Study of the influence of vanadium and niobium on the structure of Ti-Al-V and Ti-Al-Nb alloys formed by selective electron beam alloying

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Abstract. Three-component surface alloys of the Ti-Al-Nb and Ti-Al-V systems were formed by means of selective electron beam alloying; the procedure involved DC magnetron sputtering deposition of multilayer Al and Nb or Al and V films with a thickness of 1 \textmu m of each layer on a commercially-pure Ti substrate. The samples prepared were then electron-beam surface-alloyed under identical technological conditions. The specimens were examined by scanning electron microscopy (SEM); their chemical composition was studied by energy dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) was used to determine the crystallographic structure. Intermetallic alloys in the system of Ti-Al-V were successfully produced with an electron beam current of 15 mA. As the current was increased from 15 mA to 20 mA, only pure titanium was visible, probably due to the evaporation of the alloying materials. In the Ti-Al-N system, intermetallic alloys were formed when the electron beam current reached 25 mA.

1. Introduction
Titanium aluminides are widely used in the field of aircraft and automotive industries, for manufacturing of railway cars, spacecraft, light ships, etc., because of their light weight, attractive mechanical properties and excellent resistance to corrosion at high temperature [1-3]. It is known that incorporation of different transition metals, such as vanadium or niobium, significantly improves the properties discussed above and, therefore, opens a number of new potential applications of these alloys. Many researchers have investigated ternary compounds in the systems of Ti-Al-V and Ti-Al-Nb [4-6]. It is known that Ti-Al-V alloys have already been introduced for manufacturing of implants, for development of parts and prototypes for the aerospace industry, gas turbines, etc. Incorporation of niobium into Ti-Al based materials is capable of improving significantly their mechanical properties. Works [6] have been published on the microhardness of Al-Ti-Nb alloys, showing that it reaches values of about 800 HV, which significantly exceeds that of the Ti-Al-based materials.

There exist many technologies for developing the discussed alloys, including thin film deposition [7], ion implantation, etc. [8]. It should be noted that the electron-beam surface alloying technique, which belongs to the additive manufacturing technologies, is considered as one of the most promising.\textsuperscript{3}

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methods of formation of the discussed alloys. In this technique, the alloying materials preliminarily deposited on a metallic substrate are irradiated by a high-intensity electron beam. The procedure results in melting of the treated surface area and forming a melt pool where the atoms from the metallic substrate and the alloying materials interact with each other. After solidification of the melt pool, intermetallic surface alloy is formed.

The formation of surface alloys by means of electron-beam surface alloying strongly depends on the technological conditions of the process. Therefore, clarifying the exact technological parameters leading to the formation of surface alloys is of great importance.

This paper describes a study on the formation processes of Ti-Al-V and Ti-Al-Nb alloys by an electron-beam surface alloying technology. The study deals also with the phase composition of the intermetallics produced and analyzes it with respect to the technological parameters used.

2. Experimental setup

Ti-Al and Ti-Al-Nb surface alloys were produced by DC magnetron sputtering deposition of Al and V or Al and Nb coatings on pure α-Ti substrate, the thickness of each film being about 1 μm. Before deposition, the Ti substrate was cleaned by sputtering for 10 minutes. The process was realized in Ar medium at a working pressure of 1.2×10⁻³ Pa. The samples were then alloyed by scanning a continuous electron beam. During the alloying process, the accelerating voltage (U) was 55 kV, the electron beam scanning frequency (f) was 200 Hz; the speed of the specimen motion (V) was 1 cm/sec. The electron-beam current (Ie) was varied between 15 mA and 25 mA. Figure 1 presents schematically the alloying process.

The phase composition of the alloyed layers was studied by X-ray diffraction (XRD) with CuKα characteristic radiation. The measurements were performed in the range from 30° to 80° at 2θ scale with a step of 0.1° and counting time of 10 s per step. The metallographic analyses were carried out by a scanning electron microscope (SEM/FIB LYRAI XMU, TESCAN) equipped with an EDX detector (Quantax 200, Bruker), making use of back-scattered electrons (BSE).

3. Results and discussion

Figure 2 presents X-ray diffraction patterns of electron-beam alloyed Ti-Al-V specimens taken at electron-beam current (Ie) of 15 mA and 20 mA. The diffractogram of the sample fabricated by a current of 15 mA exhibits maxima corresponding to AlTi and AlTi₁ phases. When Ie was increased to 20 mA, only titanium peaks were observed. Concerning the Ti-Al-Nb (figure 3) samples, it is seen that when the current of the electron beam was 15 mA, all peaks correspond to pure Ti, Al and Nb. No intermetallic phases were registered. After increasing Ie from 15 mA to 20 mA, peaks of Al₃Ti as well as of pure Ti and Nb appeared. Therefore, using these technological parameters (i.e., the parameters discussed in the experimental setup part and electron beam current of 20 mA) an intermetallic phase consisting of Ti and Al was formed. After raising Ie from 20 mA to 25 mA, diffraction maxima of ternary Ti₃AlNb and of pure Ti were registered.

Figure 4 presents a cross-section SEM image of the Ti-Al-V sample fabricated with Ie = 15 mA. The alloyed zone and the base titanium substrate are clearly visible. The chemical composition of the intermetallic part of the specimen was studied by energy dispersive X-ray spectroscopy; the results are summarized in table 1. As seen, an intermetallic Ti-Al-V surface alloy system was formed at the technological parameters discussed above. In [9], studies on the ternary Ti-Al-V phase diagram were
reported; the results are in agreement with those obtained by our XRD and EDX investigations. According to [9], the chemical composition produced of the alloyed zone should correspond to the double-phase structure $\text{AlT}_i+\text{AlTi}_3$. We did not register peaks of vanadium-based phases, which means that the V atoms have been dissolved into $\text{AlT}_i$ and $\text{AlTi}_3$ matrices.

Figure 2. XRD patterns of Ti-Al-V alloys.

Figure 3. XRD patterns of Ti-Al-Nb alloys.

Figure 4. Cross-section SEM image of a Ti-Al-V sample alloyed with $I_c = 15$ mA.

Table 1. Chemical composition of Ti-Al-V sample fabricated with $I_c = 15$ mA.

|            | Ti, at% | Al, at% | V, at%  |
|------------|---------|---------|---------|
| Alloyed zone | 44.87±3.0 | 42.65±1.2 | 12.48±6.0 |
| Substrate  | 87.99±2.2 | 11.60±0.3 | 0.41±0.2 |

Figures 5 and 6 present cross-section SEM images of Ti-Al-Nb samples fabricated by $I_c = 20$ mA and $I_c = 25$ mA, respectively. The chemical composition of the alloyed layers was studied by EDX; the results are summarized in table 2. Points 1; 2 and 3 correspond to the sample fabricated by $I_c = 20$ mA and are indicated in figure 5. The alloyed zone and substrate, shown in figure 6 were obtained at electron-beam current of 25 mA. The results are again in agreement with those from the XRD measurements and correspond to formation of an $\text{Al}_3\text{Ti}$ intermetallic phase under the undissolved Nb layer at a beam current of 20 mA. Raising the current to 25 mA leads to the appearance of a separate alloyed zone. It consists of intermetallic $\text{Ti}_2\text{AlNb}$ and pure Ti.

The results in the present study show the possibility of formation of intermetallic alloys in the system of Ti-Al-V and Ti-Al-Nb by electron-beam surface alloying. During such a selective electron beam treatment, the kinetic energy of the electrons is transformed into heat during their interaction with the specimens [10]. As it was already mentioned in the introduction, this technique is capable of melting the surface of the samples and forming a melt pool, where the atoms from the alloying materials and the base substrate form an intermetallic surface alloy. Therefore, the parameter “input energy” is important and can be described as:

$$E = \frac{UIt}{S} \quad (1)$$
In formula (1), $E$ is the input energy (J/mm$^2$); $U$, the acceleration voltage (V); $I$, the electron beam current (A); $t$, the interaction time (s); $S$, the interaction area (mm$^2$) [11]. It is obvious that increasing the electron-beam current will increase the input energy $E$ and the temperature of the alloyed zone surface. On the other hand, the melting point of the alloyed materials is an important process parameter. For example, the melting point of Nb (2469 °C) is higher than that of V (1910 °C) [12]. This is in agreement with the results obtained in the present study, where a surface alloy of the Ti-Al-V system was formed using electron beam current of 15 mA. After increasing the beam current up to 25 mA, respectively, the input energy, we registered a pure titanium substrate only, obviously due to the evaporation of vanadium. In contrast, the intermetallic system of Ti-Al-Nb was successfully alloyed using electron beam current of 25 mA, as evidenced by the thinner undissolved Nb layer in figure 5.

### 4. Conclusions

The results of the present study show the possibility of forming intermetallic alloys of the Ti-Al-V and Ti-Al-Nb systems by a scanning continuous electron beam. In the case of alloying titanium with aluminium and vanadium, the intermetallic layers are formed by electron beam current of 15 mA. When the beam current is increased from 15 mA to 20 mA only pure titanium is present, which can be due to the evaporation of the alloying elements. However, during alloying titanium with aluminium and niobium, intermetallic layers are formed when the electron-beam current reaches 25 mA. Therefore, the melting point of the alloyed elements plays a major role in the optimization of the technological parameters of a selective electron beam technology.

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**Figure 5.** Cross-section SEM image of a Ti-Al-Nb sample alloyed with $I_c = 20$ mA.

**Figure 6.** Cross-section SEM image of a Ti-Al-Nb sample alloyed with $I_c = 25$ mA.

**Table 2.** Chemical composition of a Ti-Al-Nb sample fabricated with $I_c = 20$ mA (points 1, 2 and 3) and $I_c = 25$ mA (alloyed zone and substrate).

|                | Ti, at% | Al, at% | Nb, at% |
|----------------|---------|---------|---------|
| Point 1        | 2.96±0.1 | 7.44±0.1 | 89.59±3.5 |
| Point 2        | 25.74±0.9 | 72.78±2.5 | 1.48±0.2  |
| Point 3        | 100±2.6  | -       | -       |
| Alloyed zone   | 85.12±2.4 | 8.91±0.3 | 5.97±0.3 |
| Substrate      | 97.81±4.2 | 1.95±0.1 | 0.24±0.1 |
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] Jia M, Zhang D, Liang J and Gabbitas B 2017 Metallurgical and Materials Transactions A 48/4 2015–29
[5] Chaves J, Olmos L, Jimenez O, Bouvard D, Rodriguez E and Florez M 2017 Powder Metallurgy 60/4 257-66
[6] Valkov S, Petrov P, Lazarova R, Bezdushnyi R and Dechev D 2016 Appl. Surf. Sci. 389 768-74
[7] Hampshire J, Kelly P and Teer D 2002 Thin Solid Films 420 – 421 386 – 91
[8] Tsyganov I, Wieser E, Matz W, Mucklich A, Reuther H, Pham M and Richter E 2000 Thin Solid Films 376 188 – 97
[9] Hashimoto K, Doi H and Tsujimoto T 1986 Trans. Japan Institute of Metals 27/10 741-9
[10] Ormanova M, Petrov P and Kovacheva D 2017 Vacuum 135 7-12
[11] Fu Y, Hu J, Shen X, Wang Y and Zhao W 2017 Nuclear Instr. Methods in Phys. Res. B 410 207-14
[12] http://www.webelements.com