

STRUCTURAL-PHASE STATE OF WEAR-RESISTANT NANOCOMPOSITE Cr₃C₂-NiCr COATINGS DEPOSITED BY A NEW MULTI-CHAMBER GAS-DYNAMIC ACCELERATOR

NOVIKOV Vseslav¹, KOVALEVA Marina¹, TYURIN Yuri², PROZOROVA Mayya¹, ARSEENKO Maria¹, SIROTA Viacheslav³, VAGINA Olga¹

¹Belgorod State National Research University, Belgorod, Russian Federation, <u>kovaleva@bsu.edu.ru</u> ²E.O. Paton Electric Welding Institute NASU, Kyiv, Ukraine ³Belgorod State Technological University named after V.G. Shoukhov, Belgorod, Russian Federation

Abstract

The hardmetal Cr_3C_2 -25NiCr (180-220 μ m thick) coatings have been produced on a steel substrate by a new multi-chamber gas-dynamic accelerator. The Cr_3C_2 -25NiCr powder (POLEMA JSC, Russia) (35-140 μ m) was used as the starting material to deposit a dense layer. A detailed analysis of the features of the coatings structure on all the levels of the structure (from grain to dislocation) (phase composition, distribution of the disperse phase, grain nature, subgrains and dislocation structures) was conducted. The structural-phase state of the coatings was characterized using SEM, TEM, and XRD techniques. It was established that phase composition of Cr_3C_2 -NiCr powder under the influence of high temperatures and the atmosphere of detonation products changes with the formation of a complex heterogeneous structural-phase state in the coatings. A layered structure of the regions of carbide particles and matrix metal was found in the immediate vicinity of the "carbide-matrix" boundary with the precipitates in the matrix of dispersed secondary carbides. It was shown that the nanocomposite Cr_3C_2 -NiCr coatings are characterized by the presence of nanodispersed ceramic compounds. Lamellae in the coatings consisted of nanocrystalline grains, separated by interlayers of the amorphous phase and oxide crystalline grains.

Keywords: Gas-dynamic accelerator, Cr₃C₂ - NiCr, nanocomposite coatings, microstructure, TEM

1. INTRODUCTION

Thermally sprayed coatings based on hard carbides embedded in a metallic matrix (Cr_3C_2 -NiCr system) have been used for corrosion and wear resistant applications [1,2]. In thermal spray technology, Cr_3C_2 -NiCr cermet coatings have been extensively used to mitigate abrasive and erosive wear at high temperatures up to 850°C [3]. Cr_3C_2 -NiCr cermet coatings are deposited by the various thermal spray coating processes such as high velocity oxy fuel (HVOF), cold-spray, detonation gun spray, atmospheric plasma spraying and other [4,5]. In this study a new multi-chamber gas-dynamic accelerator (MCDS) was proposed to spray coatings [6-8]. It is considered that the properties of cermet coatings is predominately influenced by their microstructures, e.g., carbide particle size, carbide content and carbide distribution within the splats, and etc [9,10].The main aim of this contribution was to evaluate the structure of the nanocomposite Cr_3C_2 -NiCr coatings on all the levels (from grain to dislocation).

2. EXPERIMENTAL

2.1 Materials

The Cr_3C_2 -25NiCr powder (POLEMA JSC, Russia) (d(0.1):35.57 µm, d(0.5):78.34 µm, d(0.9):141.72 µm) was used as the starting material to deposit a dense layer on a plate with dimensions of 30 x 30 x 5 (mm) of the steel substrate. Corrosion-resistant steel plates (Fe-0.12C-0.90Mn-0.025P-0.01S-16Cr-0.20Cu, all in wt %)



were employed as substrates. The composite powder was prepared by solid state mixing route (Cr_3C_2 :Ni20Cr wt ratio = 75:25) (**Figure 1**). Cr_3C_2 :Ni20Cr powder consists of irregularly shaped particles with sharp facets.



Figure 1 SEM micrograph showing the morphology of the Cr₃C₂-25NiCr powder

2.2. Apparatus and Procedures

In this study, a multi-chamber, vertically mounted, gas-dynamic accelerator (MCDS) with a barrel length of 300 mm [6-8] was employed to deposit the Cr_3C_2 -25NiCr coatings. In MCDS, the realized detonation regime of the combustion of the gas mixture in the two chambers has a special profile. The Cr_3C_2 -25NiCr coatings were deposited with a frequency of 20 Hz of the snake. Speed of moving was 2000 mm/min, distance from the sample - 55 mm. The powder feed rate was 1900 g/h. The microstructure of the specimens was studied by a scanning electron microscope (SEM) and a transmission electron microscope JEOL JEM 2100 (TEM). X-ray analysis was done using a diffractometer Rigaku Ultima IV. Crystalline phases were identified by the ICDD PDF-2 (2008) powder diffraction database.

3. RESULTS AND DISCUSSION

The thickness of deposited coatings ranged about 180-220 μ m. The Cr₃C₂-25NiCr coating is uniform and dense, and has a good adhesion to the substrate. A close examination of the microstructure reveals that carbide particles were distributed in the coating evenly.



Figure 2 SEM micrographs of cross-sections of the Cr₃C₂-25NiCr coating (back-scattered electron mode)

Figure 3 shows the results of the X-ray diffraction (XRD) of the Cr_3C_2 -25NiCr powder and coatings. The detected phases for Cr_3C_2 -25NiCr powder were Cr-Ni and Cr_3C_2 phases (**Figure 3a**). As for the Cr_7C_3 phase,



it was at the lowest limit of detection (< 5 volume %). As shown in **Figure 4b**, the powder underwent a phase transformation during spraying. Specificity of the thermal spray deposition of carbide-based cermets is that under the action of high temperature (several thousands of degrees), and the atmosphere of gaseous products of combustion (detonation) of the combustible mixture occurs depletion higher carbide on carbon to lower carbides, oxidation of the carbide particles, and migration products of dissociation of carbide particles into a metal matrix [11,12]. In the Cr_3C_2 -25NiCr coating, the carbide Cr_7C_3 was present. It is generally considered that this carbide is formed through decarburization of Cr_3C_2 carbide.



Figure 3 XRD patterns of the (a) Cr_3C_2 -25NiCr powder, and (b) the Cr_3C_2 -25NiCr coating

The microstructure of the Cr₃C₂-25NiCr coating in different regions as schematically shown in **Figures 4**, **5** was examined by TEM. The features of the fine structure of the Cr₃C₂-25NiCr coatings and its parameters have been studied. It was established that the layered structure of the regions of carbide particles and matrix metal is located within the "carbide-matrix" boundary. In the center of the carbide particle is the highest carbide Cr₃C₂, around which the interlayers of carbide Cr₇C₃ and Cr₂O₃ are formed. Migration of carbon from the carbide particles to the Ni-Cr matrix with the formation of dispersed particles of secondary carbides in it was observed. In the Ni-Cr matrix, an increase in the carbon concentration and the formation of secondary carbide particles with an average size of about 47.5 nm was observed. The distance between the boundaries of the secondary carbides was not more than 190 nm. The dislocation density in the lamellar volume of the Ni-Cr matrix was 2×10^{10} , at the boundary "lamella-lamella" - 4×10^{10} , at the boundary "carbide-lamella" - $(5...6) \times 10^{10}$. It was established that the thickness of the lamellae was $1.5 \,\mu$ m, and the average size of the substructure of



the Ni-Cr matrix was 247 nm. Lamellae in the coatings consisted of nanocrystalline grains, separated by interlayers of the amorphous phase and oxide crystalline grains.



Figure 4 The structure of the Cr_3C_2 -25NiCr coating at a distance ~ 40 µm from the substrate





Lamella (Ni-Cr)



4. CONCLUSION

During the deposition of Cr₃C₂-NiCr powder under the action of high temperatures and the atmosphere of the detonation products, a change in its phase composition occurs, forming a complex heterogeneous structural-



phase state in the coatings. Within the deposited Cr_3C_2 -NiCr coating, Cr_3C_2 , C_7C_3 and Cr_2O_3 phases were present with different morphologies. In the center of the carbide particle is the highest carbide Cr_3C_2 , around which the interlayers of carbide Cr_7C_3 and Cr_2O_3 are formed. The microstructure of the matrix in the deposited coating varied with the regions. Within the coating, the grain size of the matrix changed from several nanometers to several tens nanometers. Quantitative image analysis revealed the average apparent diameter of the carbides was about 47.5 nm, the thickness of the lamellae was 1.5 μ m, and the average size of the substructure of the Ni-Cr matrix was 247 nm.

ACKNOWLEDGEMENTS

The study was financial supported by the Russian Science Foundation under grant No. 15-19-00189. All studies were carried out on the equipment of the Joint Research Center «Technology and Materials» of Belgorod State National Research University

REFERENCES

- [1] MATEOS, J., CUETOS, J.M., VIJANDE, R., FERNÁNDEZ, E., Tribological properties of plasma sprayed and laser remelted 75/25 Cr₃C₂/NiCr coatings. *Tribology International*, 2001, vol. 34, no. 5, pp. 345-351.
- [2] GUILEMANY, J.M., FERNÁNDEZ, J., DELGADO, J., BENEDETTI, A.V., CLIMENT, F., Effects of thickness coating on the electrochemical behaviour of thermal spray Cr₃C₂-NiCr coatings. *Surface and Coatings Technology*, 2002, vol. 153, no. 2-3, pp. 107-113.
- [3] TILLMANN, W, VOGLI, E, BAUMANN, I, KOPP, G, WEIHS, C. Desirability-based multi-criteria optimization of HVOF spray experiments to manufacture fine structured wear-resistant 75Cr₃C₂-25(NiCr20) coatings. *Journal of Thermal Spray Technology*, 2010, vol.19, no. 1-2, pp. 392-408.
- [4] WOLFE, D.E., EDEN, T.J., POTTER, J.K., JAROH, A.P., Investigation of Cr₃C₂-based wear-resistant coatings Applied by the cold spray process, *Journal of Thermal Spray Technology*, 2006, vol. 15, no. 4, pp. 400-412.
- [5] SIDHU, T.S., PRAKASH, S., AGRAWAL, R.D. Hot corrosion studies of HVOF sprayed Cr₃C₂-NiCr and Ni-20Cr coatings on nickel-based superalloy at 900°C. *Surface and Coatings Technology*, 2006, vol. 201, no. 3-4, pp. 792-800.
- [6] VASILIK, N., TYURIN, Y., KOLISNICHENKO, O. Method for gas-dynamic detonating speedup of powders and device for its implementation. RU Patent 2506341, 11 July 2012.
- [7] KOVALEVA, M., TYURIN, Y., KOLISNICHENKO, O., PROZOROVA, M., ARSEENKO, M. Properties of detonation nanostructured titanium-based coatings. *Journal of Thermal Spray Technology*, 2013, vol. 22, pp. 518-524.
- [8] PROZOROVA, M., TURIN, Y., VASILIK, N., KOVALEVA, M., GONCHAROV, Y., PAVLENKO, I. Alumina nanostructured coatings formed by multi-chamber gas-dynamic accelerator. In NANOCON 2013: 5th International Conference NANOCON 2013. Ostrava: TANGER, 2014, P. 140-144.
- [9] SAHRAOUI, T., FENINECHE, N.E., MONTAVON, G., CODDET, C. Structure and wear behaviour of HVOF sprayed Cr₃C₂-NiCr and WC-Co coatings. *Materials & Design*, 2003, vol. 24, no. (5), pp. 309-313.
- [10] LI, C.-J., WANG, Y.-Y., YANG, G.-J., OHMORI, A., KHOR, K.A. Effect of solid carbide particle size on deposition behaviour, microstructure and wear performance of HVOF cermet coatings. *Materials Science and Technology*, 2004, vol. 20, pp. 1087-1096.
- [11] JI, G.-C., LI, C.-J., WANG, Y.-Y., LI, W.-Y. Microstructural characterization and abrasive wear performance of HVOF sprayed Cr₃C₂-NiCr coating. *Surface and Coatings Technology*, 2006, vol. 200, pp.6749-6757.
- [12] CHATHA, S.-S., SIDHU, H.S., SIDHU, B.S. Characterisation and corrosion-erosion behaviour of carbide based thermal spray coatings. *Journal of Minerals and Materials Characterization and Engineering*, 2012, vol. 11, no. 6, pp.569-586.