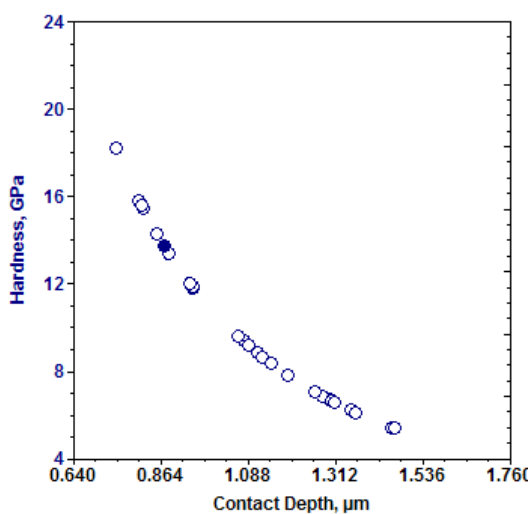


Figure 6. Nanohardness depth profile of a Ti-Al alloy.

4. Conclusions

Ti-Al alloys were successfully produced by continuous electron-beam treatment without surface melting of the Ti substrate/Ti-Al coating system with the technological parameters discussed above, in contrast with the case of electron-beam surface melting. We demonstrated that the combination of the XRD and neutron diffraction techniques is an effective method of evaluating the in-depth phase composition distribution. The results obtained showed that the surface structure of $\text{Ti}_3\text{Al}/\text{TiAl}$ was transformed to Ti/TiAl in the volume, which means that the mechanical properties on the surface are superior to those in the volume. In addition, a nanoindentation test demonstrated a decrease in the nanohardness in the depth, with the values being ~ 18.5 GPa at 0.7 μm and ~ 5 GPa at 1.5 μm .

Acknowledgments

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References

- [1] Wu X 2006 *Intermetallics* **14** 1114 - 22
- [2] Dimiduk M 1999 *Mater. Sci. Eng. A* **263/2** 281 – 8
- [3] Clements H and Mayer S 2013 *Adv. Eng. Mater.* **15** 191 – 215
- [4] Appel F, Paul J and Oehring M 2011 *Gamma Titanium Aluminide Alloys: Science and Technology* (Wiley-VCH Verlag & Co. KGaA)
- [5] Eckert J, Gao W, Golovin I, Imai Y, Li Z, Rennhofer M, Roth S, Russel A, Stoica M, Vanghan G, Zavrazhnov A and Zlomanov V 2008 *Intermetallic Research Progress* (Nova Science Publ. New York)
- [6] Hampshire J, Kelly P and Teer D 2002 *Thin Solid Films* **420 – 421** 386 – 91
- [7] Tsyganov I, Wieser E, Matz W, Mucklich A, Reuther H, Pham M and Richter E 2000 *Thin Solid Films* **376** 188 - 97
- [8] Mei X, Fu J, Li X, Rotshtein V, Koval N and Ma T 2014 *Rare Meter.* **33/2** 155 – 60
- [9] Allian-Bonasso N, Rotshtein V, Bouzy E, Germain L, Ivanov Y and Grosdidier T 2013 *J. Phys.: Conf. Series* **416**
- [10] Zabel H 1990 *Adv. Solid State Phys.* **30** 197 – 217