Layers obtained on TiCN aluminum nanocomposites
by electron-beam treatment

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Abstract. The impact of electron beam treatment on aluminum composites containing 0, 2, 5 and 10 wt.% TiCN nanoparticles was studied. Aluminum nanocomposites were produced as rods with 12 mm diameter by means of preliminary cold volume compression and succeeding hot pressing. Cylinders with a height of 10 mm were cut from the rods and their flat surfaces treated by scanning electron beam techniques. The electron-beam treatment (EBT) process was carried out using Leybold Heraeus (EWS 300/15–60) electron beam equipment. Two technological regimes were used: with low energy power input Q₁ and with high energy power input Q₂. Composite layers with a strong bond to the substrate were obtained. Light microscopy (LM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used for characterizing the microstructure. The phase composition of the obtained specimens was studied by means of X-ray diffraction (XRD) using CuKα characteristic radiation (λ=1.54 Å). The microhardness was discussed with respect to the applied technological conditions of the EBT and corresponding microstructure and crystallographic structure of the formed layers. Nanocomposite layers with improved hardness were obtained which is necessary as exploitation surface properties of automobile and aircraft parts. It was found out that the microhardness of samples treated with high energy was much lower than the one of the samples treated with low energy. The strengthening mechanism in the samples was discussed.

1. Introduction
Aluminum matrix nanocomposites are widely used in the modern automotive and aircraft construction because they have higher strength properties than aluminum alloys, maintaining good plasticity and toughness and lightweight [1-8]. Coatings and surface layers presenting aluminum nanocomposites are used as protective materials for different machine parts because of their high hardness, wear resistance and corrosion resistance [9-15]. Researchers are constantly striving to improve the exploitation properties of materials, so they are looking for new technologies to process them. In our previous works [16-19] we have found out that the aluminum nanocomposites improved their mechanical and tribological properties after electron beam treatment (EBT) with defined technological parameters with low energy and the microhardness of surface layers increases up to 21 times. These significant changes of the properties could be explained by the difficulty in the movement of the dislocations provoked by the hard TiCN nanoparticles. The dislocations form loops around the nanoparticles, the number of which increases as the applied strain increases [20]. This mechanism of strengthening known as Orowan mechanism is the main mechanism acting in the aluminum nanocomposites with TiCN nanoparticles up to 10 wt.%.

When the nanoparticles weight part exceeds this limit, then begins a process of decreasing strength and softening the material.
The aim of the present study is to investigate the microstructure and microhardness of aluminum nanocomposites layers containing 0%, 2%, 5%, and 10 wt. % TiCN nanoparticles formed after a surface treatment by electron beam irradiation with low and high energy power input.

2. Material and methods

Aluminum nanocomposites containing 0, 2, 5 and 10 wt. % TiCN nanoparticles were produced as rods with 12 mm diameter by means of preliminary cold volume compression and succeeding hot pressing. Cylinders with a height of 10mm were cut from the rods. Their flat surfaces were treated by electron beam irradiation at following parameters: voltage \( U = 50 \text{kV} \), speed of the specimen motion \( V = 50 \text{mm/sec} \) and scanning frequency \( f = 10 \text{kHz} \). When the beam current \( I_0 = 26 \text{mA} \), the regime is low energy, designed as \( Q_1 = 1300\text{W} \). When the beam current \( I_0 = 30 \text{mA} \), the regime is high energy and designed as \( Q_2 = 1500\text{W} \). The experiments were carried out with Leybold Heraeus (EWS 300/15–60) electron beam equipment.

Metallographic samples were prepared by standard procedure: mounted in acrylic resin and wet ground up to 4000 grinding paper. Then the samples were electrolytic polished with the followed electrolyte: 575 ml methyl alcohol, 25 ml HClO\(_4\) and 10 ml HNO\(_3\). The metallographic observations were carried out by microscope PolyvarMet at magnifications up to 1000x.

The microhardness was determined by means of device MicroDuromat 4000 with a load of 20g, time for reaching the load - 10s and time for holding the load - 10s.

The investigations by SEM and EDX were carried out by means of SEM/FIB LYRAI XMU.

Plates, with a thickness of \(~700 \mu\text{m}\) were mechanically thinned by grinding (SiC paper) to a thickness of \(20\sim30 \mu\text{m}\). From the as prepared foils were cut small discs of 3 mm in diameter, which were subsequently electrolytically polished at room temperature (Struers Tenupol Electropolisher, operating at 15V) in a solution of 20% HClO\(_4\) and 80% CH\(_3\)COOH. These specimens were used for TEM analysis performed by TEM JEOL-JEM 1011 with 100 kV accelerating voltage.

The phase composition of the obtained samples was studied by X-ray diffraction (XRD). The experiments were carried out using CuK\(\alpha\) characteristic radiation (1.54 Å). The measurements were conducted in the range from 5° to 90° at the 20 scale with a step of 0.02° and counting time of 5 sec. per step.

3. Results and discussion

3.1. Temperature distribution during electron beam treatment

Figure 1 presents the results of the calculated temperature field distribution along with the depth of the electron beam treated area. The calculations are made by developing a heat model that is detailed in our previous work [17]. The numerical model is based on an analytical solution of the heat transfer equation using Green’s functions.
Figure 1. Temperature distributions along the z axis (depth of the treated zone) for different energy power input (V=50 mm/s, f=10 kHz)

The results presented in figure 1 show that increasing the electron beam power leads to an increase in the alloyed layer thickness, which is expected. The molten zone depth decreases from 27 to 17 μm for energy power input variation from 1500 to 1300 W.

3.2. Samples treated with \( Q_1 \) (low energy power input)

The microstructures of samples with 0 and 10 wt. % TiCN treated with low energy power input \( Q_1 \) are shown in figure 2. The samples with (0 ÷ 10) wt. % TiCN have a clearly formed layer. The layers are too convex, so good focusing of the parent metal is impossible with a metallographic microscope. Such protrusive layers are formed during grinding and polishing samples because the hardness of layers is much higher than the hardness of the parent metal. It could be seen that the layer’s microhardness of the EBT aluminum sample is nearly two times higher than the microhardness of the parent metal. The tendency of microhardness alteration with TiCN content rising is shown in figure 3. The microhardness progressively increases with TiCN percentage and in the sample with 10 wt. % TiCN reaches a maximum of 1873HV after which it decreases. Analogic dependence of the strengthening from the weight fraction of TiCN nanoparticles contained in the parent metal is found out and explicated in [20].
Figure 3. Microhardness alteration with TiCN wt% in investigated aluminum nanocomposites

The EDX analyses show that there is 8.23 wt.% Ti in the sample with 10 wt. % TiCN - figure 4, which is an acceptable result and the observed particles with SEM are precisely nanoparticles of TiCN - figure 5 (a), (b) and (c). The chemical spectrum unambiguously shows the sharp increase in titanium, carbon and nitrogen content in the particles – figure 5 (c). We have chosen to demonstrate larger particles in order to obtain clear results. TEM image – figure 5 (d) shows increased dislocation density around the nanoparticles, the formation of dislocation walls and substructure in the aluminum matrix. The TiCN nanoparticles prevent and stop the movement of dislocations resulting in the reinforcement of composites. TiCN particles can impede the dislocation motion through a variety of interaction mechanisms, some of which can operate simultaneously. The model of internal strain hardening distinguishes two main cases depending on the distribution of the obstacles: (a) the stress fields are closely spaced and the dislocation line has to curl between them, or (b) the fields are widely spaced and the dislocation line has to pass around them, subsequently leaving a dislocation loop, known as Orowan loop [21] around each of them. The strengthening effect of the reinforcement additive on the composite is a result of the formation of multiple dislocation Orowan loops around the nanoparticles, as argued by other researchers [22-24]. When the accumulated stresses around the particles exceed the strength limit of the matrix, the strength reduction begins. The accumulated stress is then relieved by the formation of nanosized cracks usually between the nanoparticles [20]. The strengthening effect depends on the volume fraction of the additive $f$ and is limited by a critical value, $f_{\text{max}}$, beyond which the strengthening decreases. This standpoint explains very well the gradual increase of the microhardness values to the maximum at 10 wt. % TiCN, and the next decrease.
Spectrum: Acquisition 9244

| El  | AN | Series | unn. C | norm. C | Atom. C | Error [wt.%) | [wt.%) | [at.%) | [%] |
|-----|----|--------|--------|---------|---------|--------------|--------|--------|-----|
| Al  | 13 | K-series | 90.49 | 68.59 | 58.98 | 4.4 |
| O   | 8  | K-series | 25.09 | 19.02 | 27.58 | 40.8 |
| C   | 6  | K-series | 4.06  | 3.08  | 5.94  | 1.0 |
| N   | 7  | K-series | 3.42  | 2.60  | 4.30  | 6.0 |
| Ti  | 22 | K-series | 8.23  | 6.24  | 3.02  | 0.3 |
| Cu  | 29 | K-series | 0.62  | 0.47  | 0.17  | 0.1 |

Total: 131.92  100.00  100.00

Figure 4. An area in the sample with 10 wt.% TiCN nanoparticles – (a) and (b) EDX spectrum and content of chemical elements.

![Figure 4](image)

Figure 5. The area around two TiCN particles in the sample with 10 wt.%: (a); EDX spectrum of the chemical elements: (b); linear elements distribution: (c) a TEM image of nanoparticles and dislocations around them: (d)

![Figure 5](image)
3.3. Samples treated with $Q_2$ (high energy power input).

The results from light microscopy investigation of samples treated with $Q_2$ are shown in figure 6. A layer with a thickness of 25 µm nearly is formed on the aluminum sample with 0 wt. % TiCN – figure 6 (a). The layer’s microhardness is 78HV which is 2, 6 times higher than the microhardness of the parent metal. This means the EBT itself causes a hardening. The sample with 10 wt. % TiCN nanoparticles layer is with about 80 µm thickness and 102HV microhardness. The maximum micro-hardness after this type of treatment is achieved in the 5 wt. % TiCN sample. This means that the high energy displaces the maximum of microhardness to the lower values of the nanoparticles weight part. Great particles are optically registered in the sample with 10 wt. % TiCN – figure 6 (c) and (d). The TiCN nanoparticles are in principles refractory but in this case, favorable conditions are probably created for TiCN interfacial reaction with some elements from the molten matrix. Figure 6 (c) and 6 (d) register spherical nanoparticle in the layer and nanoparticles having a core and a cover. We assume that the high temperature of the liquid bath is kept in some places in the sample for a relatively long time under the electron beam impact, during which TiCN reacts with some elements of the melting and nanoparticles or a part of them do not exist yet as reinforcement. This could explain the lower microhardness of the samples treated with high energy - $Q_2$.

![Figure 6. Microstructures of samples treated with $Q_2$: (a) Al with 0 wt. % TiCN and (b) Al with 10 wt. % TiCN](image)

Figure 6 represents a SEM image of the layer of the sample with 10wt. % TiCN. The layer shows dendritic-like microstructure at higher magnification.

![Figure 7. SEM image of the layer of the sample with 10 wt. % TiCN](image)
The XRD patterns of the samples with 10 wt. % TiCN, electron beam treated with Q_1 and Q_2 are shown in figure 8 (a) and figure 8 (b), respectively. Both diffraction patterns exhibit peaks of pure Al and amorphous-like halos. In addition, at the sample treated with Q_1, peaks of TiCN phase, which means that some amount of the nanoparticles exist in the layer formed by the lower energy, contrary to the case of electron beam treatment with Q_2. This result is another proof that the high energy promotes the interaction between particles and some elements from the matrix and converts them almost entirely into an amorphous phase. The TiCN phase has body-centered cubic crystal structure where the carbon and nitrogen atoms occupied the octahedral sites of the closed-packed hexagonal Ti lattice forming TiC\textsubscript{x}N\textsubscript{1-x}. Therefore, the identification of the latter phase was done according to both TiN (ICDD PDF#38-1420) and TiC (ICDD PDF# 32-1383).

Fig. 8. XRD patterns of the samples with 10 wt. % TiCN and treated with: (a) Q_1 and (b) Q_2

4. Conclusions

- Layers obtained on aluminum nanocomposites containing 0%, 2%, 5%, and 10 wt. % TiCN nanoparticles were produced by electron beam treatment with low and high energy.
- The nanoparticles are retained in the layers obtained by low energy irradiation, whereas in the layers obtained with high energy the interaction between particles and some elements from the matrix occurs and they almost entirely convert into an amorphous phase.
- The microhardness alteration in the samples treated with low energy is expressed in progressively increasing with TiCN content and in the sample with 10 wt. % of TiCN reaches a maximum of 1873HV after which it decreases. The main strengthening mechanism in the aluminum matrix nanocomposites is the Orowan mechanism. This is the cause of higher microhardness in the samples treated with low energy where the nanoparticles remain unchanged in comparison with the samples treated with high energy where the nanoparticles are transformed into an amorphous phase.
- The microhardness alteration in the samples treated with high energy is expressed in progressively slight increasing with TiCN content and in the sample with 5% wt. TiCN reaches a maximum of 161HV after which it decreases. The slight increase in microhardness is explained in this case by the transformation of the hard TiCN nanoparticles into an amorphous phase.
- This investigation confirms the fact that the strengthening effect depends on the volume fraction of the additive f and is limited by a critical value, f_{max}, beyond which the strengthening decreases.

Acknowledgments

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