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Surface modification of an aluminum alloy by electron beam introducing TiCN nanoparticles

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Abstract. TiCN nanopowder deposited in an appropriate way on the surface of an AlSi₁₂Cu₂NiMg substrate was incorporated in the matrix using an electron beam technology. The samples were studied by means of light microscopy, SEM, and EDX; their microhardness was also determined. The formation was found of a uniform and dense coating with a thickness of 7 – 10 µm with a good adherence to the substrate. A modified zone appeared under the coating with a thickness of 100 – 150 µm containing dendrites of an α-solid solution and a fine eutectic between them, as well as primary silicon crystals. The microhardness of this modified zone was up to 2.4 times higher than that of the matrix. The results of SEM and EDX studies revealed unambiguously the presence of titanium in the coating and in the zones below it. Obviously, the electron beam treatment resulted in the TiCN nanoparticles penetrating into the coating and the substrate immediately below the coating.

1. Introduction

A large number of works reported the possibility to prepare coatings with improved properties by depositing nanoparticles in an appropriate way on a metal substrate followed by an irradiation treatment [1-6]. It is known that nanoparticles having a crystal lattice with dimensions and orientation similar to those of a metal act as nucleus centers in the melt during cooling [7]. When they are well distributed and in a sufficient concentration in the melt, they hinder the atoms' diffusion, thus limiting the grains' growth. As a result, the metal solidifies in a finer structure. Also, the nanoparticles serve as barriers to the motion of dislocations, thus increasing the strength of the solid material [8–10].

The aim of the present work was to obtain a coating with improved properties by introducing TiCN nanoparticles in an aluminum alloy substrate through electron beam irradiation. The AlSi₁₂Cu₂NiMg alloy is widely used for pistons and cylinder liners, which requires good friction and tribological properties of the surface. The above references, together with our previous experience on applications involving nanoparticles in metal melts [11-13] on the one hand, and on preparing highly wear-resistant nanosized layers by electron beam treatment [14-17] on the other, prompted us to develop the approach discussed here. In our opinion, the electron beam treatment is a technique suitable for

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incorporating nanoparticles deposited on a metal substrate. Combining a circular electron beam motion with a translational motion of the substrate, one can cause re-melting, stirring and mixing of the metal surface, thus incorporating the nanoparticles into the matrix. The result expected is reinforcement of the metal matrix by the hard and refractory nanoparticles.

2. Experimental procedure

2.1. Materials

2.1.1. Coating material. The refractory TiCN powder (Neomat Co., Latvia, mean particle size 40 ± 5 nm) was chosen as a coating material due to its excellent properties, such as high melting point, extreme hardness, and high heat conductivity [18]. Like aluminium, it has an FCC lattice, with a constant close to that of aluminium.

2.1.2. Substrate material. The chemical composition of the aluminum alloy used as a substrate is shown in table 1. This alloy is used for production of pistons operating under heavy duty conditions of friction and wear.

Table 1. Chemical composition of the substrate alloy.

Element	Cu	Mg	Si	Ni	Al
Wt %	0,930	0,331	11,31	0,109	rest

2.2. Procedure

Metallographic samples of the $\text{AlSi}_{12}\text{Cu}_2\text{NiMg}$ alloy were ground by grinding paper 1200. They were then smeared with a mixture of three drops of CHCl_3 , plastic rasping and TiCN powder to obtain a film with concentration 0.015 mg/mm^2 TiCN. The film was uniform and well adherent to the aluminum substrate. The as-prepared samples were subjected to electron-beam treatment in a type ESW300/60-15 installation (Leybold-Heraeus). The electron beam scanned the sample in a circular rotating motion, while the sample moved in a straight line. We were thus able to maintain a liquid pool for a long time, with the melt being well stirred and the nanoparticles mixing with the molten metal. The electron beam treatment conditions are given in table 2.

Following the electron beam treatment, the cross-sections of the metallographic samples perpendicular to the coating were wet-grinded by silicon carbide grinding paper 1200 and 4000 and etched by 0.5% water solution of HF. The samples were studied by means of light microscopy, SEM, and EDX. The microhardness of all samples was also determined.

The equipment used was as follows: a PolyvarMet metallographic microscope with magnification up to $1000\times$; a MicroDuromat (Reichert-Jung) HV microhardness device with a load of 20 g, time for reaching the load of 10 s and holding time of 10 s; SEM/FIB LYRAI XMU, TESCAN, equipped with an EDX detector (Quantax 200, Bruker).

Table 2. Electron beam treatment parameters.

I_b [mA]	v [cm/s]	f [kHz]	U [kv]	I_f [mA]	P [W]
30	2,5	10	52	472	1560

3. Results and discussion

3.1. Light microscopy

The microstructure of a treated sample is shown in figure 1(a) and (b). A dense coating with a uniform thickness of about $7 - 10 \mu\text{m}$ is seen on the substrate surface. It is well adherent to the underlying material. The microhardness was not measured because of the relatively small thickness and the relief. There is a modified zone with a thickness of $100 - 150 \mu\text{m}$ and a dendritic structure under the coating. It consists of α -solid solution dendrites and a fine eutectic between them, as well as of primary Si crystals. The microhardness of this modified zone was up to 2.4 times higher than that of the matrix – figure 1(c).

We should note here that the microhardness measurement unit, given as imprint in figure 1 (c) is

kgf/mm². The microhardness of the modified zone in MPa is approximately 2893 MPa, while the same parameter for the matrix is 1206 MPa.

3.2. SEM and EDX

The mapping zone and the mapping chart are presented in figure 2 (a) and (c). The titanium is distributed mainly in the coating and slightly underneath. The elements' spectra are given in figure 2 (b), where the titanium and aluminum peaks are well visible. The SEM and EDX results (figure 3) clearly show the presence of titanium in the coating and in the areas below it. Thus, the TiCN nanoparticles were embedded in the substrate material as a result of the electron beam treatment. The higher hardness of the coating is due not only to the residual stresses after the electron beam irradiation, but also to the presence of nanoparticles, which obstruct the motion of dislocations and increase the strength of the metal matrix. We believe that this is the main material strengthening mechanism, although other mechanisms are also possible in this case, such as, for example, the grain refinement mechanism, as the microstructure of the surface is visibly refined.

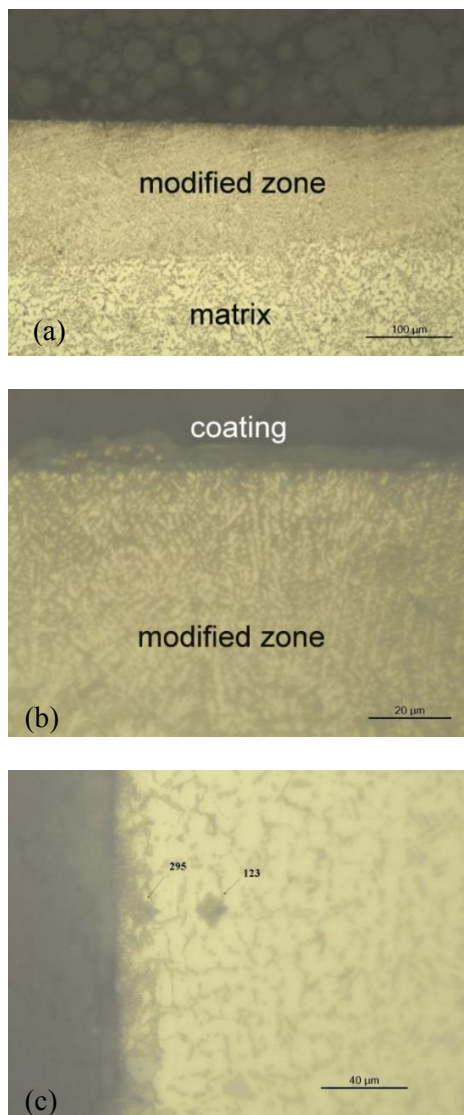


Figure 1. Microstructure of a treated sample (a, b) and microhardness imprints (c).

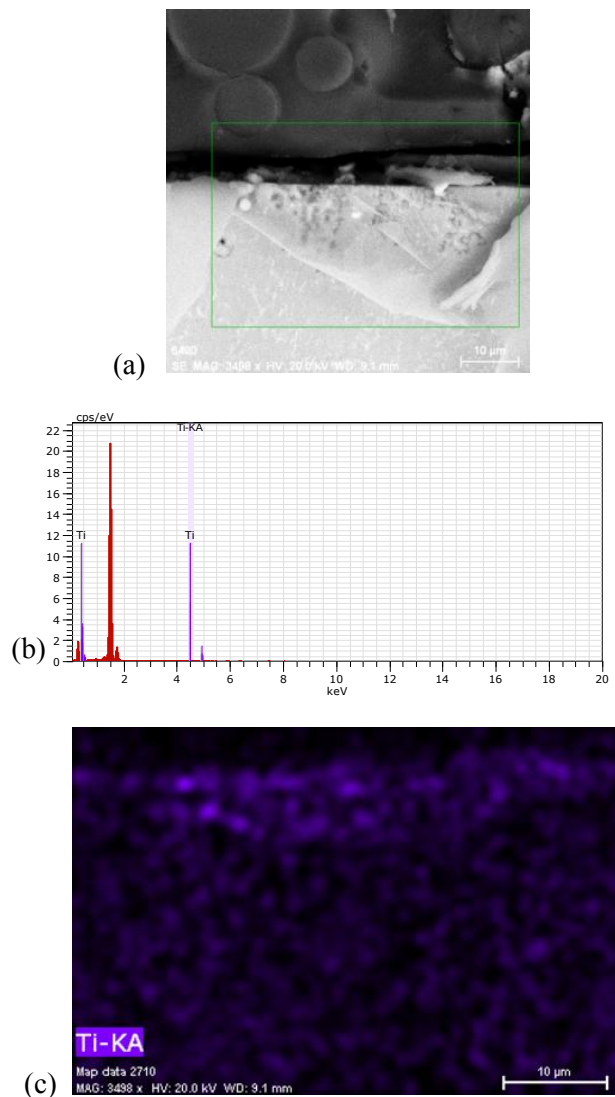
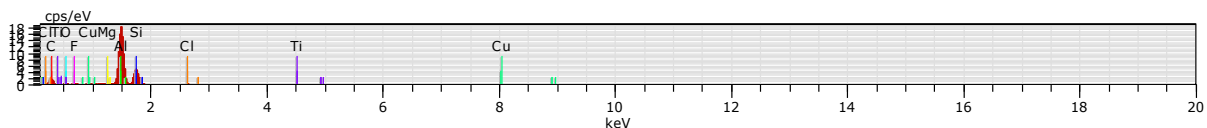


Figure 2. SEM image of TiCN coated sample with mapping zone (a), elements spectra (b) and composition map of Ti (c).

The Ti content at the marked point, which is in the substrate immediately beneath the coating, is 0.24 wt % – table 3. The conclusion one should draw is that the nanoparticles have penetrated into the substrate due to the electron beam treatment.

Table 3. Elemental composition in the marked point – figure 3 (a).

Acquisition 6531		Date:6/23/2017 11:25:05 AM		HV:20.0 kV		Puls th.:3.89 kcps	
El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error [%]	
C	6	K-series	23.09	19.21	32.18	3.9	
Al	13	K-series	49.43	41.13	30.67	2.4	
F	9	K-series	14.21	11.82	12.52	2.5	
Si	14	K-series	19.78	16.46	11.79	0.9	
O	8	K-series	10.85	9.03	11.35	16.6	
Mg	12	K-series	1.45	1.21	1.00	0.1	
Cl	17	K-series	0.44	0.37	0.21	0.0	
Cu	29	K-series	0.64	0.53	0.17	0.1	
Ti	22	K-series	0.29	0.24	0.10	0.0	
Total:			120.18	100.00	100.00		



(b)

4. Conclusions

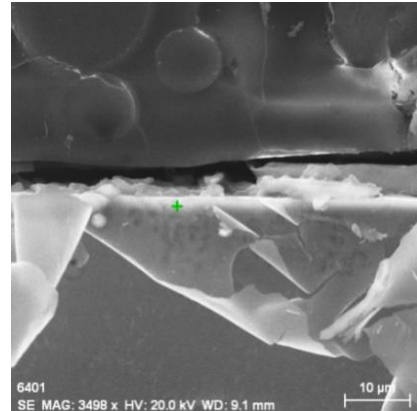
Electron beam treatment was successfully applied to produce a TiCN coating on the surface of an alloy used for fabrication of pistons.

The nanoparticles penetration in the metal matrix was proved by EDX analysis.

The coating showed good adherence to the substrate and uniform thickness.

The underlying zone beneath the coating possessed hardness higher than that of the matrix.

The major possible cause of the coatings' increased strength is the presence nanoparticles which obstruct the motion of dislocations. The grains refinement could also contribute to the improved properties of the coatings.



(a)

Figure 3. EDX analysis results in the marked point (a) and elements spectra (b).

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References

- [1] Murzakov M, Chirikov S and Markushov Y 2016 *J. Phys.: Conf. Series* **747** 012062
- [2] Xiaopeng L, Mohedano M, Blawert C, Matykina E, Arrabal R, Kainer K and Zheludkevich M 2016 *Surf. Coat. Technol.* **307** 1165–82
- [3] Petrov P 1997 *Vacuum* **48**/1 49-50
- [4] Valkov S, Petrov P, Lazarova R, Bezdushnyi R and Dechev D 2016 *Appl. Surf. Sci.* **389** 768–74

- [5] Valkov S, Petrov P and Lazarova R 2017 *Proc. SPIE* **10226** 102260I-1
- [6] Wei D, Xin W and Wang R 2010 *Proc. Int. Conf. Adv. Technol. Des. Manuf.* 357-60
- [7] Cherepanov A and Ovcharenko V 2015 *Phys. Metals and Metallography* **116**/12 1279-84
- [8] Kowalczyk B, Bishop K, Lagzi I, Wang D, Wei Y, Han S and Grzybowski B 2012 *Nat. Mater.* **11** 227
- [9] Chen L, Xu J, Choi H, Konishi H, Jin S and Li X 2014 *Nat. Commun.* **5** 3879
- [10] Wang K, Jiang H, Jia Y, Zhou H, Wang Q, Ye B and Ding W 2016 *Acta Mater.* **103** 252
- [11] Kuzmanov P, Dimitrova R, Lazarova R, Cherepanov A and Manolov V 2014 *J. Nanoeng. Nanosystems* **228**/1 11-8
- [12] Dimitrova R, Kuzmanov P, Lazarova R and Manolov V 2013 *Adv. Mater. Res.* **629** 284-91
- [13] Lazarova R, Bojanova N, Dimitrova R, Panov I and Manolov V 2016 *Int. J. Metalcasting* **10**/4 466-76
- [14] Petrov P, Parshorov S, Lazarova R, Dechev D, Ivanov N and Chobanov P 2015 *J. Mater. Sci. Technol.* **23**/3 251-6
- [15] Petrov P, Valkov S, Lazarova R, Parshorov S, Bezdushnyi R, Detchev D and Ivanov N 2016 *J. Mater. Sci. Technol.* **24**/2 92-98
- [16] Petrov P, Parshorov S, Lazarova R, Dechev D, Ivanov N and Chobanov P 2015 *J. Mater. Sci. Technol.* **23**/3 251-63
- [17] Petrov P, Ormanova M, Dechev D, Ivanov N and Chobanov P 2015 *J. Mater. Sci. Technol.* **23**/2 153-9
- [18] Caicedo J C, Amaya C, Yate L, Gómez M E, Zambrano G, Alvarado-Rivera J, Muñoz-Saldaña J and Prieto P 2010 *Appl. Surf. Sci.* **256** 5898-904