Polish Society of Composite Materials
Polskie Towarzystwo Materiałów Kompozytowych

18: 2 (2018) 121-124

COMPOSITES THEORY AND PRACTICE

**Olena Poliarus[1]*, Jerzy Morgiel[2]*, Oleksandr Umanskyi[1], Maciej Szlezynger[2], Małgorzata Pomorska[2]
Piotr Bobrowski[2], Maciej Szczerba[2]**

[1] Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine (IPMS NASU), Krzhyzhanovsky St. 3, 03680 Kyiv, Ukraine
[2] Institute of Metallurgy and Materials Science, Polish Academy of Sciences (IMIM PAN), ul. S. Reymonta 25, 30-059 Krakow, Poland
**Corresponding authors. E-mail: j.morgiel@imim.pl*

Received (Otrzymano) 5.06.2018

MICROSTRUCTURE AND PHASE COMPOSITION OF NiAl-CrB_2 COMPOSITE POWDERS USED FOR PLASMA SPRAYING

The preparation of powder agglomerates used in the plasma spray deposition processes, and especially their homogeneity, turned out to be highly important at the moment when the phase ratio in the composite coatings began to differ from that in the starting materials. The present experiment was aimed at comparing the microstructure and phase composition of hot pressed or sintered NiAl and CrB_2 powders. The use of SEM and XRD methods showed that only sintering leads to a reaction of the chromium diboride with the intermetallic matrix. As a result of this process, $Ni_{0.5}Cr_{1.5}B_3$ phase precipitates on the CrB_2 particles. Consequently, the agglomerates formed after crushing the compacts obtained by sintering are much more homogeneous than those formed by hot pressing.

Keywords: NiAl, CrB_2, $Ni_{0.5}Cr_{1.5}B_3$, hot pressing, sintering, microstructure, SEM, XRD

MIKROSTRUKTURA I SKŁAD FAZOWY PROSZKÓW KOMPOZYTOWYCH NiAl-CrB_2 WYKORZYSTYWANYCH W NATRYSKIWANIU PLAZMOWYM

Przygotowanie aglomeratów proszków wykorzystywanych w procesach natryskiwania plazmowego, a w szczególności ich ujednorodnienie, okazało się wysoce istotne w momencie, gdy skład powłok kompozytowych zaczął się znacząco różnić od stosunku udziałów proszków wyjściowych. Obecny eksperyment był nakierowany na porównanie mikrostruktury i składu fazowego proszków NiAl oraz CrB_2 spiekanych w stanie stałym pod ciśnieniem (hot pressed) oraz z przetopieniem osnowy metalicznej (sintered). Zastosowanie mikroskopii skaningowej i dyfraktometrii rentgenowskiej wykazało, że tylko przetopienie osnowy prowadzi do reakcji pomiędzy nią a dwuborkiem chromu. W rezultacie tego procesu dochodzi do wydzielania na CrB_2 fazy typu $Ni_{0.5}Cr_{1.5}B_3$. Aglomeraty powstałe po rozdrobnieniu spieków uzyskanych na drodze z przetopieniem osnowy są znacznie bardziej jednorodne niż te otrzymane z wykorzystaniem prasowania na gorąco.

Słowa kluczowe: NiAl, CrB_2, $Ni_{0.5}Cr_{1.5}B_3$, spiekanie w stanie stałym pod ciśnieniem, spiekanie, mikrostruktura, SEM, XRD

INTRODUCTION - AIM OF RESEARCH

New materials intended for use in tough operating conditions, i.e. both at high loads and temperatures are still as vigorously pursued as at their development in the second half of XX century. High performance machine parts made from them are usually intended to work under slip-friction conditions and highly corrosive environments. The above requirements could be met by the NiAl intermetallic, if not for its poor performance in friction pairs working at high temperatures caused by intense plastic deformation starting above 500°C. One of the ways to increase the high-temperature wear resistance of nickel aluminide is to reinforce it with refractory ceramic additions from the oxide, carbide, nitride or boride groups [1-5]. Previous research in this area by Umanskyi et al. [6] indicated that an optimum refractory additive for NiAl-based composites is chromium diboride.

Plasma sprayed ceramic coatings have already proved very effective as thermal barriers on the turbine blades of jet engines, which helped to further improve their efficiency. The powders used in plasma deposition processes can be heated up to several thousand degrees centigrade and therefore powder homogeneity at first seemed of secondary importance. However, experiments with a range of nanopowders proved that the finer the deposition material, the better overall properties of the coatings [7]. The explanation of this effect should be probably sought in the very short time of the powder particles in flight as well as the presence of a temperature gradient across the stream of deposited material, both acting against its proper homogenization. Therefore, the elaboration of methods enabling the production of composite powders of the most refined microstructure have gained renewed interest. The powders used in plasma spraying are injected into the plasma jet through relatively small openings, which are easily clogged, especially in case of mixtures containing elongated particles. Therefore, any powders used in this deposition method - independent of their original shape and size - have to be agglomerated up to rounded particles of a sub-millimeter range, enabling easy transfer through the plasma gun tubing. An organic binder is very effective in producing agglomerates with the proper geometric characteristics, but it is also the first constituent burned out in the plasma stream [8]. The above affects the transfer of the composite material in the plasma stream, as lighter particles are prone to drift to the stream edges and fall out before reaching the substrate. An alternative to an organic binder is hot pressing or sintering of the starting powder followed by its crushing till the required dimensions are obtained.

Therefore, the aim of this work was to compare the microstructure, phase composition and mechanical properties of NiAl-CrB_2 powders produced by hot pressing with those obtained through sintering, which should help to indicate the best method to prepare powders intended for plasma spraying.

EXPERIMENTAL TECHNIQUES

The NiAl and CrB_2 commercial powders (supplied by Polema JSC) used as the starting materials had particle sizes of of 40÷70 and 20÷40 micrometers, respectively. The initial powders were crushed for 8 hours in alcohol using WC balls (1:2 ratio) in a Sand-1 planetary mill. The obtained powders were then dried and sieved. The resulting crystallite size measured with an SK Laser Micron Sizer PRO 7000 was 16-20 micrometers for the intermetallic compound and 2-7 micrometers for the chromium diboride. After grinding, both the NiAl and CrB_2 powders were mixed in appropriate proportions for 1 hour.

The composite materials with 15 wt.% CrB_2 were obtained by one of two methods, i.e. hot pressing or sintering. In the first of the two methods the obtained mixture was placed in a graphite mold inserted into an SPD-120 induction heating unit. The fusing process started by applying a 10 MPa load and heating of the sample up to ~1310°C (monitored with a pyrometer) for 13 minutes. Next it was kept in those conditions for 5 minutes and cooled down with the system. The second method relied on sintering in a high temperature vacuum furnace system. In this case the sample was kept at ~1650°C for 30 minutes and cooled down with the furnace.

The X-ray phase analysis was performed using APD (Philips) or DIFFRACplus (Bruker AXS) programs and the ICDD crystallographic database. The microstructure and chemical composition of the composite materials was investigated using the scanning electron microscope (SEM) FEI Quanta 3D FEGSEM and the transmission electron microscope (TEM) Tecnai G2 F20 (200 kV, FEG). Thin foils for TEM observations were cut out from the central part of the composite powder particle using an FEI Dual Beam FIB.

RESULTS AND DISCUSSION

Compacted milled NiAl-15wt.%CrB_2 powders observed in the SEM/BSE mode showed that the applied refining/mixing procedure resulted in a nearly homogeneous distribution of the chromium diboride particles (only occasional small colonies of CrB_2 - differentiated by their dark gray contrast - were noticed) in the intermetallic NiAl matrix (light grey) (Fig. 1). A number of NiAl grains showed boride free-boundaries forming the denser parts of the material. Most of the void (black areas) sizes were from 1 to 3 μm. The larger of them were usually located at the crystallite triple junction points, while the smaller ones accompanied clusters of smaller particles. Between the larger diboride particles and the intermetallic matrix the presence of still one more phase characterized by an intermediate contrast (and hence chemical composition) could be discerned, but its amount is generally rather low.

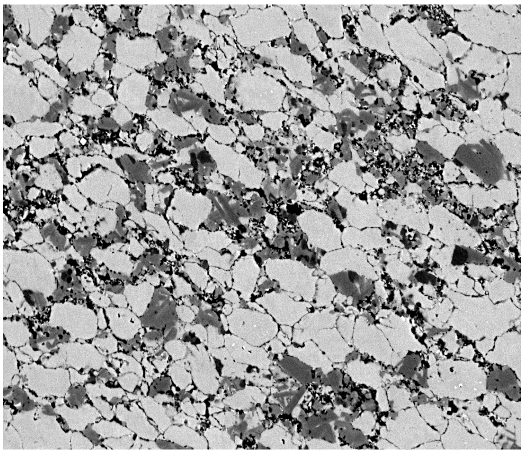

Fig. 1. SEM/BSE images of compacted NiAl-15 wt.%CrB_2 powder

Rys. 1. Obrazy SEM/BSE wyprasek z proszku NiAl-15 wt.%CrB_2

The agglomerates obtained by hot pressing (i.e. processing within the solid state range of all the involved phases) and crushing were of irregular rounded forms ranging mostly from 100 to 50 μm. They were characterized by an enlarged intermetallic crystallite size as compared to the compacted material (Fig. 2a). The borides tended to form small colonies located at the NiAl grain boundaries or within pockets at their sides, as the boride colonies offered the easiest crack propagation paths during the crushing of the material. The agglomerates obtained from the sintered (i.e. processed above the liquidus line of NiAl) powders were of a comparable size (largest of them even exceeding 100 μm), but a finer fraction was evidently better represented (Fig. 2b). However, the agglomerated particles showed a high level of homogeneity with uniformly distributed ceramic particles within the intermetallic matrix.

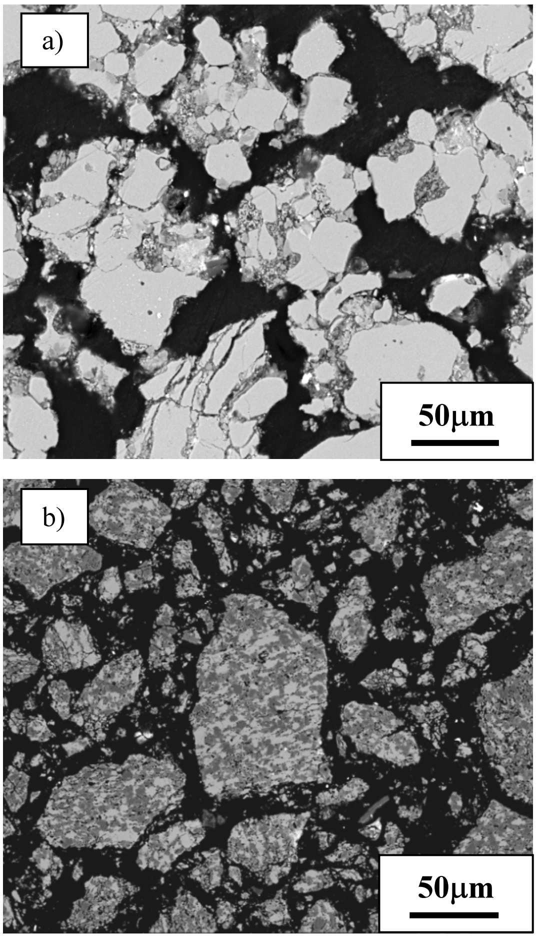

Fig. 2. SEM/BSE images of crushed: a) hot pressed and b) sintered NiAl-CrB$_2$ compacts

Rys. 2. Obrazy SEM/BSE rozdrobnionych spieków: a) prasowanych na gorąco oraz b) z udziałem przetopienia metalicznej osnowy spieków

The XRD measurements of the mixed initial powders showed peaks corresponding either to CrB$_2$ or NiAl phases, only (Fig. 3).

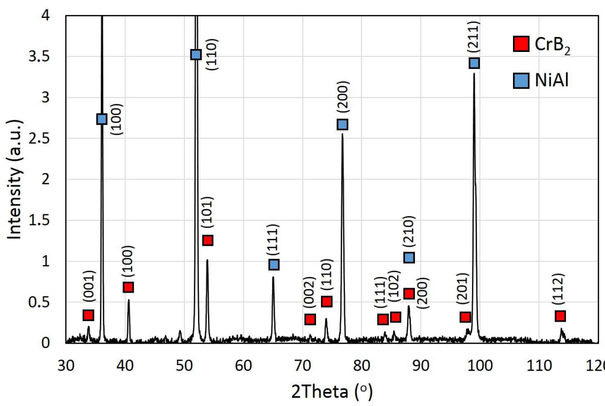

Fig. 3. XRD spectra from NiAl-15 wt %CrB$_2$ compact

Rys. 3. Obraz dyfraktogramu uzyskanego z wypraski z proszku NiAl-15 wt %CrB$_2$

The X-ray spectra obtained from the hot pressed material confirmed the presence of both the above phases through the same peaks, but with an evidently noisy background (Fig. 4a). The latter might stem from the redistribution and growth of native oxide always present on the surface of metallic powders. The spectra acquired from the sintered material showed strong peaks not only from the starting NiAl and CrB2, but also from the $Ni_{0.5}Cr_{1.5}B_3$ phase (Fig. 4b). Aside from them a series of weaker peaks could be assigned either to Cr_2B_3 or Cr_3B_4 phases.

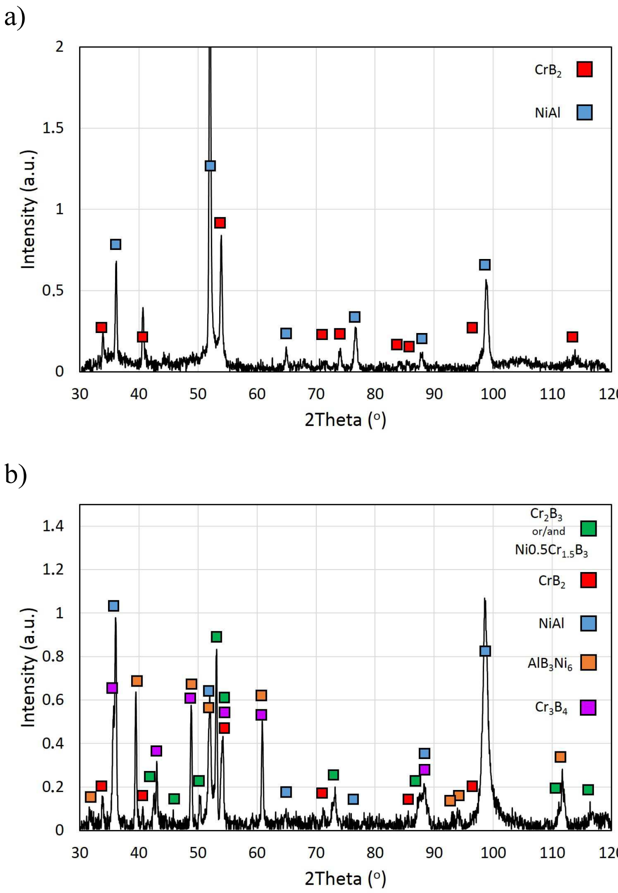

Fig. 4. XRD spectra from NiAl-15 wt %CrB$_2$ compacts after: a) hot pressing and b) sintering.

Rys. 4. Obrazy dyfraktogramów uzyskanych ze spieków: a) prasowanych na gorąco oraz b) z udziałem przetopienia metalicznej osnowy spieków

The SEM/BSE higher magnification observation of both powders indeed confirmed that both during hot pressing and sintering of the composite powders the diborides tend to react with the intermetallic matrix. In the first case, the products of this reaction are barely visibly, but in the second the CrB$_2$ particles are usually separated from the matrix by broad bands of a newly formed phase (as presented in Fig. 5). The small black areas indicate porosity and possibly some alumina formed from the native oxide usually present on the surface of intermetallic particles, while the whitish veins represent surplus nickel from the NiAl.

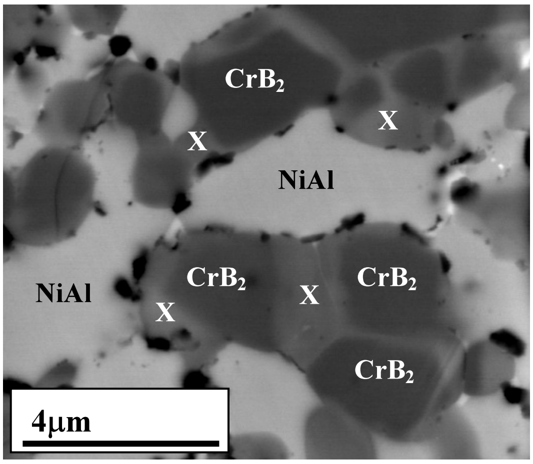

Fig. 5. SEM/BSE images presenting all three main phases (NiAl, CrB_2 and $Ni_{0.5}Cr_{1.5}B_3$ denoted as X) formed in sintered powders

Rys. 5. Obraz SEM/BSE przedstawiający trzy główne fazy (NiAl, CrB_2 oraz fazę typu $Ni_{0.5}Cr_{1.5}B_3$ oznaczona jako X) występujące w spieku uzyskanym z przetopieniem metalicznej osnowy

CONCLUSIONS

Crushing hot pressed NiAl-CrB_2 material, being a step necessary to form agglomerates for plasma spraying, practically resulted in dividing it into metal-matrix particles with adjoining pockets of boride phases. In this process, the borides are separated into numerous still smaller particles, which might be partly eliminated during plasma spraying as hard to control volatile dust. The same treatment applied to sintered compacts also leads to their breaking to particles of various sizes, but both the large and small debris are of roughly the same phase and chemical composition. Therefore, eventual loss of finer fractions is of no consequence as it concerns the final chemical composition of the plasma spray deposited coatings.

The XRD measurements of the starting powders confirmed that only pure NiAl and CrB_2 diboride were used in this experiment. The X-ray spectra obtained from the hot pressed materials showed the presence of practically both the same phases, but in the sintered one a new set of relatively strong lines was also distinguished. The analysis performed of the Ni-Al-Cr-B system indicated that the latter could be assigned to the $Ni_{0.5}Cr_{1.5}B_3$ phase. The high magnification SEM images of the sintered materials showed the presence of only one new phase of an intermediate contrast with respect to Ni and CrB_2. The above indicates that the result of the reaction of NiAl with CrB_2 is probably a quaternary $Ni_xAl_yCr_zB_v$ phase (possibly $Ni_{0.5}(Cr,Al)_{1.5}B_3$) of an $Ni_{0.5}Cr_{1.5}B_3$ elementary unit cell.

The performed investigations indicated that a deficiency of CrB_2 in an NiAl-CrB_2 plasma sprayed coating deposited using agglomerates produced with the help of hot pressing are probably caused by partial removal of the borides from the process as uncontrolled dust sediment. The agglomerates formed by the sintering process should prevent such a loss of CrB_2. Therefore, even as in the case of hot pressing the energy consumption is lower, though only the sintering enables the production of agglomerates guaranteeing the proper phase composition of NiAl-CrB_2 plasma deposition coatings.

Acknowledgments

The work was supported according to the Agreement on Scientific Cooperation between the National Academy of Sciences of the Ukraine and the Polish Academy of Sciences.

REFERENCES

[1] Whittenberger J.D., Viswanadham R.K., Mannan S.K., Sprissler B., Elevated temperature slow plastic deformation of NiAl-TiB_2 particulate composites at 1200 and 1300 K, J. Mater. Sci. 1990, 25, 35-44.

[2] Whittenberger J.D. Kumar S., Mannan S.K., Viswanadham R.K., Slow plastic deformation of extruded NiAl-10TiB_2 particulate composites at 1200 and 1300 K, J. Mater. Sci. Lett., 1990, 9, 326-328.

[3] Sheng L.Y., Yang F., Xi T.F., Guo J.T., Investigation on microstructure and wear behavior of the NiAl-TiC-Al_2O_3 composite fabricated by self-propagation high-temperature synthesis with extrusion, J. Alloys Compd. 2013, 554, 182--188.

[4] Umanskyi O., Poliarus O., Ukrainets M., Martsenyuk I., Effect of ZrB_2, CrB_2 and TiB_2 additives on the tribological characteristics of NiAl-based gas-thermal coatings, Key Eng. Mater. 2014, 604, 20-23.

[5] Miracle D.B., Darolia R., NiAl and its Alloys, Structural Applications of Intermetallic Compounds, ed. J.H. Westbrook, R.L. Fleischer, John Wiley & Sons, New York 2000. P. 20.

[6] Umanskyi O., Poliarus O.M., Ukrainets M.A., Physical-chemical interaction in NiAl-MeB_2 systems intended for tribological applications, Welding Journal 2015, 94, 225-230.

[7] Sanchez E., Bannier E., Cantavella V., Salvador M.D., Klyatskina E., Morgiel J., Grzonka J., Boccaccini A.R., Deposition of Al_2O_3-TiO_2 nanostuctured powders by atmospheric plasma spraying, Journal of Thermal Spray Technology 2008, 17, 329-337.

[8] Terentjev A., Effect of Ni-Cr-Si-B alloy based composite powder content, production technology and spraying methods on the wear resistance of gas-thermal coatings, Problems of Tribology 2014, 1, 77-83.

