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INFLUENCE OF HEAT TREATMENT ON THE MICROSTRUCTURE AND COMPOSITION OF PLASMA SPRAYED COATINGS

Plasma sprayed coatings have been used in various industries for a number of purposes. To increase their mechanical properties, different methods of thermal treatment are being applied. This work is concerned with composite coatings obtained by plasma spraying of the $Al_2O_33TiO_2$ and NiO powders (50 % and 50 % by weight), which were then reduced at an atmosphere of dissociated ammonia. Their chemical composition and morphology were determined by means of the EDS microprobe and the Joel 5400 scanning microscope respectively. It has been reported that the process of reduction contributes to the homogeneity of the coating, and that the modified structure contains Al_2O_3 and Ni.

Key words: *plasma spraying, composite coating, reduction*

1. Introduction

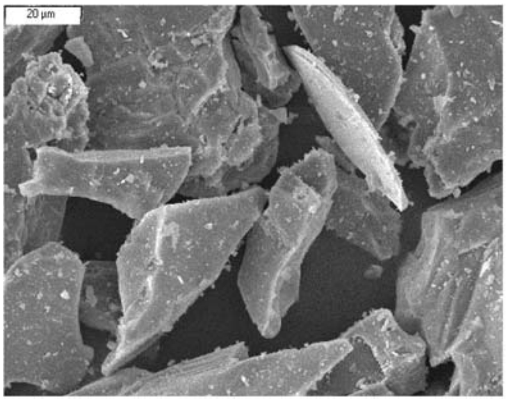
Composite ceramic coatings produced by plasma spraying have a great number of applications. The desired properties such as resistance to wear, erosion, or corrosion, as well as thermal insulation are obtained by means of various methods of plasma spraying, various techniques of powder feed, as well as various compositions of the coating material [1, 2]. Although it is possible to modify the composition and morphology, the high temperature of the plasma stream reaching 15,000 K causes that the chemical and phase composition of the coatings is different from that of the solid material. Moreover, a number of defects (i.e. porosity, microcracks, non-molten powder grains, poor cohesion between lamellae) are observed in the microstructure, all having a negative influence on the mechanical properties. Undesirable changes in the coating composition can be reduced if plasma spraying is performed in a special chamber with a regulated atmosphere, the process being extremely costly, though [3]. Another method allowing changes in the structure of coatings is thermal treatment. Numerous works, see Refs. [4, 5, 6, 7], present and discuss the results of the research into the influence of carburizing, nitriding, and laser or electron beam treatment on the properties of plasma sprayed coatings. It is possible to obtain a coating with a homogeneous structure characterised by better properties and better adhesion to the substrate. It has not yet been explained, however, what impact the process of reduction has on such structures. The investigations described in this paper aimed at determining the influence of the reduction process on the structure of plasma sprayed Al_2O_3-NiO coatings.

2. Experiment

2a. Material

The material used for the coating was a mixture of powders, the proportion by weight being 50 % $Al_2O_33TiO_2$ (Metco 101NS) and 50 % NiO. The two materials were mixed in a V type blender for 1 hour. Their morphology is shown in Fig. 1a, b. The sharp edges of the $Al_2O_33TiO_2$ grains prove that the powder was ground. The other component of the composite, the NiO powder, is a chemical reagent.

a)



b)

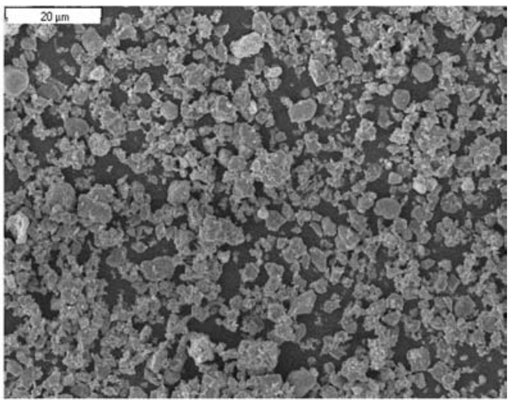


Fig. 1. Grains of the a) $Al_2O_33TiO_2$ and b) NiO powders

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The distribution of grains was determined using the Helos (Sympatec GmbH) laser particle size analyser. The range of grain size for Al_2O_3 and NiO was $-45 + 11$ μm and $-20 +5$ μm respectively.

a)

b)

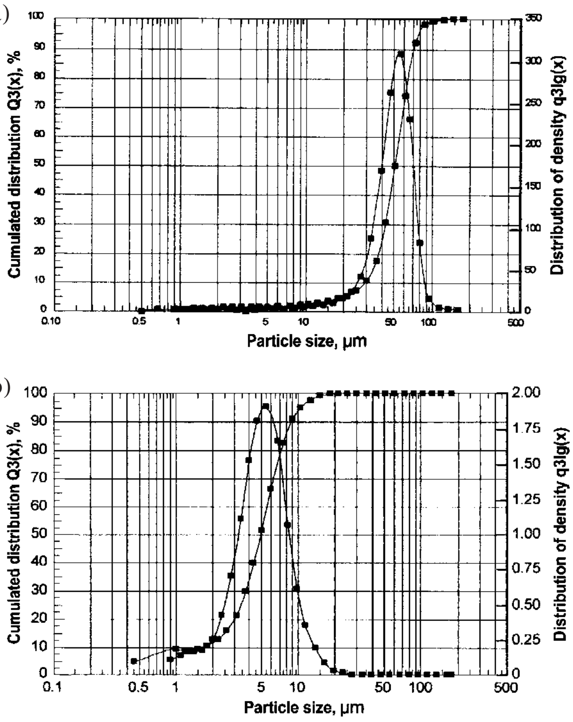

Fig. 2. Grain size distribution and relative density of the a) $Al_2O_33TiO_2$ and b) NiO powders

2b. Plasma spraying

Plasma spraying belongs to semi-molten state surface coating techniques and basically consists of the injection of selected powders into a direct current plasma jet, where they are molten, accelerated and directed onto the substrate surface. The coatings are actually splats of molten droplets instantly solidified on the substrate surface because of its lower temperature. The principles of plasma spraying are shown in Fig 3.

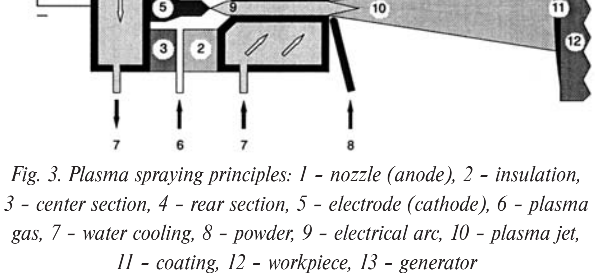

Fig. 3. Plasma spraying principles: 1 – nozzle (anode), 2 – insulation, 3 – center section, 4 – rear section, 5 – electrode (cathode), 6 – plasma gas, 7 – water cooling, 8 – powder, 9 – electrical arc, 10 – plasma jet, 11 – coating, 12 – workpiece, 13 – generator

In the experiment the composite coatings were sprayed on 3 mm thick low-carbon steel samples. Before the spraying, the samples were blasted using alundum EB 12 with a grain size of 1.5−2 mm at a pressure of 0.5 MPa. The plasma spraying was performed by means of the PLANCER set equipped with the PN 120 gun and the Thermal Miller 1264 powder feeder. Argon plasma with 7% hydrogen was used for the process. The plasma spraying parameters are given in Table1.

Plasma spraying parameters Table 1.

Voltage (V)	Current (A)	Spraying distance (mm)	Powder feed rate (g/min)
60	550	100	8

2c. Heat treatment

The process of reduction involves a reaction during which the metal valency drops to zero. The material being surrounded by a protective gas does not oxidize. The pressure of oxygen particles is smaller than the pressure of the pairs of oxides dissociating in the material at the reduction temperatures. The atmosphere of pure hydrogen is one of the most common atmospheres of sintering. Dissociated ammonia can substitute hydrogen, though it is equally costly. Ammonia is dissociated ($2NH_3 = N_2 + 3H_2$) at a temperature ranging between 600 and 950 °C. The protective atmosphere is selected depending on the chemical composition of the sintered material, the furnace type and economic factors. It is quite difficult to prevent oxidization when the materials contain oxides that are hard to reduce (Cr, Ti, Al).

For reduction purposes the plasma sprayed coatings were placed in a pipe furnace with a reducing atmosphere. The process of reduction was carried out for an hour at a temperature of 900 °C and an atmosphere of dissociated ammonia. Hydrogen being the result of the dissociation of ammonia joined the oxygen originating from the oxides reducing them to a pure metal and producing vapour.

2d. Methodology

The microstructure of the sprayed composite coatings before and after the thermal treatment was analysed by means of the Jeol JSM-5400 scanning microscope. To study their chemical composition, and perform a point or linear analysis we used the ISIS 300 Oxford Instruments microprobe. The distribution of elements, on the other hand, was determined by applying the EDS method.

3. Results and discussion

3a. Structure and composition of the coating after spraying

Some lateral microsections of the sprayed coatings were analysed for morphology (Fig. 4a,b,c) and it was reported that the structures consist of deformed particles well-adjacent to each other.

a) b) c)

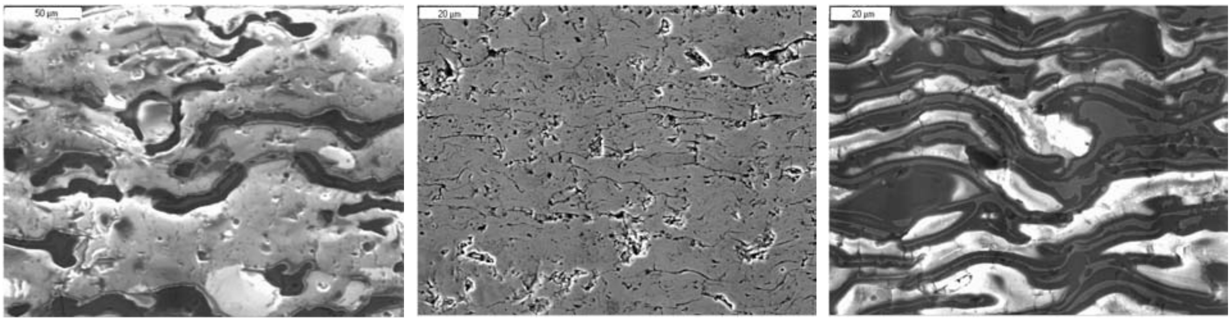

Fig.4. Microstructure of coating a) $Al_2O_33TiO_2$ b) NiO c) $Al_2O_33TiO_2/NiO$

This testifies to good remelting of the powder grains. The number of pores is small, which is characteristic of the plasma spraying technology.

In the structure of the $Al_2O_33TiO_2$ coating we distinguish between three phases: the white one, the grey one, and the dark one. In the predominant white phase, there are bands of the dark phase containing bands of the grey phase (Fig. 4a). The test results concerning the chemical composition of the phases based on the point analysis are presented in Table 2. As can be seen from the table, Al_2O_3 with minute quantities of TiO_2 constitutes the white phase. Then, TiO_2 with a considerable amount of Al_2O_3 and minute quantities of other oxides is the predominant component of the grey phase. The analysis of the dark phase in three points shows that the proportions of the main components vary, but all of them contain a considerable amount of ZrO_2 and that the chemical composition specified by the producer is quite different. The linear analysis (Fig. 5) confirmed the lamellar system of each component.

Chemical composition of the Al2O33TiO2 coating (EDS). Table 2

Compound [%wt.] / Phase	Al_2O_3	TiO_2	MgO	SiO_2	CaO	ZrO_2
white	98.71	1.25	–	–	–	–
grey	17.86	77.28	1.44	0.49	0.99	1.95
dark 1	74.49	12.11	1.76	8.11	2.42	1.11
dark 2	52.76	24.56	4.11	3.07	1.01	14.49
dark 3	40.63	31.99	3.91	2.56	0.99	19.92

As far as the NiO coating structure is concerned, we observe some lateral microcracks in the adjacent lamellae. By contrast, the Al_2O_3 coating structure exhibits no such cracks. They occur either in a single lamella or go through several lamellae. The same parameters were applied for the NiO and $Al_2O_33TiO_2$ powders. As a result, there was an excessive increase in the melting temperature of the grains of the finer NiO powder. Its melting point being 1984 °C was lower than that of Al_2O_3. Hence, some local stresses occured, which caused microcracks in the coating. The analysis of the chemical composition of the NiO coating showed some minute quantities of CoO and MgO. The composite coating obtained by spraying a mixture of the above-mentioned components is characterised by a homogeneous lamellar microstructure. The considerable difference in the size of grains of both components and more than half as great density of NiO did not cause any separation of the components during their feeding into the plasma gun or in the plasma stream. Great extension of the grey phase, i.e. nickel oxide, was observed.

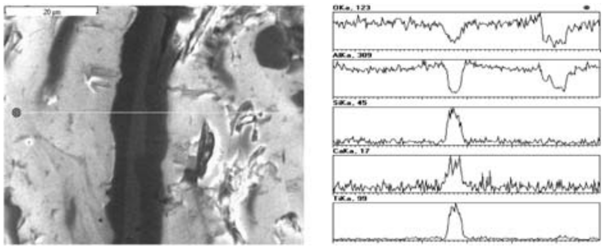

Fig. 5. Linear analysis (EDS) of the $Al_2O_33TiO_2$ coating

3b. Structure and composition of coatings after heat treatment

The analysis of the coating microstructure showed that the reduction process had influence on the particular components. The morphology of the $Al_2O_33TiO_2$ coating (Fig. 6a) did not change.

The point and linear analyses showed no difference in the composition of the phases, either. Yet, we observe some modification of the structure and the chemical composition of the NiO coating. The boundaries between the badly adherent lamellae, the pores, the micropores, and the microcracks increased considerably due to the occurrence of vapour (Fig. 6b). The hardly visible boundaries between the well adherent lamellae vanished. The analysis of the chemical composition of the NiO coating showed that it was completely reduced to pure nickel. Similar behaviour was observed after the process of reduction. (Fig. 6c). The amount of nickel oxide in the $Al_2O_33TiO_2$ matrix, not modified either structurally or chemically, was reduced. The test results concerning the chemical composition of the nickel oxide phases based on the point analysis before and after heat treatment are presented in Table 3 and in Fig. 7.

a) b) c)

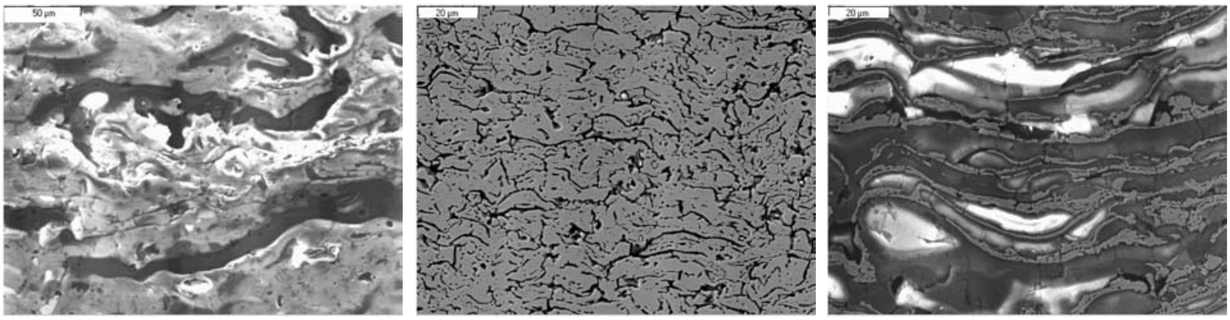

Fig. 6. Microstructure of the coating after heat treatment a) $Al_2O_33TiO_2$ b)NiO c) $Al_2O_33TiO_2$/NiO

Chemical composition of the NiO phase before and after heat treatment (EDS). Table 3.

NiO phase	
Before heat treatment [%wt.]	After heat treatment [%wt.]
NiO - 98.09	Ni - 98.97
CoO - 1.24	Co - 1.23
MgO - 0.67	–

The vapour observed in the composite structure, i.e. in the nickel lamella, caused the formation and partial defragmentation of micropores.

4. Conclusions

1. The plasma spraying process makes it possible to obtain composite coatings by mixing two or more powders, each with a different granulometeric composition.
2. Nickel oxide was reduced at an atmosphere of dissociated ammonia. The chemical composition of alumina did not change due to its greater affinity with oxygen.
3. The reduction of a plasma sprayed Al2O33TiO2/ NiO coating resulted in the formation of an Al2O3/Ni composite coating.

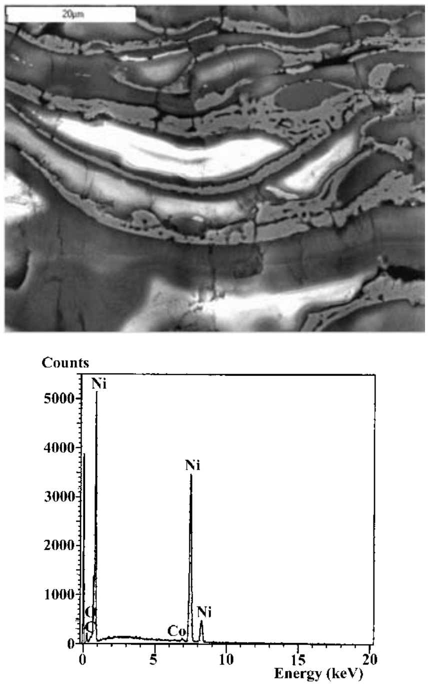

Fig. 7. Point analysis (EDS) of the $Al_2O_33TiO_2$/NiO coating after heat treatment

References

[1] PAWLOWSKI, L.: *The science and engineering of thermal spray coatings.* John Wiley & Sons Ltd, Chichester 1995.

[2] Art. LLORCA-ISERN, N., LUCCHESE, P., JEANDIN, M.: *Advances in plasma spraying technologies and applications,* Finishing 2/1997.

[3] NESTLER, M. C., SPIES, H. J., HERMAN, K.: *Improvement of coating characteristics and end-use performance of thermal spray coatings through post-treatments like hardening, nitriding or carburizing.* Proc. of United Thermal Spray Conference, Düsseldorf 1999.

[4] WIELAGE, B., STEINHÄUSER, S., PAWLOWSKI, L., SMUROV, I., COVELLI, L.: *Laser treatment of vacuum plasma sprayed CoCrAlY alloy.* Surface Engineering, Vol. 14, No 5, 1998.

[5] BINSHI, X., SHICAN, L., XIANGYANG, X., MEILING, Z.: *Structure and fretting wear resistance of electron beam remelting CoCrW coating.* Proc. of International Thermal Spray Conference, Essen 2002.

[6] MATEOS, J., CUETOS, J. M., VIJANDE, R., FERNÁNDEZ, E.: *Tribological properties of plasma sprayed and laser remelted 75/25 Cr3C2/NiCr coatings.* Tribology International 34 (2002) 345-351.

[7] ŻÓRAWSKI, W., RADEK, N.: *Influnce of laser treatment on the tribological properties of thermally sprayed nickel based alloys.* Przegląd Spawalnictwa Nr 8-10/ 2002.