THE STRUCTURE OF NiCrAlY METAL POWDERS PLASMA SPRAYED AND CAPTURED IN WATER

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The effect of plasma beam on the structure of NiCrAlY powders can be a possible source of structural inhomogeneities in plasma spray coatings. Results of structural studies performed with light microscopy, SEM, TEM, and EDX on NiCrAlY metallic powders plasma sprayed and captured in water are presented in this paper. The internal structure was found to consist of a mixture of phases including γ, γ', β-NiAl and martensitic NiAl. Y is bound in the Ni_5Y yttride localized in the grain boundary regions. Spherical caps containing O, Al, Y, and Cr are formed at the surface of powders. The depletion of bulk powders of Al due to surface oxide formation was found to be the cause of a slight decrease of microhardness of plasma sprayed powder.

ŠTRUKTÚRA KOVOVÝCH PRÁŠKOV TYPU NiCrAlY PO PLAZMOVOM NÁSTREKU DO VODY

Vplyv plazmového lúča na štruktúru práškov typu NiCrAlY môže byť zdrojom štruktúrnych nehomogenít v povlakoch nanášaných plazmou. V tomto článku uvádzame výsledky štúdia štruktúry kovových práškov typu NiCrAlY po plazmovom nástreku do vody, ktoré sa dosiahli pomocou svetelnej mikroskopie, SEM, TEM a EDX. Vnútorná štruktúra práškov pozostáva zo zmesi fáz γ, γ', β-NiAl a martenzitu NiAl. Ytrium je viazané v ytride Ni_5Y, ktorý sa nachádza na hraniciach jednotlivých fáz. Na povrchu práškov sa sformovali guľové vrchlíky, obsahujúce najmä O, Al, Y a Cr. Ochudobnenie práškov o Al, ktorý sa spotreboval pri tvorbe povrchových oxidov, sa považuje za príčinu mierneho poklesu mikrotvrdosti práškov striekaných plazmou.

1. Introduction

The investigation of the sources of inhomogeneities in plasma sprayed coatings inevitably leads to the study of initial structure of powders as well as to the study of the effect of plasma on the structure of powders. We have reported on the results of the structural studies performed on initial NiCrAlY (AMDRY 962) metal powders

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in our previous work [1]. The aim of this work is to present some results on the structure of plasma sprayed powders captured in water.

It is well known that these powders are normally sensitive to oxidizing environments and therefore are recommended by the producer to be sprayed in non-oxidizing atmosphere. However, larger sizes can be sprayed also in air, what is a very economical alternative to the vacuum spraying. Knowledge of the effect of plasma on the structure and possible degradation of NiCrAlY powders is an important precondition for a proper choice of plasma spraying technology.

2. Experimental material and procedure

AMDRY 962 is an alloy nickel base powder with a nominal composition Ni22Cr10Al1.0Y. The powder is of spherical shape with sizes ranging from 106 to 45 μm and is used for protective plasma spray coatings exposed to hot corrosive or oxidizing environments at high temperatures.

The powder was plasma sprayed at a total power input of 32 kW. Argon with a gas-flow rate of 4.2 l/min was used as a plasma carrying gas, and hydrogen and argon with gas-flow rates of 13.5 l/min and 44.0 l/min, respectively were used as plasma forming gases. Powder particles had been introduced perpendicularly into the plasma jet axis and at the distance of 135 mm from the nozzle were captured in water.

Light microscopy (LM), Vickers microhardness measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDXS) were used for the structural studies. Samples for LM and SEM studies were prepared by embedding the powder in a cold-curing resin with subsequent grinding and polishing using a conventional metallographical way. The thin foil preparation included the argon ion milling as reported elsewhere [1].

Electron microscopy observations were carried out using a JEOL JEM 100 C analytical electron microscope equipped with an ultra-high resolution scanning system EM-ASID-4D. The microscope was operated at an accelerating voltage of 20 kV for secondary electron imaging and at 100 kV for transmission electron microscopy observations including bright field (BF) and dark field (DF) observations with selected area electron diffraction (SAED). EDX analyses were performed using a Kevex Delta class IV spectrometer with an ultra-thin window detector (Kevex Quantum detector).

3. Results

Individual NiCrAlY powders plasma sprayed and captured in water are mostly of spherical shape, however, they can often be found in arrangements consisting of two or more adjacent particles with different diameters as shown in Fig. 1. Some

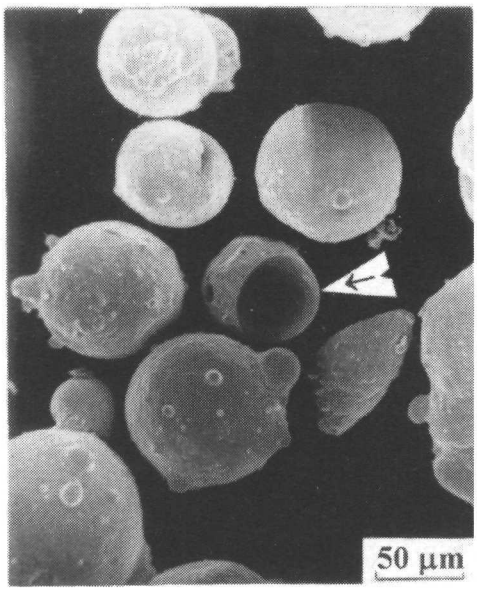

Fig. 1. NiCrAlY powder particles as passed through the plasma beam and captured in water. A well-developed spherical cap is indicated by an arrow (SEM).

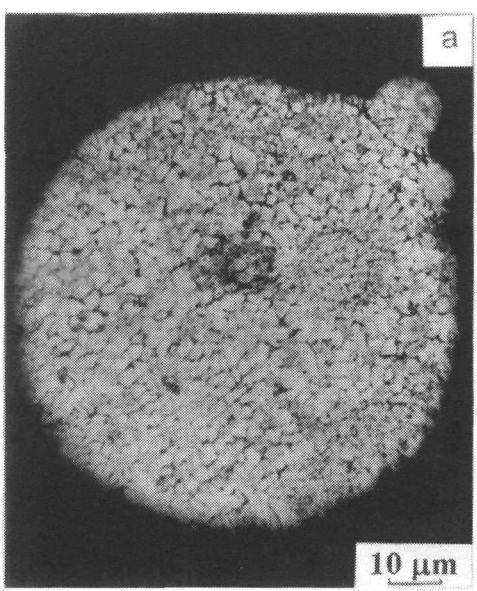

Fig. 2a. Mostly cellular solidification microstructure in a midsection of the NiCrAlY powder (light microscopy, Marble's reagent).

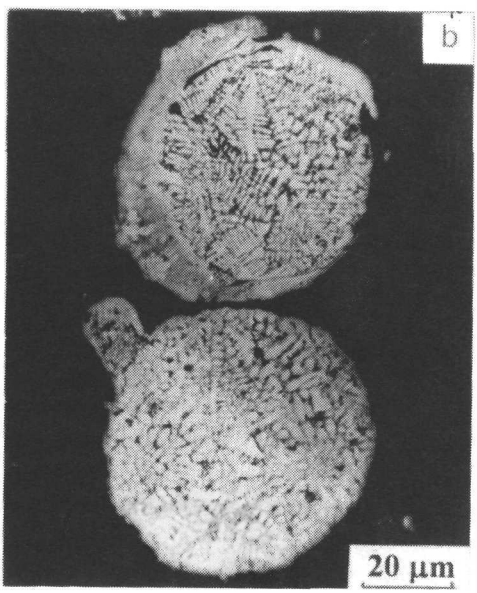

Fig. 2b. Mostly dendritic solidification microstructures in a midsection of the NiCrAlY powders (light microscopy, Marble's reagent).

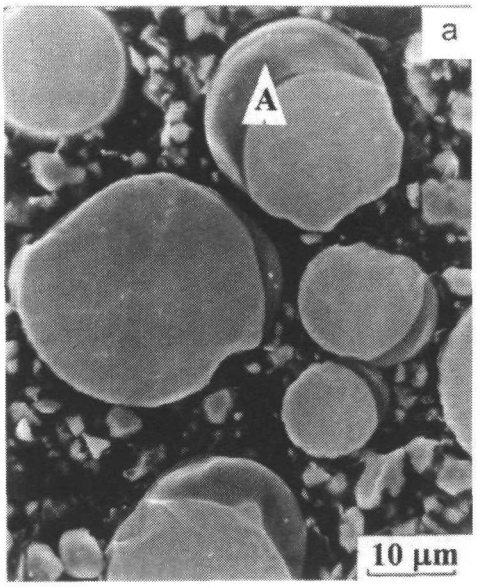

Fig. 3a. Cross sections of NiCrAlY powders (SEM, as-polished, not etched).

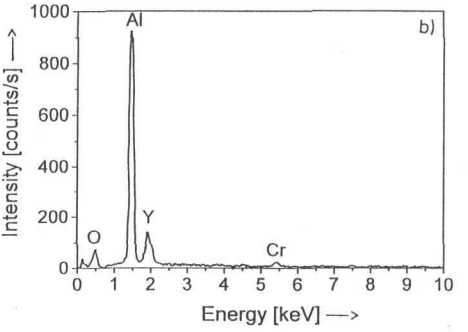

Fig. 3b. EDX spectrum acquired from the spherical cap indicated by A in Fig. 3a.

powders, predominantly of the smaller sizes have obtained spherical caps with smooth surfaces.

Light microscopy observations of the etched NiCrAlY powders cross sections revealed that both cellular and dendritic solidification structures occurred in the powders. In most cases both types of structures occupying different locations can be found within one powder particle. A specific dendritic structure with dendrites arranged in columnar blocks can be observed, too. Some typical powder structures are shown in Fig. 2. Vickers microhardness measurements showed that the hardness of NiCrAlY powders was in the range of 73–225 HV 0.01.

SEM observations and EDX analysis of the spherical caps performed on polished cross sections of powders, as shown in Fig. 3a, revealed that they were of three types. They contain mostly Al, O, and Y with a little amount of Cr as shown in Fig. 3b. Approximately about 30% of caps contain Al and O without Y but again with a little content of Cr and finally about 20% of caps contain Al, O and Cr with a little content of Y. The structure of the oxides will be treated in much more detail in the next paper.

EDX analysis of the composition of powder particles showed almost constant level of Ni content with variable concentrations of Al. The increase in Al content is accompanied by the decrease in Cr and Y content, as well. It can be seen that

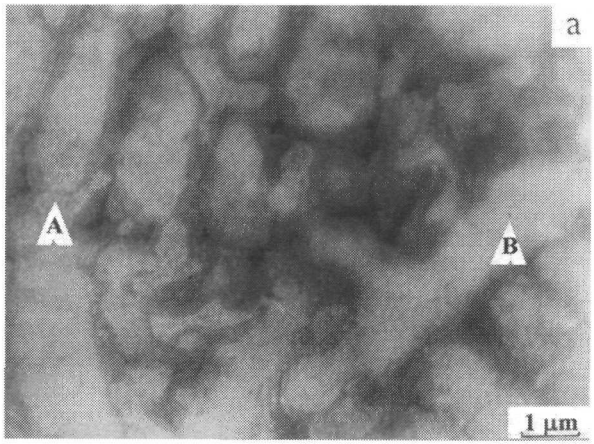

Fig. 4a. Microstructure of NiCrAlY powder particle (SEM, ion etched).

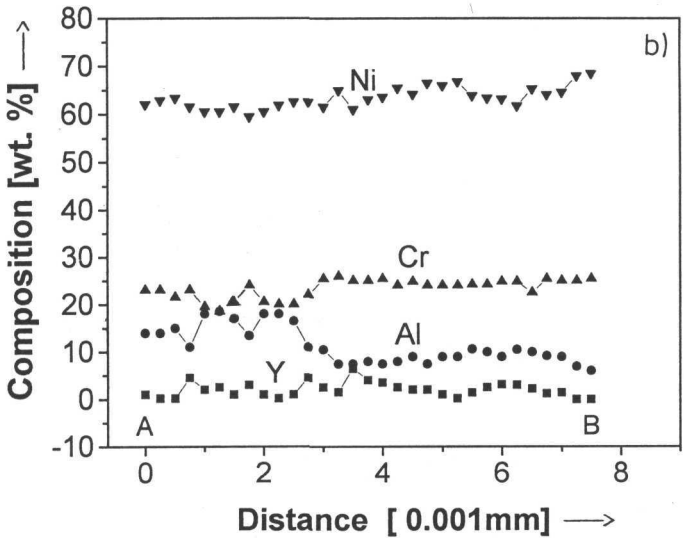

Fig. 4b. EDX semiquantitative step analysis along the A – B line in Fig. 4a.

Y shows a very high tendency to segregate at grain boundaries. Concentrations up to 6.5 wt.% of Y were obtained at the grain boundaries by the EDX step analysis along the A – B line in Fig. 4a. This tendency could have been determined only at the ion etched cross sections of powder particles as the Marble's reagent used

for light microscopy observations had selectively etched the grain boundary phases away.

TEM studies of the structure of NiCrAlY powders were performed on ion thinned samples, as shown in Fig. 5. The observations confirmed the fine grained microstructure of powders with grain sizes of only a few micrometers, normally not exceeding the 10 μm range. The typical powder microstructure is shown in Fig. 6a. Selected area electron diffraction pattern in Fig. 6b and the dark field images formed using appropriate reflexions in Fig. 6c and 6d revealed the Ni base solid solution (γ) matrix grains with a very fine coherent precipitate Ni_3Al (γ'). Weak reflections in the diffraction pattern in Fig. 6b indicated and the dark field image in Fig. 6d has finally confirmed that only very little of Ni_3Al (γ') intermetallic phase was present in the γ-Ni grains.

Y was found to be bound in the Ni_5Y yttride that appears exclusively at the grain boundaries of $\gamma, \gamma/\gamma'$, β-NiAl, and martensitic NiAl phases. The typical example is given in Fig. 7a where, with respect to the SAED pattern shown in Fig. 7b, the yttride appears at the grain boundaries of the martensitic NiAl phase with a tetragonal Ll_0 structure.

β-NiAl phase with B_2 crystal structure and a mottled appearance is shown close to the oxide in Fig. 8a. γ-Ni grains seem to be incorporated in the β-NiAl phase in this section. The appropriate electron diffraction pattern is in the Fig. 8b.

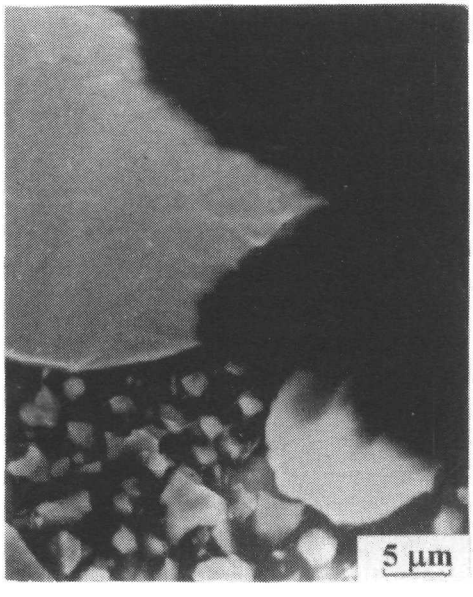

Fig. 5. Ion thinned NiCrAlY powder (SEM).

4. Discussion of results

Due to the thermal and kinetic effect of the plasma beam, the supplied powder is melted and accelerated. During the particle flight in plasma, interactions of particles with gases of surrounding atmosphere and the plasma take place resulting in gas absorption, chemical interaction, and formation of oxide layers and other bonds on the particle surface, the gas dissolution in the molten metal of particle, and the diffusion process and mechanical mixing of the interaction products [2]. All these characteristics of the process should be taken into account when the effect of plasma on the structure of powders is under investigation.

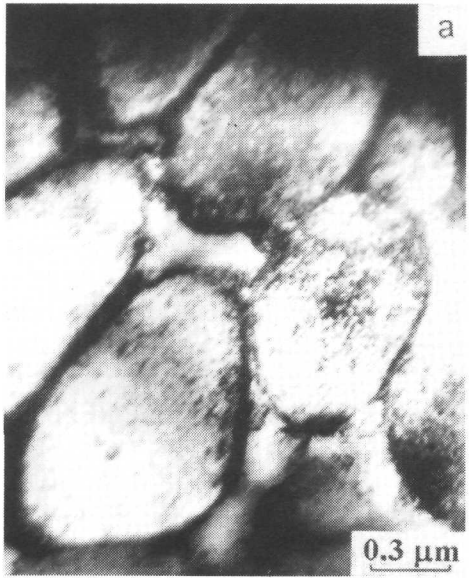

Fig. 6a. Microstructure of NiCrAlY powders (TEM, bright field image).

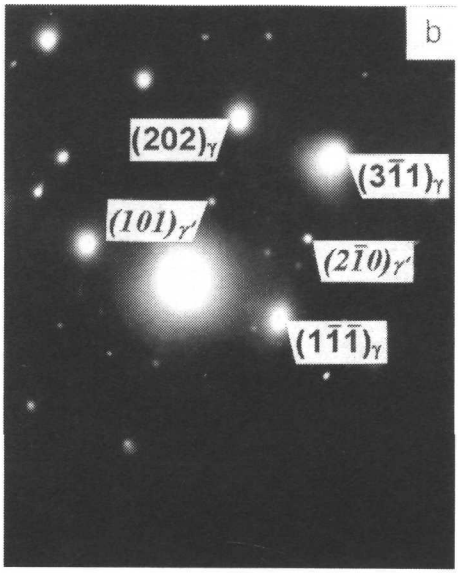

Fig. 6b. A selected area electron diffraction pattern showing the γ-Ni and γ'-Ni_3Al diffraction spots.

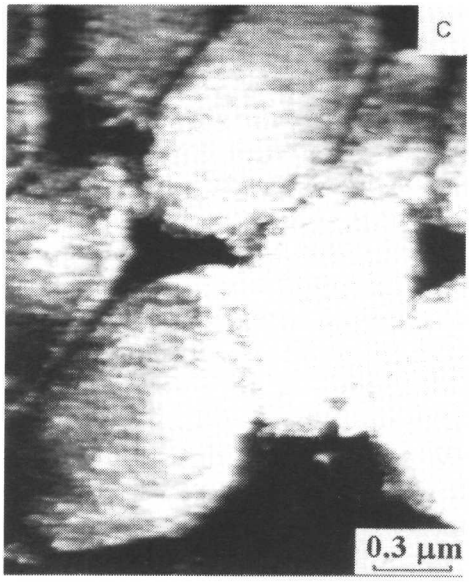

Fig. 6c. A dark-field image formed using a γ-Ni reflection (TEM).

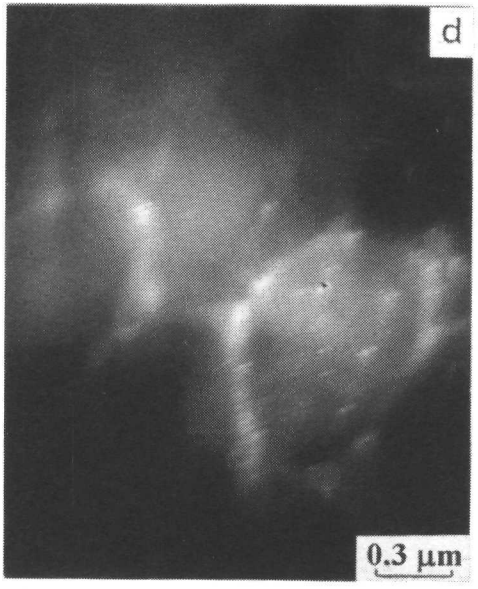

Fig. 6d. A dark-field image formed using a γ'-Ni_3Al reflection (TEM).

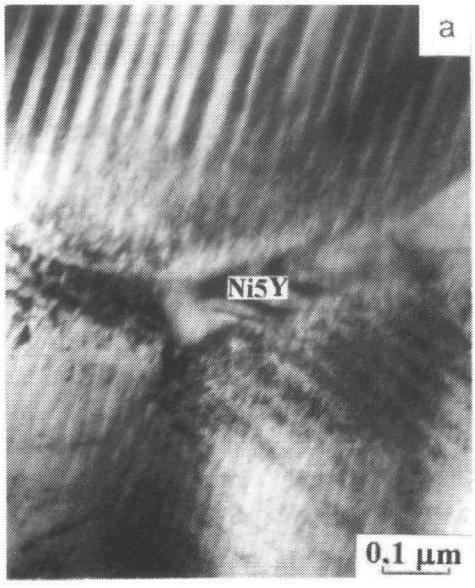

Fig. 7a. Ni_5Y yttride at the grain boundaries of NiAl-martensitic phases (TEM, bright field image).

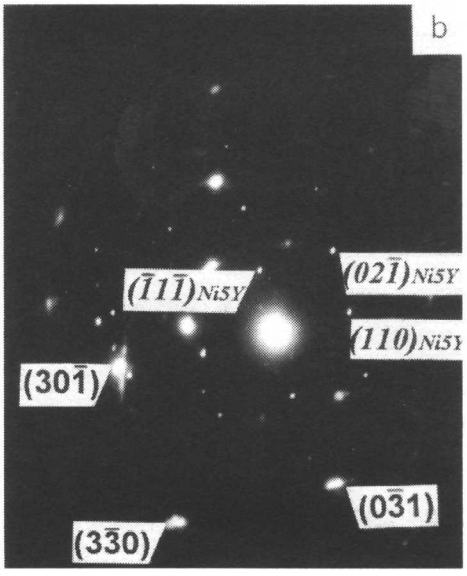

Fig. 7b. A selected area electron diffraction pattern showing the NiAl-martensite and Ni_5Y diffraction spots.

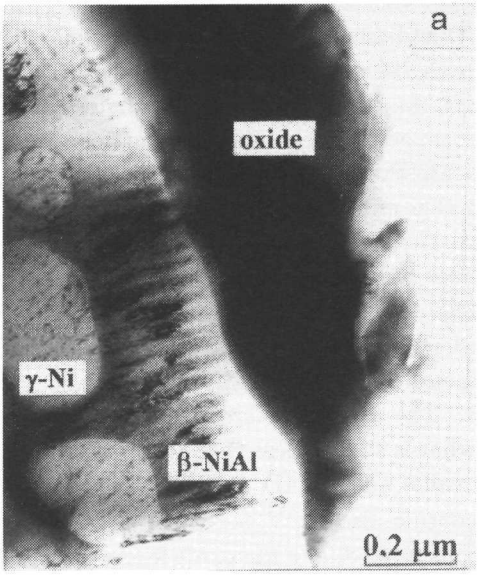

Fig. 8a. β-NiAl and γ-Ni grains close to the surface oxide in the structure of NiCrAlY powder (TEM, bright field image).

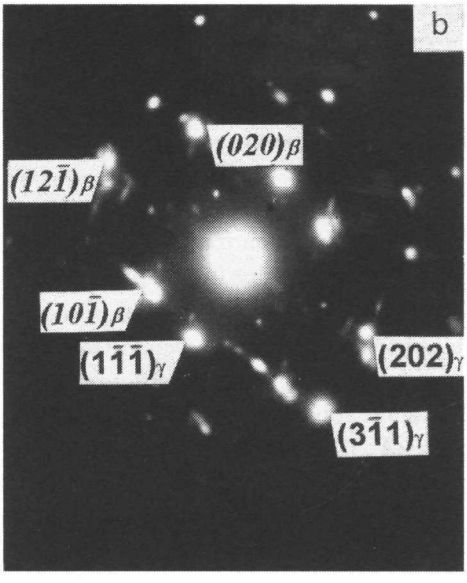

Fig. 8b. A selected area electron diffraction pattern showing the β-NiAl and γ-Ni diffraction spots.

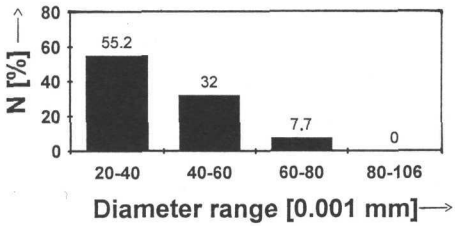

Fig. 9. Frequency of spherical caps appearance vs. the diameter range of powders.

As the NiCrAlY powders as-produced are already of spherical shape, it is not possible to evaluate the number of particles that were re-melted in the plasma beam according to their newly obtained spherical shape. However, the SEM observations of these particles revealed the spherical caps on some of them, that were not observed on the surfaces of initial powders. EDX analysis confirmed that these caps according to their composition belong to the oxide family of compounds. These results are consistent with the observations of authors [3] who performed some pilot work concerning the structure of NiCrAlY powders.

Though the structure of these oxides is not treated in this paper, 220 particles had been observed, and the frequency of spherical caps appearance was evaluated. The results are presented in the Fig. 9. It can be concluded that particles of smaller sizes are much more sensitive to oxidation in the plasma beam than the particles of larger sizes. A numerous fraction of particles with diameters smaller than 40 μm was found among the observed powders. This diameter range is smaller than the minimal limit given by the producer. From all 220 observed particles only 2 particles were in the diameter range 80–106 μm, 13 particles were in the diameter range 60–80 μm, 47 particles were in the diameter range 40–60 μm and 154 particles were in the diameter range up to 40 μm. This means that the particles are disassociated in the plasma beam and the number of smaller sizes increases. As these particles are evidently much more oxidation sensitive, the significant structural degradation of NiCrAlY powder in the plasma beam takes place.

The various solidification structures observed by light microscopy can be related to inhomogeneous conditions of powder solidification. The wide microhardness range is the result of different phase appearance in the powder structure including solid solution and intermetallic phases. The average microhardness value for plasma sprayed powders was 145 HV 0.01 what is slightly less than for as-produced powders where the average microhardness value was 162 HV 0.01.

Though the spherical caps besides O contain also Al, Y, and Cr, it was shown that these constituents had not been fully consumed due to the oxide formation. As shown by the EDX step analysis, Y remains located in the grain boundary regions and so it can be further expected to improve the adherence of alumina or chromia scales formed at the surface of the coating when exposed to higher temperatures.

Finally, TEM observations confirmed the presence of principally the same phases as in the initial powders including γ-Ni, γ'-Ni_3Al, β-NiAl, and martensitic NiAl with Y bound in the Ni_5Y yttride. The cooling rate of powder particles plasma sprayed and captured in water is undoubtedly high and the appearance of non-equilibrium structures including NiAl-martensitic decomposition product is not surprising as it was already determined in the as-produced powders [1]. Moreover, the mottled appearance of the β-NiAl phase in Fig. 8a with diffuse intensity distribution and the anomalous diffuse streaks in Fig. 8b can be related to the premartensitic lattice instability as shown by Enami et al. [4]. However, the slight decrease of microhardness when compared with as-produced powders can be due to the depletion of bulk powders with Al that was found to be very active in the oxide formation on the surface of plasma sprayed NiCrAlY powders.

5. Conclusions

The structure of NiCrAlY (AMDRY 962) powders plasma sprayed and captured in water was studied in this paper. The internal powder structure was found to consist of γ-Ni, γ/γ', β-NiAl, and martensitic NiAl grains with Y bound in the Ni_5Y yttride located in the grain boundary regions.

Powders disassociated in the plasma beam and a numerous fraction of powders with diameters lower than 40 μm appeared. Intensive formation of spherical caps predominantly on the surface of smaller sizes powders was observed.

Spherical caps contain besides O above all Al, Y, and Cr. The consumption of Al for the spherical caps formation is assumed to be the main reason for the slight decrease of microhardness of plasma sprayed NiCrAlY powders.

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