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MICROSTRUCTURE OF NIAI + 15 WT.% CrB₂ NANO-CRYSTALLINE COMPOSITE COATINGS OBTAINED THROUGH CO-MILLING OF NIAI AND CrB₂ POWDERS

The development of a new deposition method allowing to obtain thick composite coatings is of both scientifically and practical importance. The one presented in this paper is based on a negative side effect taking place during the mechanical synthesis of alloys, i.e. sticking of milled material to the surfaces of both the vial and balls. The experiment covered the co-milling of NiAl (~45 μ m) with 15 wt.% CrB₂ (~40 μ m) powders together with nickel platelets used as the substrates and steel balls. The above processing performed at 200 rpm resulted in a steady increase in the thickness of the rubbed-in buildup on the platelet surfaces allowing coatings of 4, 11, 22 and 33 μ m to be produced after 4, 8, 16 and 32 hours. The OM, XRD and TEM investigations showed that such coatings are characterized by a gradient microstructure with heavily dislocated but coarser grains near the substrate and a more porous inner part formed with rounded well fused agglomerates of greatly refined crystallites. The CrB₂ were only slightly larger than the NiAl ones and were distributed quite uniformly. Most of the coating was found well fused with the substrate, but occasional voids and porosity at the substrate/coating interface were also noted. It is worth noting that applying the proposed method allowed the authors to produce a thick, gradient and mostly nano-crystalline NiAl and CrB₂ composite coating.

Keywords: NiAl, NiAl CrB₂ composite coatings, mechanical alloying, TEM

MIKROSTRUKTURA NANOKOMPOZYTOWYCH POWŁOK NIAI + 15% WAG. CrB₂ OTRZYMANYCH PRZEZ WSPÓŁMIELENIE PROSZKÓW NIAI ORAZ CrB₂

Rozwój nowych metod osadzania powłok kompozytowych jest istotny z naukowego i praktycznego punktu widzenia. Metoda proponowana obecnie bazuje na negatywnym zjawisku zachodzącym w czasie mechanicznej syntezy stopów, tj. oklejaniem mielonym materiałem kul i naczynia w którym prowadzony jest proces. Obecny eksperyment obejmował współmielenie stalowymi kulami proszków NiAl (~45 µm) z 15 wt.% CrB₂ (~40 µm) z płytkami Ni zastosowanymi jako podłoża. Proces ten, prowadzony przy 200 obr./min, skutkował ciągłym powiększaniem grubości powłok do 4, 11, 22 i 33 µm odpowiednio po 4, 8, 16 i 32 godz. Badania z wykorzystaniem mikroskopii optycznej, transmisyjnej oraz dyfraktometrii rentgenowskiej wykazały, że powłoki te charakteryzuje budowa gradientowa z warstwą silnie zdefektowanych, ale stosunkowo dużych krystalitów przy podłożu stopniowo zastępowanych nanokrystalicznym porowatym materiałem w formie silnie spojonych aglomeratów. Krystality CrB₂ wykazywały niewiele mniejsze rozdrobnienie od NiAl oraz w przybliżeniu równomierny rozkład w intermetalicznej osnowie. Powłoki w większej części wykazywały dobre spojenie z podłożem, ale obecność pustek oraz porowatości penetrującej od granic z podłożem była dokumentowana. Należy podkreślić, że zastosowanie proponowanej metody umożliwia wytworzenie grubych, gradientowych i w przeważającej części nano-krystalicznych kompozytowych powłok.

Słowa kluczowe: NiAl, kompozytowe powłoki NiAl CrB2, mechaniczna synteza, TEM

INTRODUCTION

NiAl coatings draw a strong interest as they are characterized by high both hardness and oxidation resistance [1, 2]. Practically, their only drawback is a relatively low wear resistance at high temperature. A way to circumvent this disadvantage in the case of bulk materials is usually sought through the addition of ceramic particles. They help to distribute external loads throughout the matrix as long as they are well fused with it. Experiments with plasma spraying showed that coatings with an admixture of titanium, zirconium or chromium diboride particles in an NiAl intermetallic matrix significantly lower its wear [3-10]. An addition of ~15 wt.% of CrB_2 turned out to be especially effective in that case by lowering the wear by four times at 500°C as compared with unmodified NiAl coatings [10-14]. These investigations also indicated that the simultaneous transfer of both light borides and significantly heavier intermetallics result in significant loss of the former fraction. Therefore, either new powder agglomeration procedures will have to be elaborated or another coating deposition method will have to be sought.

The mechanical synthesis of alloys through milling elemental powders routinely forms a thick coating both on the balls and sides of containers used in this process even with an addition of anti-sticking agents. It has already been shown that this undesired phenomenon might be turned into an advantage, i.e. used as a new NiAl intermetallic coating deposition method [4, 5, 10, 15]. An obvious limitation of such rubbing of materials is a problem of the geometry of the process, as the best form of substrates are the inner sides of cylinders of diameters in a low decimeter range. Simultaneously, neither the substrates nor the deposited materials are excessively heated and all the starting fractions are transformed into a coating in the original ratio. However, the applicability of this new deposition method to produce much harder and brittle composite coatings has to be evaluated.

The aim of the presently described experiments was to assess the possibility of depositing a composite coating through milling NiAl and CrB_2 powders. The milling was performed together with Ni platelets used as the substrates and at settings used as standard for mechanical synthesis of alloys starting from elemental powders. The obtained coatings were characterized by X-ray diffraction (XRD) as well as light and transmission electron microscopy (LM, TEM) methods.

EXPERIMENTAL PROCEDURE

NiAl (99.97% purity/45 μ m av. size) and CrB₂ (99.99 purity/40 μ m av. size) powders supplied by Polema JSC were used in the present experiment. Up to 40 g of NiAl-15 wt.% CrB₂ mixed powders were loaded under argon atmosphere into 0.5 l stainless steel containers together with Ni platelets (10 mm x 10 mm x 2 mm) serving as the substrates and 10 mm steel balls (the ratio of ball weight to powder was 10:1). Next the containers were rotated at 200 rpm in a high energy Fritsch mill in 15 min cycles separated by 45 min breaks necessary to cool them down. The NiAl and CrB₂ used as the starting materials were of 40÷70 micrometers and 20÷40 micrometers, respectively.

The milled Ni platelets were first examined via visual observations. Next they were cut in half and cross-sections of the obtained coatings were observed using light microscopy. Finally, the coatings were characterized by X-ray diffraction using an APD (Philips)

system and transmission electron microscope Tecnai G2 F20 (200 kV). Thin foils for TEM observations were prepared from the substrate/coating interface area by cutting them out with the Ga^+ ions with the help of the FEI Quanta Dual Beam Focused Ion Beam (FIB) system. In the first step, a selected site was protected by depositing a 20 μ m x 2 μ m platinum strip, which determined the initial length and thickness of the thin foil, respectively. The in-depth dimension of the thin foil was set at $\sim 8 \ \mu m$ and controlled by the milling time and current of the Ga⁺ ion beam. Then, the produced platelet was lifted from the sample with the Omniprobe system, mounted to a Cu grid. Next, it was subjected to final thinning with Ga⁺ beams of low current till the thickness of the thin foil was reduced to ~100 nm.

RESULTS

The milling of NiAl and CrB₂ powders caused a quick formation of deposit on the nickel platelets added together with steel balls, i.e. the development of roughness was evident even after 4 hours of such processing (see inserts in Fig. 1). Additionally, at the beginning of this process parts of the substrates were still deposit-free. The result of balls hitting the platelets is especially well visible at their rounded edges. The observations of the cross-section of the coatings indicated that the surface roughness is to a large extent reproduced at the coating/substrate interface (Fig. 1). It was found that the coating thickness increased at a roughly similar rate for both the NiAl and NiAl with the 15 wt.% addition of CrB₂ (Fig. 2). Simultaneously, the deposition rate was evidently higher at the beginning of the process rising up to 1.5 µm/h after 8 hours only to fall to $\sim 1 \ \mu m/h$ after 32 hours. The thickest coatings obtained after longest processing lasting 32 hours were for both type of powders close to 30 µm.

The TEM observations of sections of the coatings proved that in all cases they are well fused with the substrate even though occasional defects in the form of voids or cracks are also present after the long set milling time, i.e. 32 hours (Figs. 3 and 4). Close to the nickel substrate a 1 to 2 µm band of fine, frequently elongated grains develops. The NiAl coatings show an evident gradient type microstructure with highly dislocated but evidently coarser grains closer to the interface (Fig. 3a), followed by bends of roughly fused rounded agglomerates of nanocrystallites (Fig. 3b). The size of these crystallites changes from ~50 to ~10 nm present closer and farther from the interface, respectively (Fig. 3c). The diffraction pattern, acquired from that area, contains uniform rings of intensity which also proves its nano-crystaline character. Indexing the SAED pattern confirmed that it corresponds to the β -NiAl intermetallic phase (Fig. 3d).



Fig. 1. Light microscopy (LM) images of coatings formed on sections of Ni platelets milled for 4, 8, 16 and 32 hours in NiAl (a-d) and NiAl+CrB₂ (e-h) powders (photographs of platelets in inserts)

Rys. 1. Obrazy uzyskane z wykorzystaniem mikroskopu optycznego przekrojów powłok wytworzonych na płytkach NiAl po 4, 8, 16 i 32 godz. mielenia w proszkach: Ni (a-d) i NiAl+CrB₂ (e-h) (fotografie płytek umieszczone na wklejkach)



Fig. 2. Deposition rate for NiAl and NiAl+CrB₂ coatings Rys. 2. Szybkość osadzania dla NiAl oraz NiAl+CrB₂



Fig. 3. TEM images of microstructure of NiAl coating: a) near substrate, b) far from substrate and c) inside of rounded agglomerates, d) SAED pattern acquired using 40 µm aperture, e) radial plot of circumferential integration of SAED pattern intensity

0 5488

0.8632

k (1/Å)

0.00

Rys. 3. Obrazy TEM mikrostruktury powłok NiAI: a) przy podłożu, b) daleko od podłoża oraz c) wewnątrz zaokrąglonych aglomeratów, d) dyfrakcja SAED uzyskana za pomocą apertury o średnicy 40 μm, e) widmo uzyskane poprzez scałkowanie intensywności pierścieni dyfrakcyjnych SAED

The NiAl coatings with the addition of chromium diboride bear strong resemblance to the NiAl ones, with the exception that closer to the interface large chromium diboride crystallites are surrounded by refined NiAl grains (Fig. 4a), hence the gradient microstructure is less developed. However, away from the coating/substrate interface, again the presence of rounded nano-crystalline agglomerates (this time imbedded with slightly larger and of whitish contrast chromium diboride particles) was documented (Fig. 4b). Simultaneously, the nano-crystallite size of NiAl in the composite coating is significantly smaller than that in the NiAl coating, as could be compared by looking at Figures 3c and 4c. Namely, the size of the NiAl nanocrystallites and chromium diboride particles stayed below 15 and 200 nm, respectively (again, measured away from the substrate/coating interface). The selected area of electron diffraction allowed the authors to prove that the whitish particles visible in Figure 4c correspond to the CrB₂ phase and they are surrounded by nanocrystallites of the β -NiAl intermetallic phase (Fig. 4d and 4e).



Fig. 4. TEM images of microstructure of NiAl+15 wt.% CrB₂ coating: a) near substrate, b) far from substrate and c) inside of rounded agglomerate, d) SAED pattern acquired using 40 μm aperture, e) radial plot of circumferential integration of SAED pattern intensity

Rys. 4. Obrazy TEM mikrostruktury powłok NiAl+CrB₂: a) przy podłożu, b) daleko od podłoża oraz c) wewnątrz zaokrąglonych aglomeratów, d) dyfrakcja SAED uzyskana za pomocą apertury o średnicy 40 μm, e) widmo uzyskane poprzez scałkowanie intensywności pierścieni dyfrakcyjnych SAED

The XRD spectra acquired from the nickel platelets milled in NiAl powder were dominated by Ni peaks from the substrate accompanied by a series of much weaker ones characteristic of the NiAl phase, which persists even for the longest processing times (Fig. 5).

Comparing the spectra acquired from the coatings obtained after 8 and 32 h of milling, diminished by 30% resulting from smaller penetration of the X-ray beam and increased absorption of characteristic X-ray radiation by the thicker coating. The peaks representing the NiAl intermetallic are both lower and wider, which could be explained by progressive refinement of the coating grain size.

The spectra obtained from the platelets milled in NiAl + 15 wt.% CrB_2 showed a similar decrease (~25%) in the intensity of the lines originating from the substrate (Fig. 6). Nonetheless, the peaks from NiAl not only diminish in intensity in-between both processing runs but were also much smaller compared with that obtained from the NiAl coating at respective times. Such an effect agrees with the microstructure observation pointing toward a significantly finer crystallite size of the NiAl matrix in the NiAl+CrB₂ coating.



Fig. 5. XRD spectra from NiAl coatings obtained after 8 hrs and 32 hrs of milling





Fig. 6. XRD spectra from NiAl+CrB₂ coatings obtained after 8 hrs and 32 hrs of milling

Fig. 6. Widma XRD mierzone dla powłok NiAl+CrB₂ po 8 i 32 godz. mielenia

DISCUSSION

The experiments aimed at taking advantage of the negative effect taking place during the mechanical synthesis of alloys, i.e. sticking of the milled materials on the container sides and balls, and using it as a new method for depositing composite coatings, turned out to be successful, as documented in the result section. Even milling of the square nickel platelets serving as the substrates together with either NiAl or the NiAl intermetallic and CrB₂, powders helped to deposit on the surface of the former, well adhering intermetallic NiAl or composite NiAl+CrB₂ coatings. Developing this method aimed at substituting the present platelet substrates with the inner walls of metallic cylinders fitting milling vials should be an easy way to increase the rate of kinetic energy transfer of the balls, rising both the coating deposition rate as well as its adhesion. A comparable deposition rate for intermetallic and composite coatings may at first seem strange. However, NiAl is quite hard by itself and a 15 wt.% addition of CrB₂ is in the case of composite materials a relatively small addition. Therefore, at first the deposition process is dominated by sticking to the nickel substrate of intermetallic particles with occasional crushing of the CrB₂ particles in the case of milled mixtures of ceramic and metallic powders. Next, the mechanisms operating during the mechanical synthesis of alloys [12, 16] causes gradual refining of both the intermetallic and ceramic particles, with the latter predominantly located inside rounded agglomerates. Again, at that stage, deposition of both the intermetallic and composite milled powders will depend on the brittleness of these agglomerates of the metallic matrix, which in both cases showed a similar nanocrystalline character.

The higher deposition rates measured in the first few hours of milling can be explained by the fact that at this stage of the process the metallic matrix is relatively coarse crystalline and has the ability to disperse most of the impact energy from the balls impact both by generating dislocations and plastic deformation. Therefore, whole new particles are steadily added to those already attached to the substrate resulting in fast growth of the coating. Nevertheless, continued milling causes the accumulation of defects in the milled particles, causing fast grain refinement accompanied by hardening. At that stage, sticking of the powder policrystalline particles to the substrate will compete with crushing of the already attached material and its partial removal, effectively lowering the deposition rate.

Evidently, the steel balls heating the metallic and ceramic powder particles during the milling process could serve as a new composite coating deposition method. From the start, it is limited to small substrates like the presently applied nickel platelets or the inner walls of small cylinders resembling milling containers. Simultaneously, it is a process run at relatively low temperatures. It allows gradient nano-crystalline type coatings to be obtained, which is not so easy to obtain by means of other techniques like plasma coating. The additional knowledge including ball optimum energy (applied rev./min), milling time, metallic to ceramic fraction ratio and its effect on the coating deposition rate are definitely necessary before an assessment of this method could be made.

CONCLUSIONS

The performed OM, XRD and TEM examinations helped to establish, that:

- both coatings presented a gradient microstructure with the presence of highly defected but relatively coarse crystallites near the substrate/coating interface, followed by porous but rounded wellbonded/fused nano-crystalline agglomerates in the coating,
- 2. all the features characterizing the intermetallic coating were slightly coarser than those of the composite one obtain after the same milling time, i.e. dislocation walls were observed in the NiAl grains near the substrate, while the nano-crystalline material was surrounded by crushed CrB_2 crystallites in the composite,

 the substrate/coating interfaces showed mostly good cohesion degraded only locally by voids or porosity extending into the coatings, while their significant roughness was similar to that of the surface.

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REFERENCES

- Sierra C., Vazquez A.J., NiAl coating on carbon steel with an intermediate Ni gradient layer, Surface Coatings Technology 2006, 200, 4383-4388.
- [2] Prevot G., Schmausa D., Le Moal S., Epitaxial alloyed films out of the bulk stability domain: surface structure and composition of Ni3Al and NiAl films, Surface Science 2010, 604, 770-777.
- [3] Poliarus O., Morgiel J., Umanskyi O., Szlezynger M., Pomorska M., Bobrowski P., Szczerba M., Microstructure and phase composition of NiAl-CrB₂ composite powders used for plasma spraying, Composite Theory and Practice 2018, 18, 121-124.
- [4] Umanskyi O., Poliarus O., Ukrainets M., Kostenko O., Terentyev O., Influence of CrB₂ additives into NiAl intermetallics on tribological properties of thermal spray coatings at high temperature friction, Conference MET-2013: Materials, Environment, Technology, Latvia, Riga 2013, 37-43.
- [5] Umanskyi O., Poliarus O., Ukrainets M., Martsenyuk I., Effect of ZrB₂, CrB₂ and TiB₂ additives on the tribological characteristics of NiAl-based plasma coatings, Key Eng. Mat. 2014, 604, pp. 20-23.
- [6] Bhatt B., Murethy T.S.R.C., Limaye P.K., Nagaraj A., Singh K., Sonber J.K., Sairam K., Sashanka A., Nageswara Rao G.V.S., Srinivasa Rao T.S., Tribological studies of monolithic chromium diboride against tungsten carbide (WC-Co) under dry condition, Ceramic Int. 2016, 42, 15536-15546.

- [7] Xiaoli C., Yuying W., Tong G., Chong L., Jinfeng N., Xiangfa L., In situ CrB₂ and its effect on the mechanical properties of A390 alloy, Materials Characterization 2013, 86, 296-302.
- [8] Audronis M., Rosli Z.M., Leyland A., Kelly P.J., Matthews A., Tribological behaviour of pulsed magnetron sputtered CrB₂ coatings examined by reciprocating sliding wear testing against aluminium alloy and steel, Surf. Coat. Technol. 2008, 202, 1470-1478.
- [9] Bedse R.D., Sonber J.K., Sairam K., Murthy T.S.R.C., Hubli R.C., Processing and characterization of CrB₂-based novel composites, High Temp. Mater. Process. 2015, 34(7), 683-687.
- [10] Umanskyi O., Poliarus O., Ukrainets M., Antonov M., Hussainova I., High temperature sliding wear of NiAl-based coating reinforced by borides, Materials Science 2016, 22, 1.
- [11] Zadorozhnyy V., Kaloshkin S., Kaevitser E., Romankov S., Coating of metals with intermetallics by mechanical alloying, Journal of Alloys and Compounds 2011, 509S, 8507--8509.
- [12] Zadorozhnyy V., Kaloshkin S., Tcherdyntsev V., Gorshenkov M., Komissarov A., Zadorozhnyy M., Formation of intermetallic Ni-Al coatings by mechanical alloying on the different hardness substrates, Journal of Alloys and Compounds 2014, 586, S373-S376.
- [13] Kubaski E.T., Cintho O.M., Antoniassi J.L., Kahn H., Obtaining NiAl intermetallic compound using different milling devices, Adv. Powder Tech. 2012, 23, 5, 667-672.
- [14] Mohammadnezhad M., Shamanian M., Enayati M.H., Formation of nano structured NiAl coating on carbon steel by using mechanical alloying, Applied Surface Science 2012, 263, 730-736.
- [15] Mohammadnezhad M., Shamanian M., Enayati M.H., Salehi M., Influence of annealing temperature on the structure and properties of the nanograined NiAl intermetallic coatings produced by using mechanical alloying, Surface & Coatings Technology 2013, 217, 64-69.
- [16] Suryanarayana C., Mechanical alloying and milling, Prog. in Mat. Science 2001, 46, 1-184.