

Analysis of NiCrAl powder doped by Fe and Si after high temperature exposure

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Received 23 January 2015, received in revised form 15 July 2015, accepted 9 November 2015

Abstract

In this work structural changes of NiCrAl doped by Fe and Si powder after annealing at high temperatures are observed. The material under study was annealed at 800, 1000 and 1200 °C in an air atmosphere for 24 h and the structures obtained were compared with the as-received state. Phase analyses were performed based on X-ray diffraction measurements. The lattice parameters of current phases were measured and quantitative analyses were carried out by the Rietveld refinement from the XRD patterns measured. The character and size of powder particles as well as their chemical composition were studied by SEM equipped with EDX. After exposure at 800 °C for 24 h, the major part of whole material still in a primer solid solution formed, unlike after exposure at 1200 °C whole volume of material transformed into oxides. The presence of different oxides was observed after heating at different temperatures with dominance of NiO. Change of lattice parameters of present phases was observed, what can be concluded as a dissolution effect.

Key words: high-temperature oxidation, NiCrAl powder, phase transformation

1. Introduction

The aim of our work is to study high-temperature oxidation of MCrAl powders commonly used as material for thermal barrier coating systems. The current work is focused on NiCrAl, doped by Fe and Si; NiCrAlY and CoNiCrAlY powders will be studied in the following research.

Material formed into a layer usually exhibits a high number of deviations from the theoretical ideal state in consequence of the manufacturing process, for example, preferred orientation, lattice distortions, etc. When oxidation occurs, the newly formed phases are often affected by the above defects of preliminary phases, which can then cause complications with analysing and correctly and accurately quantifying the phases within the structure. The analysis is the more problematic, the smaller the quantity of the phase is in the whole analysed volume of material.

The idea of and the motivation for the work are to observe oxidation of the material in the form of as-received powder and to study phase transformations

in the basic state with reduced number of defects, and later on to compare obtained results with oxidation of material in the form of layers prepared by different technologies (plasma, cold spray, etc.) [1–3].

2. Materials and methods

For the experiment commercially obtainable NiCrAl powder was used. The chemical analysis showed the powder also contained minor volume of Fe and Si beside expected Ni, Cr and Al. Exact chemical composition of powder is shown in Table 1. The powder on a fireclay plate was put into a pre-heated furnace and then exposed for 24 h in air atmosphere. The temperatures studied in this work were set to 800, 1000 and 1200 °C. The highest set temperature, 1200 °C is out of range of common use for NiCrAl, such temperature was chosen to make comparison with other studied materials, NiCrAlY and CoNiCrAlY. After heating, the powders were slowly cooled down and then analysed. Some of the samples

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Table 1. Chemical composition of NiCrAl powder in as-received state and after exposure at 800, 1000, and 1200 °C for 24 h

Element (wt.%)	O	Al	Si	Cr	Fe	Ni
As-received	–	1.13	3.65	8.85	2.31	84.06
800 °C	20.79	4.91	2.12	17.52	1.97	52.69
1000 °C	23.34	1.3	5.27	9.65	2.45	57.99
1200 °C	25.47	1.39	3.72	7.46	2.09	59.87

studied were sintered at higher temperatures; they were ground back to powder in an agate bowl. Chemical analyses were performed and the size and morphology of particles were analysed with an aid of SEM Philips equipped with EDX. X-ray diffraction of powders after exposure was measured and refined and results were compared to an as-received state.

Phase analyses were performed from the diffraction pattern measured on obtained specimen, lattice parameters and quantitative analyses were calculated by the Rietveld refinement.

X-ray diffraction was measured at 3kW Smartlab from Rigaku. Diffractometer was set up in Bragg-Brentano geometry using Cu K α radiation ($l = 1.54 \text{ \AA}$) equipped with linear detector Dtex Ultra. The Cu lamp was operated at a current of 30 mA and a voltage 40 kV. The diffraction of specimens was measured in the 2-Theta range from 15° to 150° with a step size of 0.02° and a speed of 0.3 s/step.

The phase analysis was performed based on chemical composition and using the PDF2 and ICSD databases. The Rietveld refinement was used for the evaluation of lattice parameters and quantity of present phases. Peak profiles were fitted by the Pseudo-Voigt function, the background was refined using the polynomial function of 5th order. Lattice parameters of current phases were calculated using the equation describing Bragg's law:

$$n\lambda = 2d \sin \theta, \quad (1)$$

where n is an integer, λ is the wavelength of incident wave, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident X-ray and the scattering planes.

The quantitative phase analysis was performed using the formalism described by Hill and Howard [4]. The general scattering cross-section for Bragg scattering is proportional to N/V , where N is the number of unit cells contributing to the scattering and V is the unit cell volume. The scale factor S is then proportional to N/V . The weight fraction of phase p can then be derived as:

$$W_p = \frac{(SZMV)_p}{\sum_i (SZMV)_i}, \quad (2)$$

where S is the scale factor, Z is the number of formula

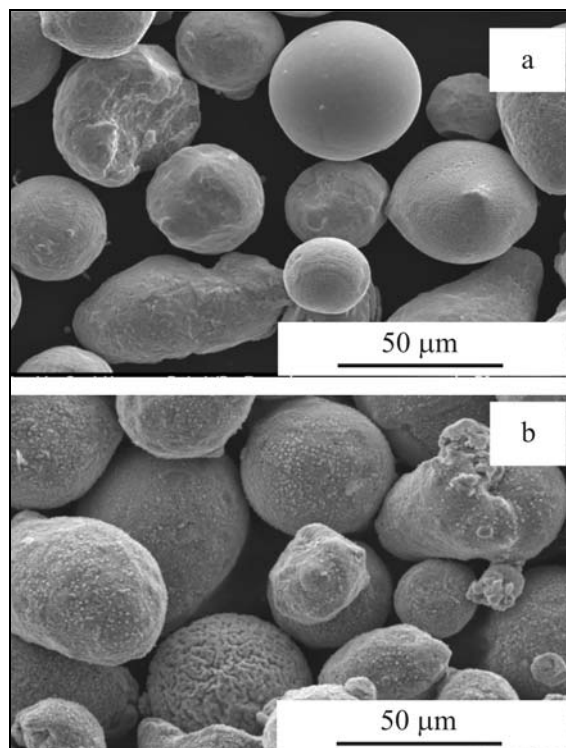


Fig. 1. SEM image of NiCrAl powder in as-received state a) and after exposition to 800 °C b).

units per unit cell, M is the molecular weight of the formula unit, V is the unit cell volume and i is an index running over all phases.

It is worth noting that $S \times V$ is proportional to the number of diffracting unit cells (N) and $Z \times M$ is just the molecular weight of the unit cell, hence $S \times V \times Z \times M$ is proportional to the weight of the diffracting sample. Other fractions, such as volume fraction are also easily calculated, e.g., volume fraction:

$$V_p = \frac{(SV^2)_p}{\sum_i (SV^2)_i}. \quad (3)$$

3. Results and discussion

The powder in as-received state comprises uniform ball-like particles of about 43 μm in size (see Fig. 1).

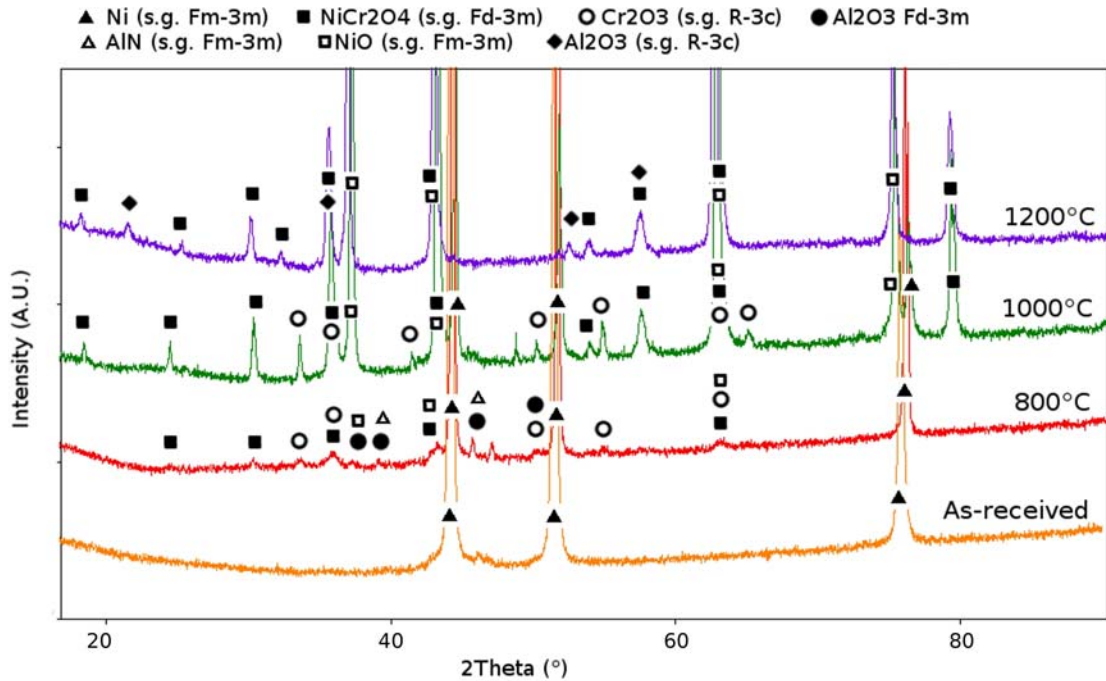


Fig. 2. XRD patterns of NiCrAl in as-received state and after 24-hours exposure at 800, 1000 and 1200°C (s.g. as space group).

The character and size of the particles after heating at 800°C have not been changed, while after exposition at 1000 and 1200°C the powder was sintered. The material consists mainly of Ni (84 wt.%) with additions of Cr, Fe, Si and Al with uniform distribution. The results of chemical analysis of the powder in as-received state and after thermal exposure are shown in Table 1.

Diffraction patterns of the material after three different thermal exposures are compared to the as-received state in Fig. 2. The NiCrAl powder in as-received state consists of one phase, solid solution face-centred cubic Ni, space group (s.g.) Fm-3m, with the lattice parameter $a = 3.548 \text{ \AA}$. The measured lattice parameter is slightly bigger compared to the literature value for pure Ni (3.532 \AA) due to the presence of substitutional alloying elements ($a_{\text{Cr}} = 1.249 \text{ \AA}$, $a_{\text{Al}} = 1.431 \text{ \AA}$) [5].

Annealing for 24 h at 800°C leads to the formation of five new phases in addition to the initial Ni-based solid solution (91 wt.%): NiCr₂O₄ (1 wt.%), Cr₂O₃ (1 wt.%), Al₂O₃ (4 wt.%), NiO (2 wt.%) and AlN (1 wt.%); the lattice parameters and space groups (s.g.) of phases are given in Table 2.

NiCrAl powder after annealing for 24 h at 1000°C shows presence of four phases: original Ni-based solid solution (19 wt.%), NiCr₂O₄ (13 wt.%), Cr₂O₃ (4 wt.%), NiO (64 wt.%). Lattice parameters and space groups are noticed in Table 2.

After annealing for 24 h at 1200°C, whole volume of material oxidised. The initial one-phase structure transformed completely into three other phases:

NiCr₂O₄ (23 wt.%), NiO (75 wt.%) and Al₂O₃ (1 wt.%) with different lattice than after exposure at 800°C; the lattice parameters and space groups are given in Table 2.

The different temperatures of annealing of NiCrAl ranging from 800°C to 1200°C then resulted in the transformation of different phases. After the 24 h exposition at temperatures between 800°C and 1200°C, NiCr₂O₄ and NiO formed in the whole temperature range in different fractions. With increasing annealing temperature, an increase of quantities was observed for the two oxidic phases NiCr₂O₄ and NiO, from 1 to 23 wt.% and from 2 to 75 wt.%, respectively. After a 24 h exposure at 1200°C, the original cubic Ni-based solid solution disappeared, the material transformed into mainly oxidic phases with NiO predominating (75 wt.%). After thermal expositions up to 1000°C, Cr₂O₃ was formed too, with the volume slightly increasing with higher temperature, 1 wt.% for 800°C and 4 wt.% for 1000°C. Presence of Al₂O₃ was observed after annealing at 800 and 1200°C but not at 1000°C. At different temperatures the Al₂O₃ phase formed with different lattices, cubic face-centred at 800°C and rhombohedral at 1200°C, with a slightly higher amount of 4 wt.% at 800°C compared to 1 wt.% at 1200°C. Unlike the lower temperature exposition at 1200°C another phase was formed, rhomboedral Al₂O₃ in a volume of 2 wt.%.

A change in the lattice parameter of Ni-based solid solution was observed after thermal exposure. With increasing temperature of exposure, the lattice para-

Table 2. Analysis of NiCrAl powder after 24 h exposition at 800, 1000 and 1200 °C: current phases (s.g. as space groups), their quantity and lattice parameters

NiCrAl		As-received	800 °C, 24 h	1000 °C, 24 h	1200 °C, 24 h
Ni. s.g. Fm-3m	(wt.%)	100	91	19	
	<i>a</i> (Å)	3.548	3.532	3.524	
NiCr ₂ O ₄ . s.g. Fd-3m	(wt.%)		1	13	23
	<i>a</i> (Å)		8.335	8.312	8.282
Cr ₂ O ₃ . s.g. R-3c	(wt.%)		1	4	
	<i>a</i> (Å)		4.987	4.958	
	<i>c</i> (Å)		13.483	13.578	
Al ₂ O ₃ . s.g. Fd-3m	(wt.%)		4		
	<i>a</i> (Å)		7.921		
AlN. s.g. Fm-3m	(wt.%)		1		
	<i>a</i> (Å)		3.852		
NiO. s.g. Fm-3m	(wt.%)		2	64	75
	<i>a</i> (Å)		4.147	4.176	4.167
Al ₂ O ₃ . s.g. R-3c	(wt.%)				2
	<i>a</i> (Å)				4.747
	<i>c</i> (Å)				13.001

meter of Ni-based phase shows a decreasing trend, which can be explained by the dissolution of solid solution. An evaluation of atomic parameters of elements present in the material leads to the conclusion that the dissolution of substitutional Al atoms has the most significant effect. Also the decreasing lattice parameter of Ni solid solution corresponds to the increasing amount of NiO, with NiO lattice parameter increasing with exposure to higher temperatures.

4. Conclusions

Oxidation of NiCrAl powder at different temperatures was compared. After 24 h exposure the presence of the oxides NiO and NiCr₂O₄ was observed in the whole range of the temperatures used, from 800 to 1200 °C. From the change in the quantity of the initial Ni-based solid solution it can be concluded that the oxidation rate increased greatly with increasing temperatures, from 91 wt.% of Ni at 800 °C to 19 wt.% of Ni at 1000 °C with no presence of Ni-based solid solution being observed after 1200 °C exposition. The dominant oxidic phase was NiO with 64 wt.% and 75 wt.% after 1000 and 1200 °C exposures, respectively; another significant oxidic phase was NiCr₂O₄ with 13 wt.% and 23 wt.% after 1000 and 1200 °C exposures, respectively. A decrease in the lattice parameter of the initial Ni-based solid solution was observed after different temperature exposures, corres-

ponding to the increasing amount of newly formed oxidic phases and also to the increase in the lattice parameter of NiO which is supposedly the result of chemical dissolution.

Acknowledgement

This work was supported by the project “Excellent young researcher at BUT” CZ.1.07/2.3.00/30.0039 from European Social Fund.

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