MICROSTRUCTURE OF PLASMA SPRAYED NiCrAlY COATING ISOTHERMALLY EXPOSED AT 850 °C FOR 1, 10 AND 100 HOURS

KAROL IŽDINSKÝ[1*], JOZEF IVAN[1], MILINA ZEMÁNKOVÁ[1]

Results of structural studies performed with light microscopy and transmission electron microscopy on plasma sprayed NiCrAlY coatings isothermally exposed at 850 °C for 1, 10 and 100 hours are presented in this paper. The applied thermal treatment led to the decomposition of initial phases and to precipitation of α-Cr and γ'-Ni_3Al. It is shown that the precipitation of α-Cr in the γ/γ' matrix obeys orientation relationships.

Complete transformation of amorphous oxides into crystalline structures takes place within the 100 hour exposure. Spinel structures with spacings close to γ-Al_2O_3 are mostly formed, however, Cr_2O_3 and CrO_3 oxides were found too. No transformation to stable α-Al_2O_3 oxide has been observed.

Key words: NiCrAlY coating, microstructure, thermal treatment, TEM studies

MIKROŠTRUKTÚRA PLAZMOVÉHO POVLAKU TYPU NiCrAlY PO 1, 10 A 100 HODINÁCH IZOTERMICKEJ EXPOZÍCIE PRI TEPLOTE 850 °C

V práci sú uvedené výsledky štúdia štruktúry plazmového povlaku typu NiCrAlY po 1, 10 a 100 hodinách izotermickej expozície pri teplote 850 °C. Výsledky získané pomocou svetelnej mikroskopie a transmisnej elektrónovej mikroskopie ukázali, že uvedené tepelné spracovanie viedlo k rozpadu pôvodnej štruktúry nástreku a k precipitácii α-Cr a γ'-Ni_3Al. V práci je ukázané, že precipitácia α-Cr v matrici γ/γ' sa riadi orientačnými vzťahmi.

Po 100-hodinovej expozícii sa dosiahne kompletná transformácia amorfných oxidov na kryštalické. Najčastejšie pritom vznikajú spinelové štruktúry s parametrami blízkymi γ-Al_2O_3. Oxidy Cr_2O_3 a CrO_3 boli v štruktúre nástreku taktiež identifikované. Transformácia na stabilný oxid α-Al_2O_3 sa nezistila.

[1] Ústav materiálov a mechaniky strojov SAV, Račianska 75, 831 02 Bratislava 3, Slovak Republic

[*] corresponding author

1. Introduction

The microstructure of as-plasma sprayed NiCrAlY coating is formed by a heterogeneous mixture of matrix metal, non-molten powders and oxide inclusions [1]. The microstructure of the matrix metal is fine-grained with the grain sizes not exceeding 1 μm. It was found to consist of nickel based solid solution γ-Ni with bcc structure, martensitic NiAl with tetragonal Ll_0 structure and β-NiAl with B_2 crystal structure. Y is predominantly bound in the Ni_5Y yttride located in the grain boundary regions. Oxide inclusions are mostly aluminium base oxides with different amounts of Y, Cr or Ni. Chromium base oxides were rarely observed, too. All the oxide inclusions independently of their composition were determined as amorphous structures.

As shown in our latest work [2], isothermal exposure at the temperature 850 °C for 6 minutes leads to decomposition of nearly all initial phases and to precipitation of α-Cr and γ'-Ni_3Al. Precipitation of coherent phases, predominantly γ'--Ni_3Al is responsible for the dramatic increase of hardness to 384 HV10. However, all the oxide inclusions remained amorphous and their transformation into crystalline structures is expected after longer exposures at 850 °C or at higher exposure temperatures.

The aim of this work is to present the results obtained by microstructural studies performed on plasma sprayed NiCrAlY coating isothermally exposed at 850 °C for 1, 10 and 100 hours.

2. Experimental material and procedure

Nickel base powder AMDRY 962, with a nominal composition Ni22Cr10Al1.0Y and dimensions ranging from 106 to 45 μm, was plasma sprayed in air onto a steel substrate at a total power input of 32 kW. The coating was removed from the substrate and further isothermally exposed at 850 °C for 1, 10 and 100 hours. The heating rate was 20 °C/minute and subsequent cooling of samples was performed in air.

The same plasma spraying procedure, as well as analytical equipment and techniques including light microscopy (LM) and transmission electron microscopy (TEM), as reported in previous studies [1, 3–5], were used also in the present work and so the details will not be repeated here.

3. Results

Microstructures of NiCrAlY coatings isothermally exposed at 850 °C for 1, 10 and 100 hours are quite similar and are typically formed by a heterogeneous mixture of light matrix metal and numerous darkly appearing oxide inclusions. Large particles known from microstructural studies performed on as-plasma sprayed coating [1] did not appear in currently studied microstructures. Oxide inclusions are of

Table 1. Results of Vickers hardness measurements performed at NiCrAlY coatings isothermally exposed at the temperature of 850 °C

Hardness	Exposure time [hours]				
	0	0.1	1	10	100
HV 10	223	384	375	366	365

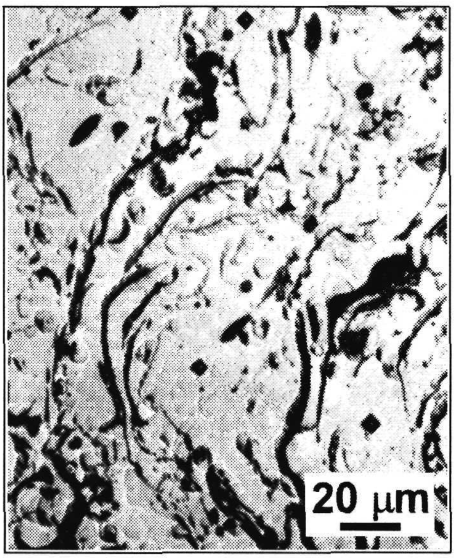


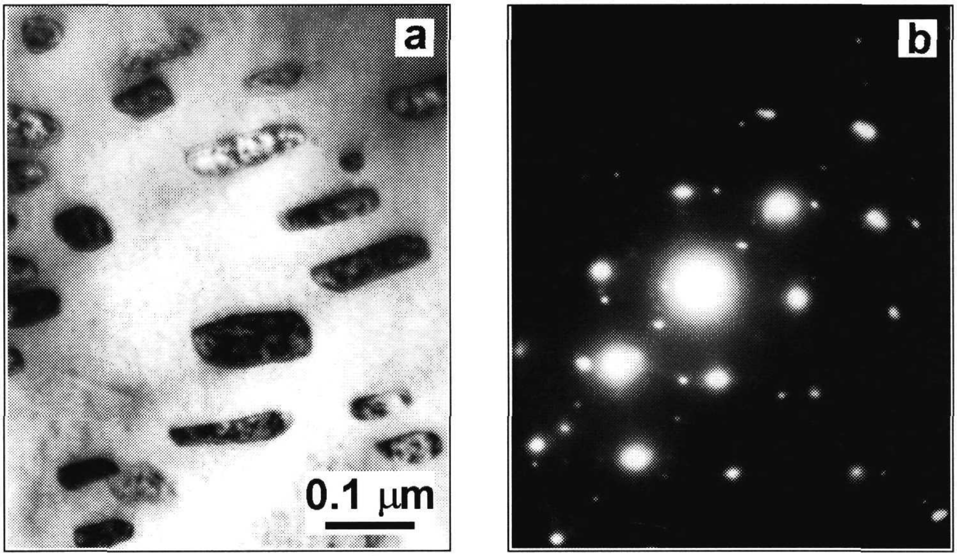
Fig. 1. Light micrograph revealing the typical microstructure of NiCrAlY coating isothermally exposed at 850 °C for 100 hours (ion etched).

various, predominantly elongated shapes, that do not change in dependence on the total time of exposure.

Results of Vickers hardness measurements are summarized in Table 1. Typical structure of NiCrAlY coating isothermally exposed at 850 °C for 100 hours is shown in Fig. 1.

TEM observations revealed that the metal matrix of the coating was formed by α-Cr and γ'-Ni_3Al precipitates distributed in the nickel based solid solution γ-Ni. α-Cr precipitates receive mostly platelet like morphology. Typical examples are shown in Figs. 2 and 3. Although the size of α-Cr precipitates generally grows with increasing time of exposure, many differences with respect to size and distribution were observed within each sample. This is because the actual growth is obviously governed by the local chemistry. Small α-Cr precipitates are coherent with the γ/γ' matrix obeying various orientation relationships as shown in Figs. 2c, 3c.

Besides γ-Ni reflections SAED patterns always show also forbidden reflections corresponding to coherent precipitates of γ'-Ni_3Al. They mostly appear in the



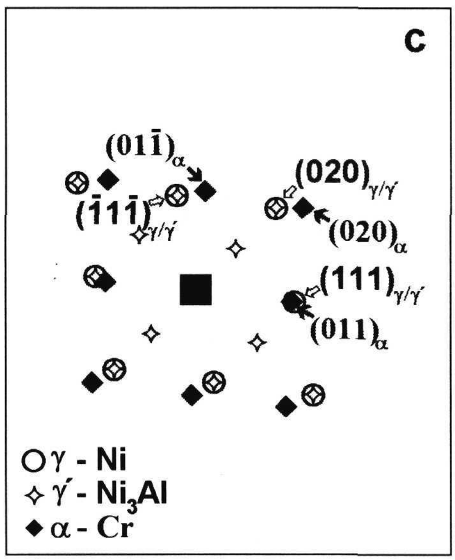
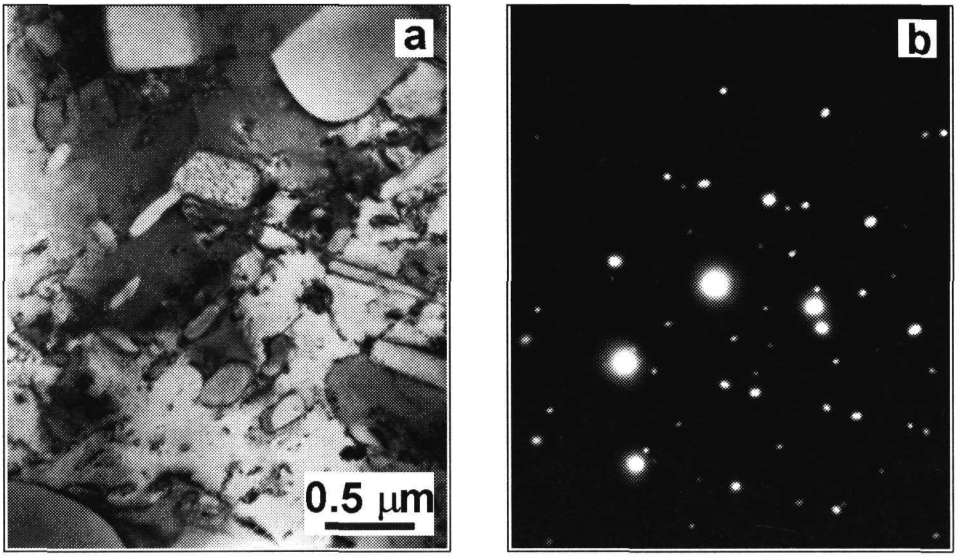


Fig. 2a. α-Cr platelets in the γ/γ' matrix of NiCrAlY coating isothermally exposed at 850 °C for 10 hours (TEM, bright field image).
Fig. 2b. SAED patterns corresponding to [$\bar{1}$00] zone of α-Cr superimposed on [$\bar{1}$01] zone of γ/γ'.
Fig. 2c. Indexed scheme corresponding to the SAED patterns in Fig. 2b showing the $(011)[\bar{1}00]_\alpha \| (111)[\bar{1}01]_{\gamma/\gamma'}$ orientation relationship.

form of discrete particles or subgrains separated by both antiphase boundaries and thin regions of disordered γ-Ni. Lamellar, cuboidal, and spherical morphology of γ'-Ni_3Al particles were observed. Typical example of γ'-Ni_3Al particles with cuboidal features is shown in Fig. 4.

Neither β-NiAl phase nor martensitic NiAl were observed in the microstructure of the thermally treated coatings. The presence of Ni_5Y yttride was not recognized



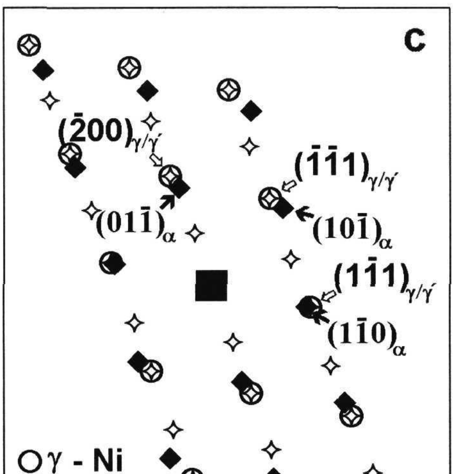


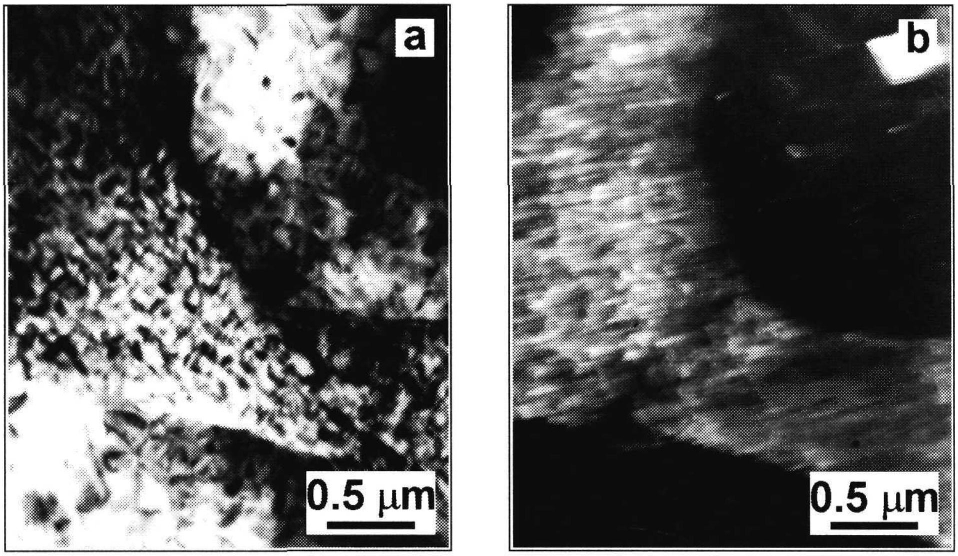
Fig. 3a. α-Cr platelets in the γ/γ' matrix of NiCrAlY coating isothermally exposed at 850 °C for 100 hours (TEM, bright field image).

Fig. 3b. SAED patterns corresponding to [111] zone of α-Cr superimposed on $[0\bar{1}\bar{1}]$ zone of γ/γ'.

Fig. 3c. Indexed scheme corresponding to the SAED patterns in Fig. 3b showing the $(1\bar{1}0)[111]_{\alpha} \| (1\bar{1}1)[0\bar{1}\bar{1}]_{\gamma/\gamma'}$ orientation relationship.

in the analysed SAED patterns, however, no particular attention has been paid to determination of this phase expected logically in the observed microstructures. Occasionally, $M_{23}C_6$ carbides coherent with the γ/γ' matrix were observed. A typical example is shown in Fig. 5.

The early transformation of amorphous oxides in the structure of NiCrAlY coating into crystalline structures was observed in samples exposed at 850 °C for 1



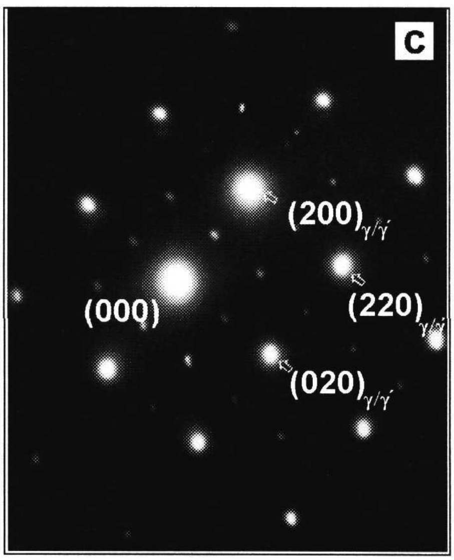


Fig. 4a. γ/γ' grain with γ'-Ni_3Al cuboids separated by both the antiphase boundaries and thin regions of disordered γ-Ni in the microstructure of NiCrAlY coating isothermally exposed at 850 °C for 1 hour (TEM, bright field image).
Fig. 4b. Dark field image of the $(020)_{\gamma/\gamma'}$ reflection (TEM).
Fig. 4c. SAED pattern corresponding to $[00\bar{1}]$ zone of γ/γ'.

hour. A typical example is shown in Fig. 6. As can be seen, numerous crystalline nuclei with random orientation appear in the original amorphous oxide. The SAED ring patterns correspond well to spacings close to γ-Al_2O_3 spinel structure.

Crystalline nuclei grow with increasing time of exposure as seen in Figs. 7 and 8. Most of the appearing oxides can be identified as γ-Al_2O_3 spinel type structures. Amorphous or only partially transformed oxides could have been found in samples

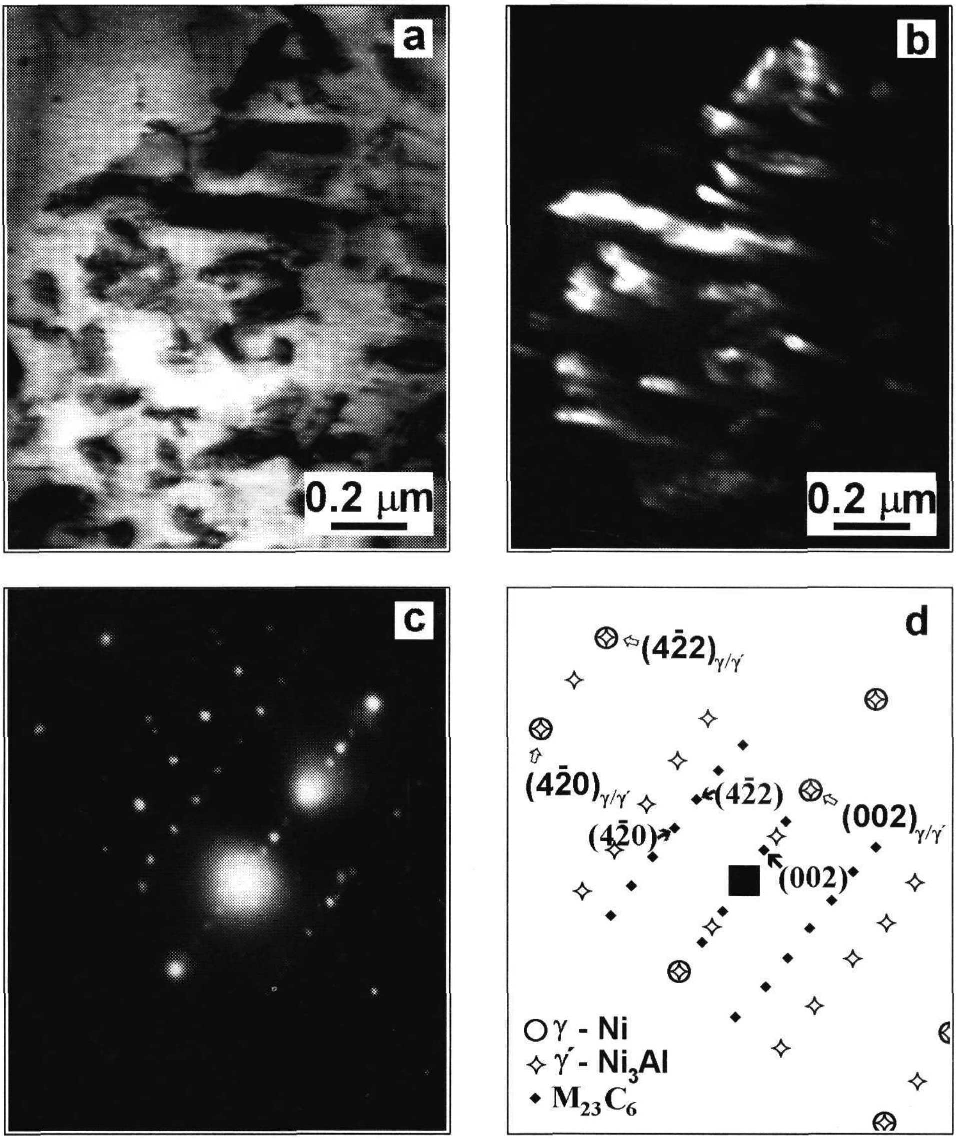


Fig. 5a. $M_{23}C_6$ carbides in the microstructure of NiCrAlY coating isothermally exposed at 850 °C for 10 hours (TEM, bright field image).

Fig. 5b. Dark field image of the $(4\bar{2}0)_{M23C6}$ reflection (TEM).

Fig. 5c. SAED patterns corresponding to [120] zone of $M_{23}C_6$ superimposed on [120] zone of γ/γ'.

Fig. 5d. Indexed scheme corresponding to the SAED patterns in Fig. 5c.

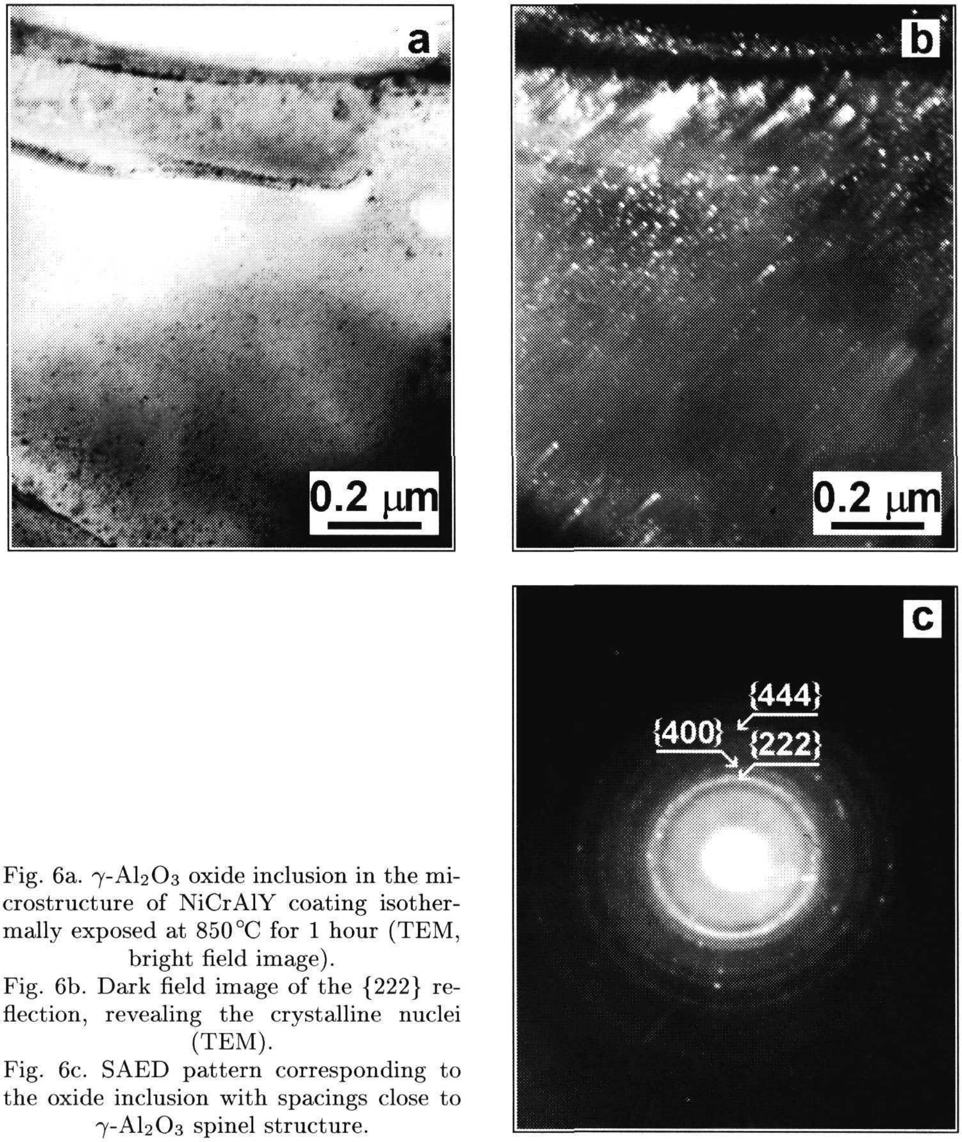


Fig. 6a. γ-Al_2O_3 oxide inclusion in the microstructure of NiCrAlY coating isothermally exposed at 850 °C for 1 hour (TEM, bright field image).
Fig. 6b. Dark field image of the {222} reflection, revealing the crystalline nuclei (TEM).
Fig. 6c. SAED pattern corresponding to the oxide inclusion with spacings close to γ-Al_2O_3 spinel structure.

exposed for 1 and 10 hours. Microstructure of the coating exposed for 100 hours contained only crystalline oxides.

Rarely, also other than alumina oxides were identified by electron diffraction. These were mostly chromia scales of both types, i.e., Cr_2O_3 and CrO_3. Typical examples are shown in Figs. 9 and 10. However, it should be stressed that no α-Al_2O_3 oxides were observed in any of the exposed structures.

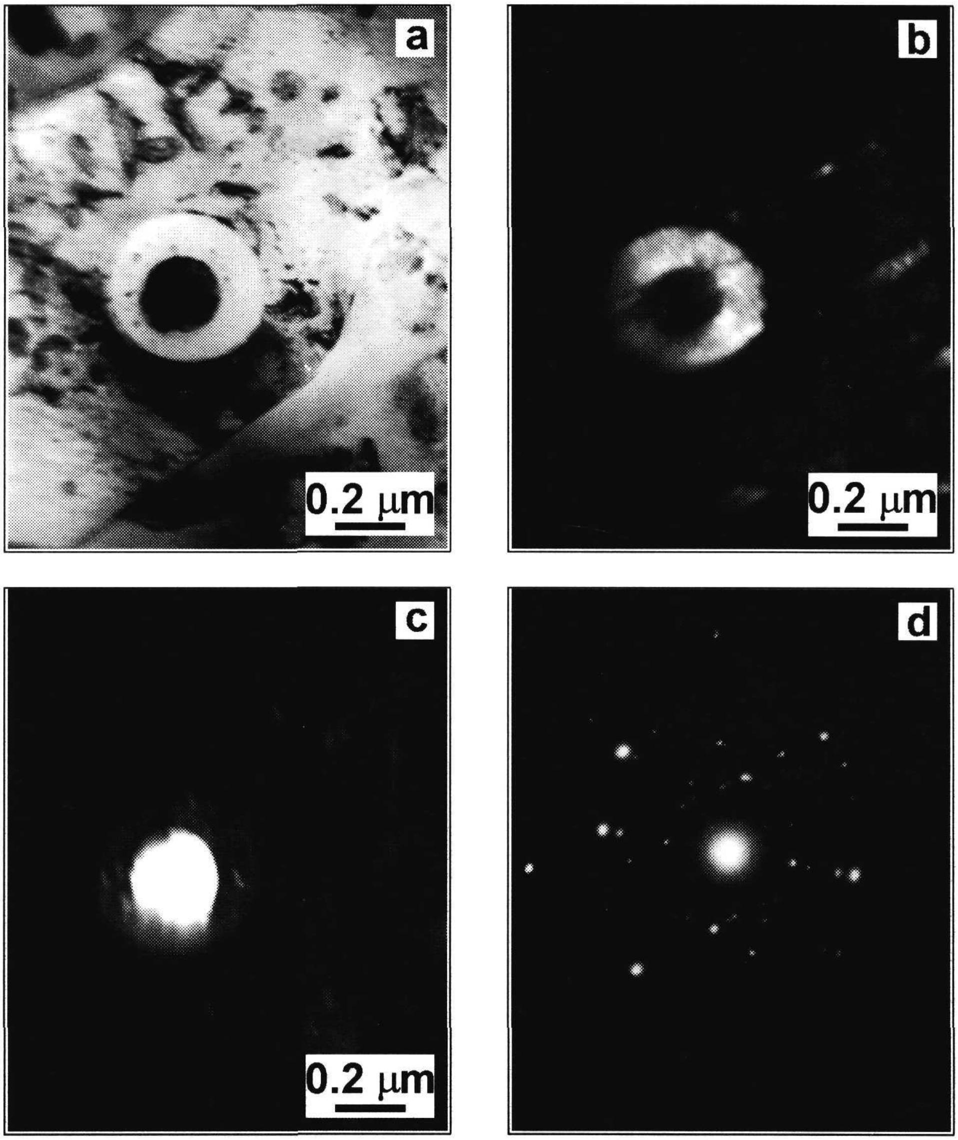


Fig. 7a. γ-Al_2O_3 oxide inclusion in the microstructure of NiCrAlY coating isothermally exposed at 850 °C for 10 hours (TEM, bright field image).
Fig. 7b. Dark field image of the $(400)_{\gamma-Al2O3}$ reflection (TEM).
Fig. 7c. Dark field image of the $(\bar{1}31)_{\gamma/\gamma'}$ reflection (TEM).
Fig. 7d. SAED patterns corresponding to $[01\bar{1}]$ zone of γ-Al_2O_3 superimposed on $[2\bar{1}5]$ zone of γ/γ'.

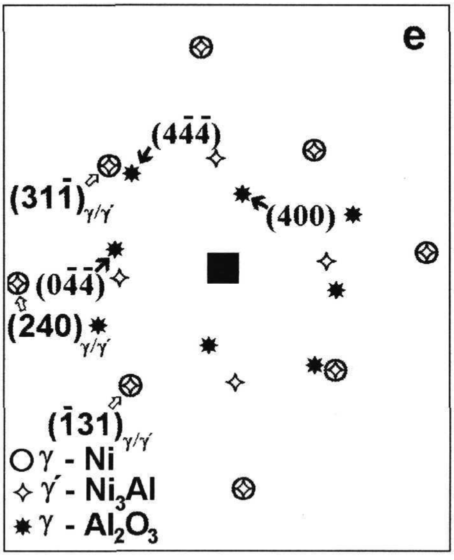


Fig. 7e. Indexed schematic corresponding to the SAED patterns shown in the Fig. 7d.

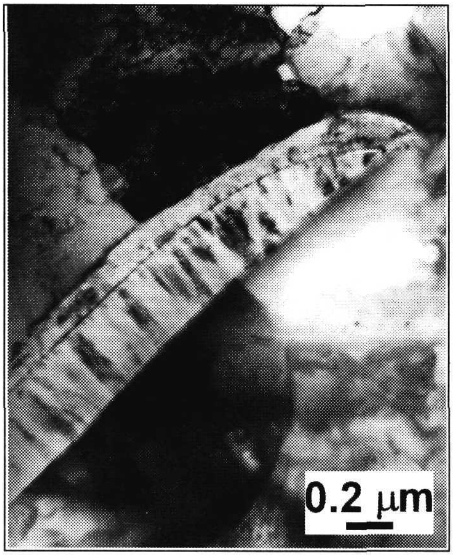


Fig. 8. γ-Al_2O_3 oxide inclusion in the microstructure of NiCrAlY coating isothermally exposed at 850 °C for 100 hours (TEM, bright field image).

4. Discussion of results

As shown in our previous work [2], already a very short time isothermal exposure at 850 °C leads to dramatic changes in the microstructure of the as-plasma sprayed NiCrAlY coating. Present results confirmed that microstructures after 1, 10 and 100 hour exposures are quite similar to that obtained after the 6 minute exposure, as revealed by light microscopy. Independently of the applied thermal treatment, microstructures are always formed by relatively homogeneous light matrix metal and darkly appearing oxide inclusions. The absence of initial casting microstructure of non-molten particles [1], due to phase transformations initiated by the applied thermal treatment, was also confirmed in this work.

The obtained hardness values are very close, although slightly below, the hardness measured in the previous work [2]. Comparison of hardness of as-plasma sprayed and as-thermally treated coatings is shown in Table 1.

The dominant role of temperature and not that of time on the hardness of the coating is quite evident. It can be assumed that the non-equilibrium as-plasma

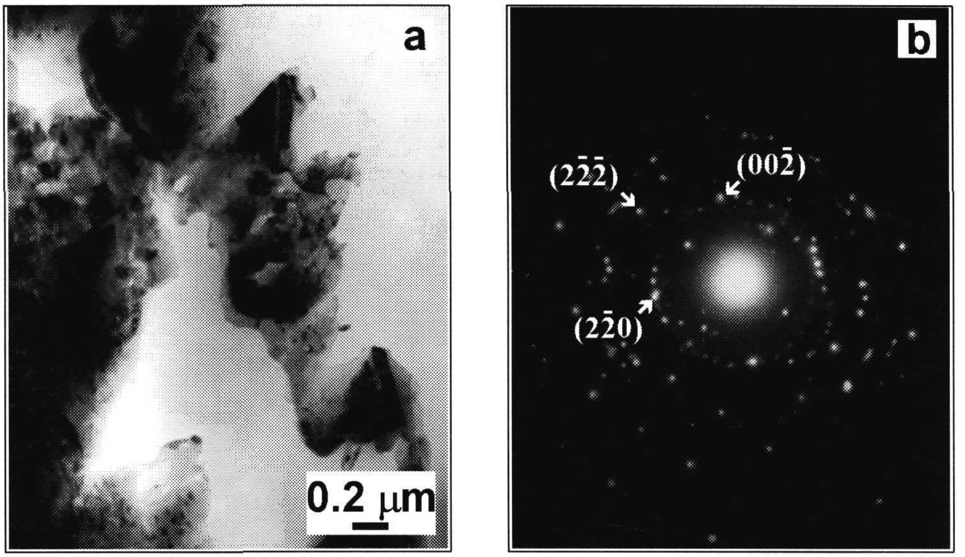
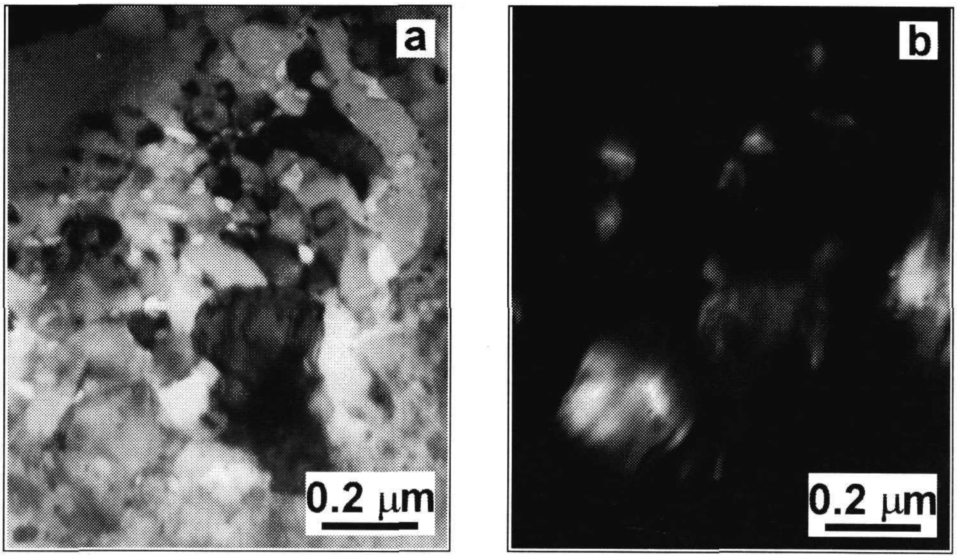


Fig. 9a. CrO_3 oxide in the microstructure of NiCrAlY coating isothermally exposed at 850 °C for 10 hours (TEM, bright field image).
Fig. 9b. SAED pattern corresponding to [$\bar{1}\bar{1}$0] zone of CrO_3.

sprayed microstructure transforms rapidly during early stages of isothermal exposure at 850 °C into more stable microstructure that does not dramatically change by subsequent long time exposures.

However, this assumption has been confirmed by present results above all with respect to the metal matrix. It was repeatedly determined that the decomposition of initial phases including NiAl had been completed in early stages of exposure, as none of them was observed in any of the analysed samples. α-Cr or γ'-Ni_3Al appear in all the investigated microstructures exhibiting typical morphologies. Generally, no dramatic change in their morphologies was observed, however, the impression, that with increasing time of exposure the size of precipitates grows, is quite clear. On the other hand, quite a big differences can be found within each sample and so these results are to be accepted rather qualitatively than quantitatively. This is undoubtedly due to extensive heterogeneity that is intrinsic to plasma sprayed coatings.

The origin of the increased hardness of the thermally treated coating is to be related to phase transformations observed already in [2]. No further increase was determined in the present work what is in a good agreement with the general knowledge [6] that the highest hardness is achieved in early stages of precipitation. The efficiency of hardening decreases with increasing size of precipitates. No dramatic



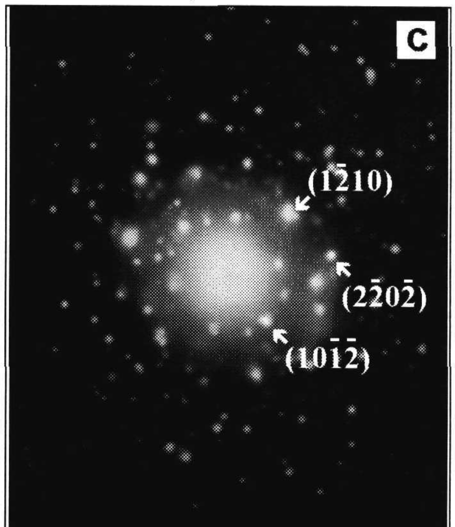


Fig. 10a. Cr_2O_3 oxide in the microstructure of NiCrAlY coating isothermally exposed at 850 °C for 100 hours (TEM, bright field image).
Fig. 10b. Dark field image of $(10\overline{1}\overline{2})$ reflection of Cr_2O_3 oxide (TEM).
Fig. 10c. SAED pattern corresponding to $[\overline{2}\overline{1}3\overline{1}]$ zone of Cr_2O_3.

increase in the size of γ'-Ni_3Al and α-Cr phases was observed what corresponds well to only very small decrease of hardness of thermally exposed coatings when compared with [2].

Orientation relationship between α-Cr and γ/γ' as determined already in [2] and its variants (Figs. 2c, 3c) were observed in this work. This orientation relationship is based on the close interplanar distances of (110) of α-Cr where $d_{(110)} = 0.2036$ nm and (111) of γ/γ' where $d_{(111)} = 0.2031$ nm, what gives the d-spacing mismatch less than 0.25%.

TEM observations [1–4] confirmed the presence of Ni_5Y yttride in the microstructure of initial and as-plasma sprayed NiCrAlY powders as well as in as-plasma sprayed and isothermally exposed coating. This is in a good agreement with the results presented by the authors [7] as Ni_5Y yttride dissolves at temperatures higher than 1000 °C. This is why we assume that, though not directly determined, the yttride is still present in the analysed samples subjected also to longer exposures.

Carbides of $M_{23}C_6$ were observed exclusively in the microstructure of NiCrAlY coating subjected to isothermal exposure for 10 hours. They were not observed in other samples. Therefore we assume that the appearance of carbides can be considered as a local event related to the applied technology of plasma spraying.

No really rapid transformation of amorphous oxides into crystalline structures was observed. Even after the exposure for 10 hours the majority of oxides still exhibits amorphous structures. The oxides differ in size, shape and chemical composition what undoubtedly affects the kinetics of their transformation. Anyway after 100 hour exposition no amorphous oxide was observed what confirms that the transformation had been completed.

Small crystalline oxide nuclei with random orientation initially provided ring diffraction patterns. As they grew, also some monocrystalline patterns could have been obtained. They were predominantly identified as spinel structures with spacings close to γ-Al_2O_3. However, as reported already in [1] the oxides contain besides Al also different amounts of Ni, Cr and Y. The differentiation of cubic γ-Al_2O_3 ($a = 0.7908$ nm) from cubic $Ni(Al,Cr)_2O_4$ ($a = 0.8048$ nm) is hardly possible analysing the obtained SAED patterns. Therefore with respect to chemical heterogeneity of oxides we assume that both types are formed and that this process is governed by the local chemistry. 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 $Al_5Y_3O_{12}$).

Some of the amorphous oxides with large amounts of Cr transform into Cr_2O_3 and CrO_3 as determined by electron diffraction. These oxides, that are predominantly formed in the temperature range below 1000 °C, were determined also by the authors [7].

Finally, the actual position of Y and Cr atoms in the spinel crystal structure may attract some attention. As already discussed [5], γ-Al_2O_3 fits 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 0.094 nm or as small as 0.04 nm. The octahedral ion can be as small as 0.068 nm or as large as 0.129 nm [8]. As the ion radii of Cr^{3+} and Y^{3+} are equal to 0.0755 nm and 0.104 nm, respectively, these ions can be principally accommodated by the spinel structure.

5. Conclusions

The microstructure of NiCrAlY (AMDRY 962) plasma sprayed coating isothermally exposed at the temperature 850 °C for 1, 10 and 100 hours was studied in this paper. The applied thermal treatments led to the decomposition of initial microstructure of the coating and to precipitation of α-Cr and γ'-Ni_3Al in the γ-Ni matrix.

Following orientation relationships between α-Cr and γ/γ' were observed:

$$(011)[\bar{1}00]_{\alpha}||(111)[\bar{1}01]_{\gamma/\gamma'},$$
$$(1\bar{1}0)[111]_{\alpha}||(1\bar{1}1)[0\bar{1}\bar{1}]_{\gamma/\gamma'}.$$

No significant coarsening of α-Cr and γ'-Ni_3Al precipitates within the applied exposures was observed. The hardness achieved in early stages of precipitation was attained also after longer exposure times.

Complete transformation of amorphous oxides into crystalline structures takes place within the 100 hour exposure. Spinel structures with spacings close to γ-Al_2O_3 are mostly formed, however, Cr_2O_3 and CrO_3 oxides were found, too. No transformation to stable α-Al_2O_3 oxide has been observed.

Acknowledgements

The authors gratefully acknowledge the Scientific Grant Agency of Ministry of Education of the Slovak Republic and Slovak Academy of Sciences (Grant project No. 5096/98) for the financial support of this work and Mr. V. Kolenčiak for the preparation of plasma sprayed samples.

REFERENCES

[1] IŽDINSKÝ, K.—IVAN, J.—ZEMÁNKOVÁ, M.—KOLENČIAK, V.: Kovove Mater., *36*, 1998, p. 367.
[2] IŽDINSKÝ, K.—IVAN, J.—ZEMÁNKOVÁ, M.: Kovove Mater., *38*, 2000, p. 329.
[3] IŽDINSKÝ, K.—IVAN, J.—ZEMÁNKOVÁ, M.—KOLENČIAK, V.: Kovove Mater., *35*, 1997, p. 188.
[4] IŽDINSKÝ, K.—IVAN, J.—ZEMÁNKOVÁ, M.—KOLENČIAK, V.: Kovove Mater., *35*, 1997, p. 322.
[5] IŽDINSKÝ, K.—IVAN, J.—ZEMÁNKOVÁ, M.—KOLENČIAK, V.: Kovove Mater., *36*, 1998, p. 87.

[6] BARRETT, C. S.: Structure of Metals. New York, McGraw-Hill 1952.
[7] SACRÉ, S.—WIENSTROTH, U.—FELLER, G.—THOMAS, L. K.: Journal of Materials Science, *28*, 1993, p. 1843.
[8] MULLER, O.—ROY, R.: The Major Ternary Structural Families. Berlin, Springer Verlag 1974.

Received: 14.3.2001