Formation and characterization of Al-Hf alloys by selective electron-beam surface alloying

S Valkov¹ and P Petrov
Acad. Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
E-mail: stsvalkov@gmail.com

Abstract. We report electron-beam surface alloying of Al substrates with Hf. The Al substrates were covered by a Hf coating with a thickness of 2 μm; the samples were alloyed by means of a scanning electron beam with circular geometry of the beam deflection. The phase composition of the obtained specimens was studied by X-ray diffraction (XRD); their microstructure and chemical composition were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively. The results showed that the phase composition did not depend on the speed of sample motion. However, their microstructure was significantly finer and more homogeneous in the case of the lower speed of motion \( V_1 = 0.5 \text{ cm/s} \) in comparison with the higher speed \( V_2 = 1 \text{ cm/s} \).

1. Introduction

Aluminum and its alloys have a number of applications due to their low weight, attractive mechanical properties, resistance to corrosion, etc. However, some drawbacks, such as low hardness and wear resistance limit the range of their applications. Since these limitations depend mostly on the surface properties, they can be overcome by applying appropriate technologies for surface modification [1].

There exist a number of techniques for surface modification of materials, including thin film deposition [2] and surface treatment by high-energy fluxes (HEFs), such as laser or electron beams [3], etc. In recent years, the treatment of the materials by HEFs received strong attention in modern materials science for the development of surface alloys since it has several advantages in comparison with the other methods, such as low cost, significantly shorter time of treatment, etc. In these technologies, the flux interacts with the treated area of the surface and forms a heat distribution from the surface to the bulk. The technological conditions can be selected so as to melt the surface and form a melt pool. The alloying elements are incorporated into the molten material; after solidification, a surface alloy is formed [4].

A number of studies have been published describing the modification of Al and aluminum alloys by formation of surface alloys by electron or laser beam surface treatment. In [5], laser beam alloying and remelting of Al substrates with Nb were carried out using a CO₂ laser; the results showed that the structure of the surface layers formed consisted of fine dendrites of Al₃Nb and small fractions of pure Al. The hardness varied in the range from 480 HV to 650 HV. A similar study was performed by the authors of [6], where a laser beam alloying and remelting of Al with Cr was studied; the results showed a significant increase in the microhardness of the obtained surface alloy in comparison with

¹ To whom any correspondence should be addressed.
the base Al substrate. In works [3,4,7], Al substrates electron-beam alloyed with Fe, Cr, Co and Ni powders were studied. The results showed that the microhardness of the formed layers was significantly higher in comparison with the base Al substrate.

It is clear that the formation of intermetallic coatings on the surface of Al substrates leads to a significant improvement of the functional properties of the material. However, results of alloying of aluminum substrate with hafnium are currently lacking in the scientific literature.

The aim of this study is to investigate the process of synthesis of Al-Hf surface alloys on aluminum substrates by means of selective electron-beam alloying. The phase composition and microstructure were studied and discussed with respect to the speed of the specimen motion.

2. Experimental setup

As a first step of our experiments, Hf coatings with a thickness of about 2 μm were deposited on pure Al substrates by DC magnetron sputtering in Ar at a working pressure of 1.2×10⁻¹ Pa. Al-Hf surface alloys were then produced by scanning with a continuous electron beam. During the alloying process, the accelerating voltage (U) was 52 kV, the electron-beam scanning rate (f) was 200 Hz, and the electron beam current (Ic) was 25 mA. Two speed of the specimen motion (V) were chosen, namely, V₁ = 0.5 cm/s and V₂ = 1 cm/s. Figure 1 presents schematically the alloying process.

The phase composition of the alloyed layers was studied by X-ray diffraction (XRD) with Cu Kα (1.54 Å) characteristic radiation. The measurements were carried out from 30° to 80° at 2θ scale with a step of 0.02 and counting time of 2 s per step.

The microstructure and chemical composition of the alloyed layers were studied by scanning electron microscopy (SEM/FIB LYRA XMU, TESCAN) equipped with an EDX microanalyzer (Quantax 200, Bruker), which integrates a true standardless analysis with P/B ZAF correction (Z being atomic number correction factor; A, X-ray adsorption correction factor; F, fluorescence correction factor).

3. Results and discussion

Figure 2 presents the experimentally obtained XRD patterns of the specimens alloyed with V₁ = 0.5 cm/s and V₂ = 1 cm/s. The results show that an intermetallic surface alloy in the system of Al-Hf has been successfully formed under these technological conditions. The phase composition of the alloyed layers is in the form of a double-phase structure of Al₃Hf and pure Al. Also, some traces of an oxide phase, namely Al₂O₃, are visible due to the strong affinity of Al to oxidation. Al₃Hf has a body-centered tetragonal structure. No changes in the phase composition were observed, which means that the speed of the specimen motion did not affect the phase composition. The formation of the Al₂O₃ phase can be explained by the fact that the samples were retrieved from the vacuum chamber immediately after the electron-beam treatment before being cooled down to room temperature. The existence of oxide phases can be beneficial, since they act as a protective barrier to other reactive agents and organic pollutants.
The microstructure and chemical composition of the obtained surface alloys were studied by scanning electron microscopy (see figure 3 and figure 4) and energy-dispersive X-ray spectroscopy (EDX). Figure 3 presents a cross-sectional SEM image of the alloyed layer at the speed of the electron beam of 1 cm/s. It is obvious that in the case of the higher speed of specimen motion during the electron beam alloying process ($V=1$ cm/s in the present particular investigation) the intermetallic phase is mainly in the form of coarse fractions distributed on the surface of the Al substrate. The results obtained from the EDX measurements are summarized in Table 1 and Table 2. It should be noted that according to the binary Al-Hf phase diagram [8], the surface alloy obtained is in the form of a double phase structure of Al$_3$Hf fractions randomly distributed in the Al solid solution. A small amount of oxygen was also detected. Figure 4 presents a cross-sectional SEM image of the sample obtained at a speed of the specimen motion $V=0.5$ cm/s. The structure of the alloyed layer consists of fine intermetallic particles dispersed in the Al matrix; a very small amount of coarse fractions can be seen in the alloyed zone. Obviously, by applying the lower speed of specimen motion, a significantly higher degree of homogeneity of the surface alloy obtained is achieved, in contrast to the case of higher velocity of the sample motion.

The microstructure and chemical composition of the obtained surface alloys were studied by scanning electron microscopy (see figure 3 and figure 4) and energy-dispersive X-ray spectroscopy (EDX). Figure 3 presents a cross-sectional SEM image of the alloyed layer at the speed of the specimen motion of 1 cm/s. It is obvious that in the case of the higher speed of specimen motion during the electron beam alloying process ($V=1$ cm/s in the present particular investigation) the intermetallic phase is mainly in the form of coarse fractions distributed on the surface of the Al substrate. The results obtained from the EDX measurements are summarized in Table 1 and Table 2. It should be noted that according to the binary Al-Hf phase diagram [8], the surface alloy obtained is in the form of a double phase structure of Al$_3$Hf fractions randomly distributed in the Al solid solution. A small amount of oxygen was also detected. Figure 4 presents a cross-sectional SEM image of the sample obtained at a speed of the specimen motion $V=0.5$ cm/s. The structure of the alloyed layer consists of fine intermetallic particles dispersed in the Al matrix; a very small amount of coarse fractions can be seen in the alloyed zone. Obviously, by applying the lower speed of specimen motion, a significantly higher degree of homogeneity of the surface alloy obtained is achieved, in contrast to the case of higher velocity of the sample motion.

### Table 1. Chemical composition of Al-Hf surface alloy fabricated at $V=1$ cm/s.

|       | Al, at%  | Hf, at%  | O, at% |
|-------|----------|----------|--------|
| Point 1 | 54.62±1.1 | 24.15±1.8 | 21.23±1.1 |
| Point 2 | 59.19±3.1 | 1.43±0.4  | 39.38±4.9  |
| Point 3 | 100±2.6  | -        | -      |

### Table 2. Chemical composition of Al-Hf surface alloy fabricated with $V=0.5$ cm/s.

|       | Al, at%  | Hf, at%  | O, at% |
|-------|----------|----------|--------|
| Point 1 | 58.59±2.1 | 8.75±1.2 | 32.66±3.0 |
| Point 2 | 70.50±2.9 | 3.84±0.7 | 25.65±2.4 |
| Point 3 | 100±3.6  | -        | -      |

The results obtained in the present study show the possibility of forming intermetallic Al-Hf surface alloys. It is shown that the speed of specimen motion does not affect the phase composition. However, this speed strongly influences the microstructure of the alloyed layers. According to the numerical model [9], which studies the mass transport, the distribution of the alloying elements and homogenization process is based on the intense Marangoni convection, which is caused by the high temperature gradient in the melt pool. The homogenization process can be expressed by the surface tension number, which can be defined as follows:

$$S = \frac{\langle d\sigma/dT \rangle q d}{\mu u_0 k}$$

(1)
In (1), \((d\sigma/dT)\) is the temperature coefficient of the surface tension; \(q\) is the net heat flow from the e-beam; \(d\) is the diameter of the beam; \(\mu\) is the viscosity; \(u_0\), the speed of specimen motion; \(k\), the thermal conductivity. According to (1), it is obvious that the surface tension number increases with a decrease in the speed of the sample motion and vice-versa. For lower values of the surface tension number, the convection becomes negligible. Furthermore, by using the speed of sample motion of 0.5 cm/sec, the specimen was exposed for twice the electron beam interaction time in comparison with the speed of 1 cm/sec, leading to longer lifetime of the melt pool and sufficient mass transport for melt homogenization. These statements are in agreement with the results in the present study where the higher speed of the specimen motion during the electron beam alloying process leads to a significantly inhomogeneous structure of the surface alloy obtained.

4. Conclusions
The results obtained in the present study show the possibility of forming intermetallic surface alloys in the Al-Hf system by selective electron beam surface alloying of Al substrate with Hf. The phase composition remains unchanged with respect to the speed of sample motion. The parameters of the process, namely, speed of specimen motion, strongly influences the microstructure. Thus, the lower speed of sample motion leads to a significantly finer and more homogeneous microstructure in comparison with the higher speed. The conclusion is drawn that the surface tension is of major importance for melt homogenization of the surface alloys formed by selective electron-beam alloying, which can be controlled by the speed of specimen motion.

Acknowledgements
This work was supported by the Bulgarian Ministry of Education and Science under the National Research Program "Young scientists and postdoctoral students" approved by DCM #577/17.08.2018.

References
[1] Kartal G, Timur S, Urgen M and Erdemir A 2010 Surf. Coat. Technol. 204 3935–9
[2] Kelly P and Arnell R 2000 Vacuum 56 159-72
[3] Petrov P and Dimitroff D 1993 Vacuum 44 857-61
[4] Petrov P 1997 Vacuum 48 49-50
[5] Almeida A, Petrov P, Nogueira I and Vilar R 2001 Mater. Sci. Eng. A 303 273-80
[6] Almeida A, Carvalho P and Vilar R 2017 J. Metall. Sci. 1 1-12
[7] Petrov P 2012 J. Phys.: Conf. Series 356 012035
[8] Wang T, Jin Z and Zhao J 2002 J. Phase Equilibria 23 416-23
[9] Chan C, Mazumder M and Chen M 1984 Metal. Trans. A 15 2175-84