

STUDY OF OXIDE STRUCTURES FORMED ON THE SURFACE OF NiCrAlY POWDERS AS-PASSED THROUGH THE PLASMA BEAM

KAROL IŽDINSKÝ, JOZEF IVAN, MILINA ZEMÁNKOVÁ,
VLADIMÍR KOLENČIAK

The structure of oxides formed on the surface of NiCrAlY (AMDRY 962) powders plasma sprayed and captured in water was studied. Results of TEM have shown that these oxides were not amorphous but crystalline structures. All the investigated oxides, quite independent on the chemical composition, had spinel structures with spacings close to those of $\gamma\text{-Al}_2\text{O}_3$. Inhomogeneous thermal conditions due to the effect of plasma beam are assumed to be responsible for slight lattice distortions of oxides and superlattice reflexions caused by cation ordering. No transformations to the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ were observed.

ŠTÚDIUM ŠTRUKTÚRY OXIDOV VZNIKAJÚCICH NA POVRCHU PRÁŠKOV TYPU NiCrAlY PO PRECHODE PLAZMOVÝM LÚČOM

Predmetom článku je štúdium štruktúry oxidov vznikajúcich na povrchu práškov typu NiCrAlY (AMDRY 962) po prechode plazmovým lúčom. Výsledky štúdia pomocou TEM ukázali, že tieto oxidy nemajú amorfnú, ale kryštalickú štruktúru. Všetky skúmané oxidy, bez ohľadu na ich chemické zloženie, boli spinelového typu s parametrami blízкими $\gamma\text{-Al}_2\text{O}_3$. Predpokladá sa, že nehomogénne teplotné podmienky vyvolané plazmovým lúčom spôsobili mierne mriežkové deformácie oxidov a vyššiu mieru usporiadania katiónov, ktorá sa prejavila vznikom superreflexií v niektorých difraktogramoch. Transformácia oxidov na termodynamicky stabilnú fázu $\alpha\text{-Al}_2\text{O}_3$ sa nepozorovala.

1. Introduction

The study of NiCrAlY (AMDRY 962) powders plasma sprayed and captured in water reveals that disintegration of powders and extensive formation of spherical caps due to the effect of plasma beam take place. These caps contain significant

amounts of oxygen and so they can be regarded as oxidic products of mutual reaction of powders with the surrounding atmosphere. We have reported on the results of structural studies performed on plasma sprayed powders in our previous work [1]. The aim of this work is to present the results achieved by the study of the structure of oxidic spherical caps formed on the surface of NiCrAlY powders as-passed through the plasma beam.

2. Experimental material and procedure

NiCrAlY powders were plasma sprayed and captured in water. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) and conventional transmission electron microscopy (TEM) including bright field (BF) and dark field (DF) image observations and selected area electron diffraction (SAED) have been used for the structural studies.

All experiments and analytical work have been carried out with the same samples and equipment as mentioned in the papers [1, 2]. Therefore, details of experimental material and procedure will not be repeated here.

3. Results

Typical NiCrAlY powder with a well developed spherical cap is shown in

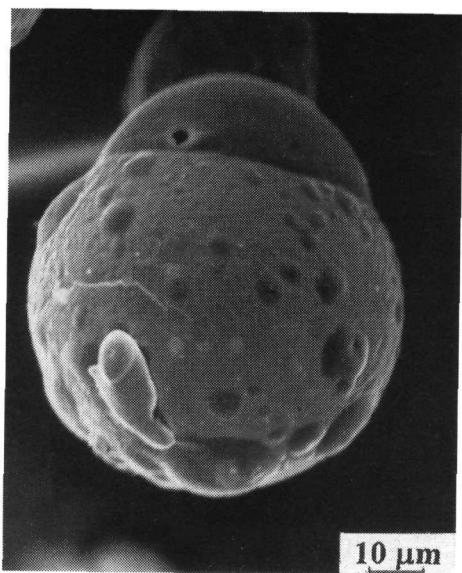


Fig. 1. NiCrAlY powder particle as-passed through the plasma beam with a well developed spherical cap (SEM).

the Fig. 1. Caps were typically of very smooth surfaces. Numerous locations with an analogous appearance, occupying much smaller powder surface areas than the dominant cap can be also observed.

EDX analysis revealed that spherical caps contain in particular Al and O. Beside these elements, Y and Cr are often present, too. Approximately 50% of particles contain Al, O, Y, and a little amount of Cr, about 30% of caps contain Al and O with a little content of Cr, and finally about 20% of caps contain Al, O, and Cr with a little content of Y [1]. In any case, as shown in Fig. 2a,b, the concentration of elements throughout the cap does not significantly change and is nearly constant. Ni was detected in none of the investigated oxide caps.

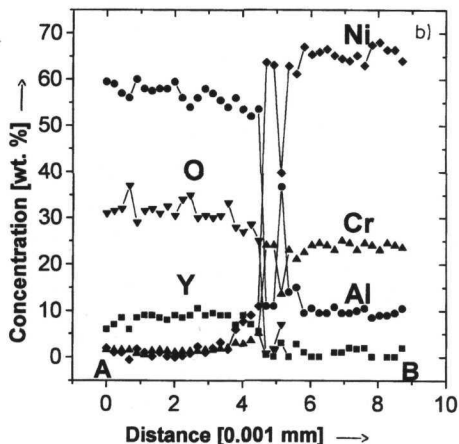
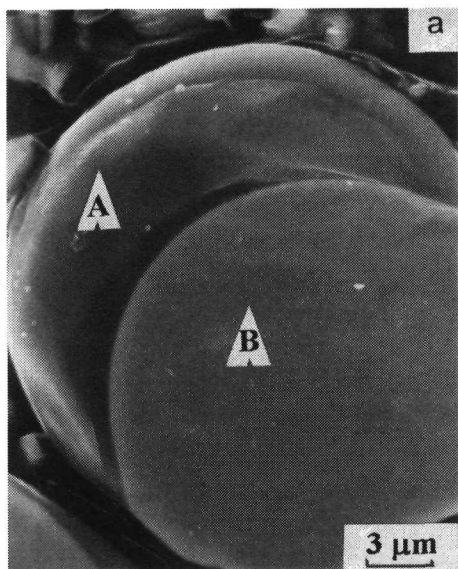


Fig. 2a. Cross section of NiCrAlY powder with a spherical cap (SEM, as-polished, not etched).

Fig. 2b. EDX semiquantitative step analysis along the A-B line in the Fig. 2a.

TEM studies were performed on ion thinned samples as shown in Fig. 3. Careful control of the thinning process yielded samples with transparent metal-oxide interfaces as well as transparent regions of individual oxide caps.

The oxide cap shown in Fig. 4a contained Al, O, and Y as determined by EDX analysis. The structure of the $[1\bar{1}1]$ oriented oxide is shown in Fig. 4b. The appropriate electron diffraction pattern from this area shown in Fig. 4c corresponds to a spinel structure with the lattice spacings approximately of $\gamma\text{-Al}_2\text{O}_3$.

The microstructure of metal-oxide interface is shown in Fig. 5a. The SAED patterns shown in Fig. 5b and dark field image observations revealed fcc $\gamma\text{-Ni}$ and martensitic NiAl phase



Fig. 3. Ion thinned NiCrAlY powder with a spherical cap (SEM).

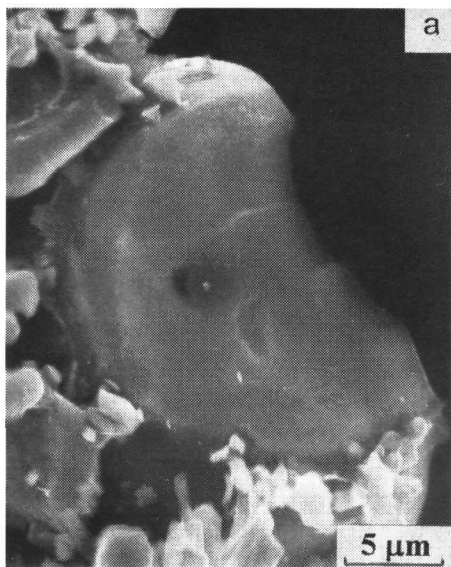


Fig. 4a. Ion thinned spherical cap (SEM).

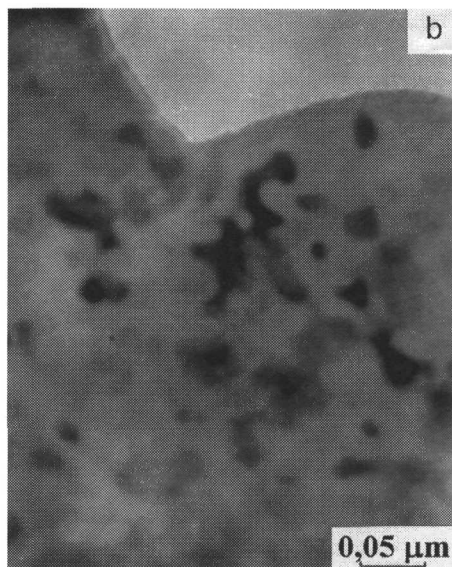


Fig. 4b. Microstructure of the spherical cap (TEM, BF image).

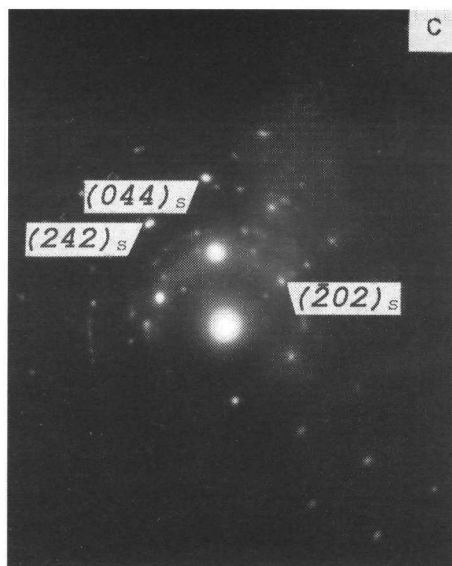


Fig. 4c. SAED pattern of spherical cap corresponding to $[\bar{1}\bar{1}1]$ zone of γ - Al_2O_3 spinel.

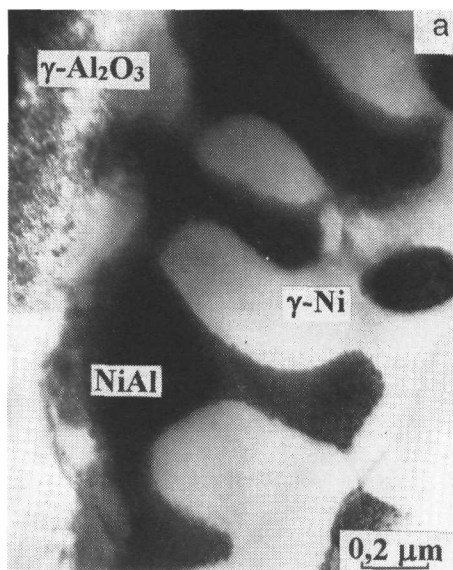


Fig. 5a. Microstructure of NiCrAlY metal-oxide interface (TEM, BF image).

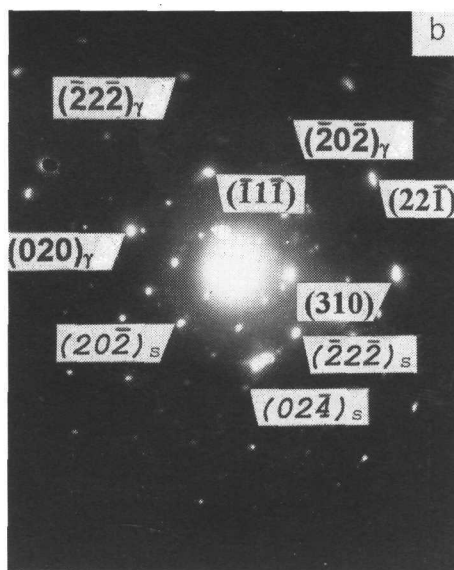


Fig. 5b. SAED patterns of metal-oxide interface corresponding to $[\bar{1}01]$ zone of $\gamma\text{-Ni}$ superimposed on $[\bar{1}34]$ zone of martensitic NiAl and $[121]$ zone of $\gamma\text{-Al}_2\text{O}_3$ spinel.

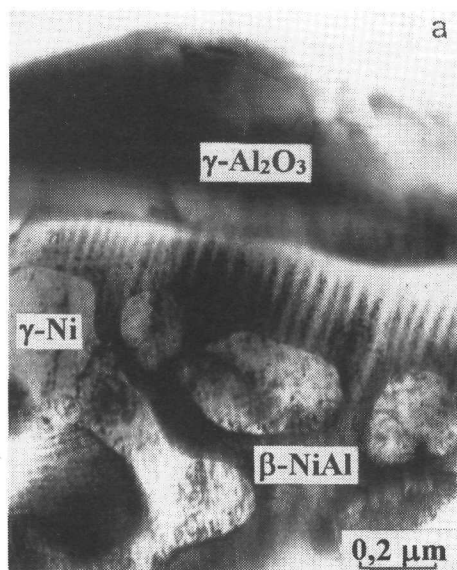


Fig. 6a. Microstructure of NiCrAlY metal-oxide interface (TEM, BF image).

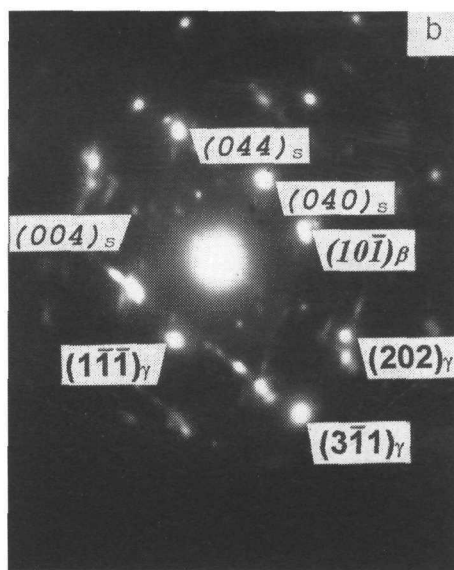


Fig. 6b. SAED patterns of metal-oxide interface corresponding to $[121]$ zone of $\gamma\text{-Ni}$ superimposed on $[\bar{1}0\bar{1}]$ zone of $\beta\text{-NiAl}$ and



Fig. 7a. Microstructure of NiCrAlY metal-oxide interface (TEM, BF image).

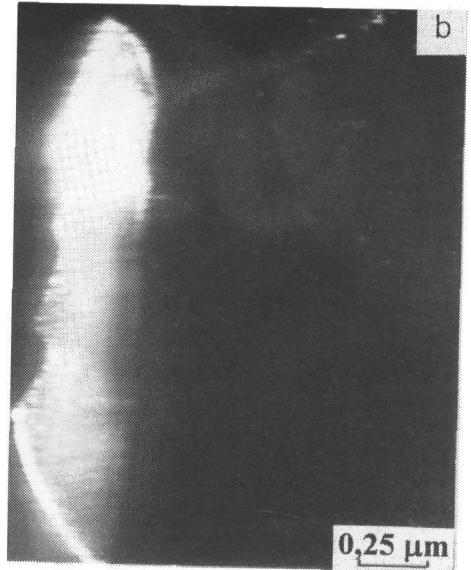


Fig. 7b. DF image formed using a $(11\bar{3})$ γ - Al_2O_3 spinel reflection (TEM).

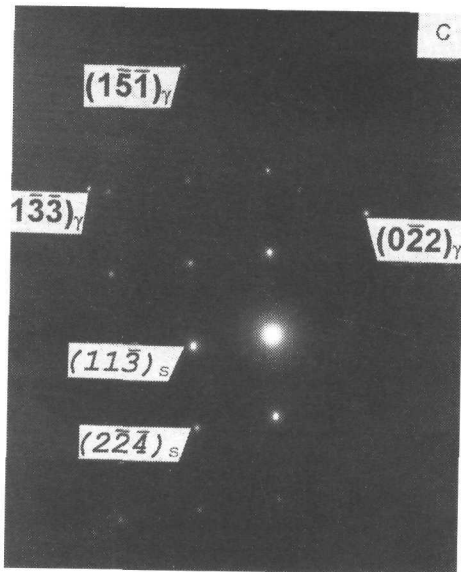


Fig. 7c. SAED patterns of metal-oxide interface corresponding to $[\bar{6}1\bar{1}]$ zone of γ -Ni superimposed on $[\bar{5}1\bar{2}]$ zone of γ - Al_2O_3 spinel.

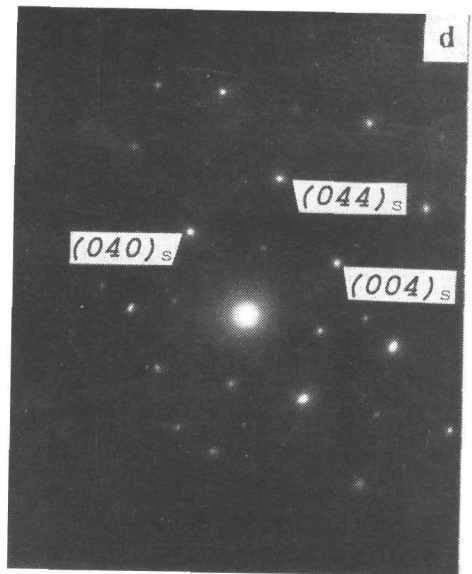


Fig. 7d. SAED pattern corresponding to $[\bar{1}11]$ zone of γ - Al_2O_3 spinel structure.

with a tetragonal Ll_0 structure adjacent to the oxide. The oxide structure could have been indexed only in terms of spinel structure with parameters close to γ - Al_2O_3 . However, superlattice reflections of the spinel structure can be easily distinguished, too.

The structures of β -NiAl grains with B_2 crystal structure and γ -Ni phases adjacent to the oxide cap are shown in the microstructure of the metal-oxide interface in Fig. 6a. The appropriate SAED patterns shown in Fig. 6b reveal that the oxide corresponds to the [100] zone of a slightly tetragonally distorted γ - Al_2O_3 spinel structure.

The metal-oxide interface is finally shown in Fig. 7a. SAED patterns shown in Fig. 7c reveal the presence of γ -Ni and γ - Al_2O_3 spinel in the interface microstructure. (11 $\bar{3}$) dark field image of oxide cap is shown in Fig. 7b. An appropriate tilting of the sample yields pattern of low index zone axis. A [$\bar{1}11$] SAED pattern of oxide alone corresponding to the γ - Al_2O_3 spinel structure is shown in Fig. 7d.

4. Discussion of results

Spherical caps are formed on the surface of the plasma sprayed NiCrAlY powders due to the interaction of melted particles with the surrounding atmosphere and the plasma. With respect to the chemical composition determined by EDX analyses, these caps belong to the oxide family of compounds.

The results of TEM have shown that these oxides were not amorphous, as they could be expected taking into account the high cooling rates of the plasma sprayed powders captured in water, but crystalline structures. The SAED patterns obtained from the oxides were nearly single crystal patterns. The size of oxide grains was found to be within the micrometer range. Selected area diffraction of the metal and oxide grains at one time showed no distinctive crystallographic alignment of oxide and metal planes.

Several caps with different chemical composition were investigated and their SAED patterns were analysed. All these patterns, quite independent on the chemical composition of caps, using γ -Ni reflections as internal calibration, could have been indexed only as spinel structures with parameters close to γ - Al_2O_3 . The differentiation of cubic γ - Al_2O_3 ($a = 0.7908$ nm) from cubic $NiAl_2O_4$ ($a = 0.8048$ nm) was concluded as EDX measurements indicated only negligible amounts of nickel in the oxides.

No possible indexing scheme allowed for the existence of hexagonal α - Al_2O_3 neither of any known Y containing ternary oxides (hexagonal $AlYO_3$, monoclinic $Al_2Y_4O_9$, cubic $Al_5Y_3O_{12}$). This implies the question of the position of Y and Cr detected by the EDX analysis in the crystal structure of oxide caps.

Metastable Al_2O_3 phases including γ - Al_2O_3 fit into the category of defect spinels. Spinel structure is known to be able to accommodate a great variety of ions, different in kind, charge, and size. In oxide spinels, the tetrahedral ion can

be as large as Cd^{2+} (0.094 nm) or as small as Si^{4+} (0.04 nm). The octahedral ion can be as small as Ge^{4+} (0.068 nm) or as large as Ag^{1+} (0.129 nm) [3]. As the ion radii of Cr^{3+} , and Y^{3+} are equal to 0.0755 and 0.104 nm, respectively, these ions can be in principle accommodated by the spinel structure.

However, in some SAED patterns arrays of superlattice spots were observed. Generally, diffraction patterns taken in different regions of the oxide showed different intensities of superlattice reflections.

Similar phenomenon has been observed in several other experiments. Investigation of plasma sprayed aluminas revealed superlattice structures in $\gamma\text{-Al}_2\text{O}_3$ [4] after annealing 50 h at 1223 K. Similar superlattices have been found using electron diffraction in metastable alumina evolved from the melt [5].

The initial formation of metastable Al_2O_3 phases seems to be a general phenomenon of alumina forming alloys as reported in [6–8]. Various metastable Al_2O_3 phases including $\gamma\text{-Al}_2\text{O}_3$, $\delta\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$ have been reported as intermediate steps on the way to the transformation to thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ [9]. However, it is the ordering of cations that principally gives rise to different Al_2O_3 polymorphs. Particularly, in $\gamma\text{-Al}_2\text{O}_3$ the aluminium ions are considered to be arranged randomly on the octahedral and tetrahedral sites. The term $\delta\text{-Al}_2\text{O}_3$ has been used in general to label a tetragonal phase ($c \cong 3a$) that is based on the same fcc packing of anions as in spinel, but with a higher ordering of the cationic sites [5]. $\theta\text{-Al}_2\text{O}_3$ is a monoclinic metastable Al_2O_3 polymorph that is also an ordered form of the $\gamma\text{-Al}_2\text{O}_3$ spinel phase [6]. The formation of γ , δ , and θ alumina may be seen as a part of the gradual transition from disordered to fully ordered structures.

For the ideal spinel lattice it appears that the reflections, the indices of which after division by two still belong to a face centred lattice, originate both from the oxygen sublattice and the cation sublattice. Reflections with odd indices originate from the total cation sublattice while the contributions from the oxygen sublattice are negligible. Reflections with even indices, which upon division by two do not belong any more to a face-centred lattice, originate only from the cations in tetrahedral positions; the contributions from the oxygen sublattice and the cations in octahedral positions are negligible [10]. Superlattice reflections found in the SAED patterns [6–8] are understood to be caused by cation ordering and arise as a result of the transformation of the cubic structure of $\gamma\text{-Al}_2\text{O}_3$ to $\delta\text{-Al}_2\text{O}_3$ or $\theta\text{-Al}_2\text{O}_3$. Thus, the cation ordering due to thermal activation resulting from the effect of plasma beam can be the main reason for the superlattice reflections in the investigated SAED patterns.

Oxide caps on NiCrAlY powders plasma sprayed and captured in water were formed in inhomogeneous thermal conditions. These conditions effected the structure, cation ordering, and lattice distortions of oxides. Anyhow, as shown by the electron diffraction measurements, all these effects could have been accommodated

by the spinel structure of the γ -Al₂O₃. The transformation to the α -Al₂O₃ was not observed.

5. Conclusions

The structure of oxides formed on the surface of NiCrAlY (AMDRY 962) powders, plasma sprayed and captured in water, was studied in this paper.

The results of TEM have shown that these oxides were not amorphous but crystalline structures.

All the investigated oxides quite independent on the chemical composition had spinel structures with spacings close to those of γ -Al₂O₃.

No distinctive crystallographic alignment of oxide and metal planes has been observed.

Due to the effect of plasma beam inhomogeneous thermal conditions were assumed to be responsible for slight lattice distortions of oxides and superlattice reflections caused by cation ordering.

No transformations to the thermodynamically stable α -Al₂O₃ were observed.

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