77/14

Archives of Foundry,
Year 2004, Volume 4, № 14
Archiwum Odlewnictwa,
Rok 2004, Rocznik 4, Nr 14
PAN – Katowice PL ISSN 1642-5308

SOLIDIFICATION OF THE ZrO_2-Y_2O_3 CERAMICS ONTO THE Ni-SUBSTRATE

W. WOŁCZYŃSKI[1], J. SZAJNAR[2], A. PAWŁOWSKI[3]
[1, 3] Institute of Metallurgy and Materials Science, Polish Academy of Sciences,
Reymonta 25, 30 059 Kraków, Poland
[2] Institute of Engineering Materials and Biomaterials,
Silesian University of Technology, Towarowa 7, 44 100 Gliwice, Poland

SUMMARY

A theory for solute microsegregation and solute redistribution has been applied to describe the behaviour of ZrO_2 solute within the three regions visible in a ceramic layer morphology. The theory allowed for selecting measurement points, which can be analysed by means of some equations taking into account both phenomena partitioning and back-diffusion. The theoretical profiles of solute redistribution have been plotted to fit selected measurement points. The plotted curves of ZrO_2 solute redistribution allowed to deduce the geometry of growth within the analysed sub-layers obtained during the atmospheric plasma spraying and solidification of ZrO_2-Y_2O_3 ceramics onto Ni-substrate. A model of a structure formation during solidification of ceramic onto the metallic substrate is worked out. The 2D and 3D types of structure are taken into account in the model. The model contains also the sub-layer of chilled fine structure from the side of air as well as amorphous sub-layer from the side of Ni-substrate. The deduced model is compared with real morphology observed within the ceramic layer. EDX technique was applied to measurement of ZrO_2 solute redistribution.

Key words: segregation, ceramic plasma spraying, multi-layers structure

---

[1] *prof. dr hab. inż., nmwolczy@imim-pan.krakow.pl*
[2] *dr hab. inż., prof. Pol. Śl.*
[3] *prof. dr hab. inż.*

1. INTRODUCTION

Ceramic layers of the ZrO_2-Y_2O_3 type are usually produced by atmospheric plasma spraying (APS) on the metallic substrate. The layers are found as a good thermal barrier. This quite new technology is usually applied for gas turbines and engines, [3]. Ceramic powder is injected into plasma flame and next is propelled onto substrate during several milliseconds by plasma gas of Ar at the temperature of 10^4 [K]. The liquid or partially liquid ceramic strikes against the cold Ni-substrate, which is additionally cooled by the air stream. In effect, the rapid solidification of ceramic occurs. The cooling rate is estimated to be about 10^5 - 10^6 [K/s]. The Ni – substrate is initially coated by the NiCrAlY layer, which ensure good adherence of the solidifying ceramic.

The morphology of a coating depends on the nominal concentration of applied ceramic as well as on the solidification rate. The important role play also gun power, spray distance to substrate from which ceramic is sprayed, size of grains and temperature of substrate, [2].

The morphology of such a coating has already been analysed by means of High Resolution Electron Microscopy, (HREM), [3]. Chraska and King [3] have revealed both columnar and equiaxed grains of sprayed ceramic ZrO_2-Y_2O_3. The mentioned grains were accompanied by two layers: fine chilled crystals of the size of 30-100 [nm] and amorphous layer from the side of Ni-substrate.

An attempt is made in the current analysis to describe as precisely as possible the ceramic morphology due to ZrO_2-solute redistribution measured by means of the EDX technique. Finally, a model of ceramic coating should be made. The analysis of solute measurement will be done applying a theoretical model of solute microsegregation and solute redistribution after back-diffusion. A model will be related to adequate phase diagram, [1]. The calculated model of morphology will be related to the real morphology observed within the ceramic multi-layer.

2. FUNDAMENTALS OF THE APPLIED THEORY

The theory of solute microsegregation is based on the description of solute partitioning. The theory of solute redistribution takes into account both solute partitioning and back-diffusion into the solid, [4].

Physical fundamentals for both models are:

- complete mixing in the liquid,
- constant slope of the liquidus line and constant partition ratio of solute,
- liquid and solid compositions are then linear functions of temperature,
- constant density of the primary solid,
- negligibility of solid state diffusion along the cell axis,
- flat isotherms, which are perpendicular to the growth direction,
- s/l interface is at the equilibrium and interface undercooling is negligible,

- growth is plate-like, 1D, directional: cellular/dendritic, 2D or equiaxed, 3D,
- postulated equations do not depend on the geometry of crystal growth,
- densities of liquid and solid phases are equal to one another,
- increase of solute in advance of the tips of cells or dendrites is negligible,
- equilibrium growth and non-equilibrium freezing are integral parts of model.

A formation of the segregation profiles across a given sub-layer is a result of two different phenomena taking part in solidification. At first partitioning between *liquidus* and *solidus* lines is to be considered. As a result of partitioning microsegregation

$N_i^S(x,\alpha_i^D,L_i,N_{i-1},k_i)$, ($i=1,\ldots,n$) is formed.

$$N_i^S(x,\alpha_i^D,L_i,N_{i-1},k_i)=k_i\,N_i^L(x,\alpha_i^D,L_i,N_{i-1},k_i) \tag{1}$$

where

$$N_i^L(x,\alpha_i^D,L_i,N_{i-1},k_i)=N_{i-1}\left[(L_i+\alpha_i^D\,k_i\,x-x)/L_i\right]^{\frac{k_i-1}{1-\alpha_i^D k_i}} \tag{2}$$

is the solute concentration in the liquid at a given step of solidification, [4].

The phenomenon of back-diffusion smoothes a microsegregation. In a result, solute redistribution $N_i^B(x,X_i^0,\alpha_i^D,L_i,N_{i-1},k_i)$ is formed:

$$N_i^B(x,X_i^0,\alpha_i^D,L_i,N_{i-1},k_i)=\left[1+\beta_i^{ex}(x,X_i^0,L_i,k_i)\;\beta_i^{in}(X_i^0,\alpha_i^D,L_i,k_i)\right]\times N_i^S(x,\alpha_i^D,L_i,N_{i-1},k_i) \tag{3}$$

Symbols used in the mathematical formulations are denoted as follows:

k_i	partition ratio for a given range of solidification, i,
L_i	amount of liquid at a beginning of a given range of solidification, $L_1=1$,
n	number of ranges of solidification, $n=2$,
N_{i-1}	solute concentration at a beginning of a given range of solidification, i, N_0 - nominal concentration of the solute, $N_K=1$ - solute concentration in the liquid for the second step solidification,
x -	amount of a growing sub-layer related to 1 mole of a considered alloy,
X_i^0 -	amount of a growing sub-layer for an imposed freezing procedure,
α_i^D -	parameter of back-diffusion for partitioning and redistribution,
β_i^{ex} -	coefficient of the extent of redistribution,
β_i^{in} -	coefficient of the intensity of redistribution.

3. RESULTS AND DISCUSSION

The ZrO_2-solute redistribution was measured across the ceramic coating perpendicularly to the surface of Ni-substrate, within three distinguished regions of structures: AC – from the side of air, EG – middle region, SC – from the side of nickel substrate, Fig. 1, Fig. 2, Fig. 3.

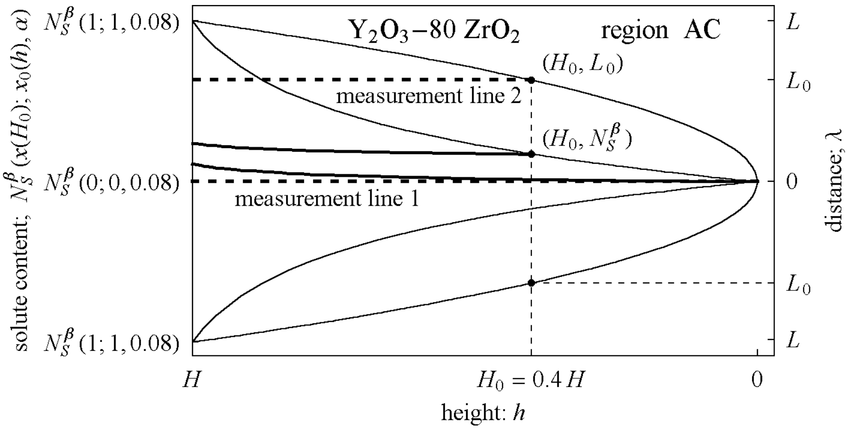

Fig. 1. Solute redistribution along cell envelope; the cell shape reproduced.
Rys. 1. Redystrybucja po obwiedni komórki oraz odtworzony jej kształt

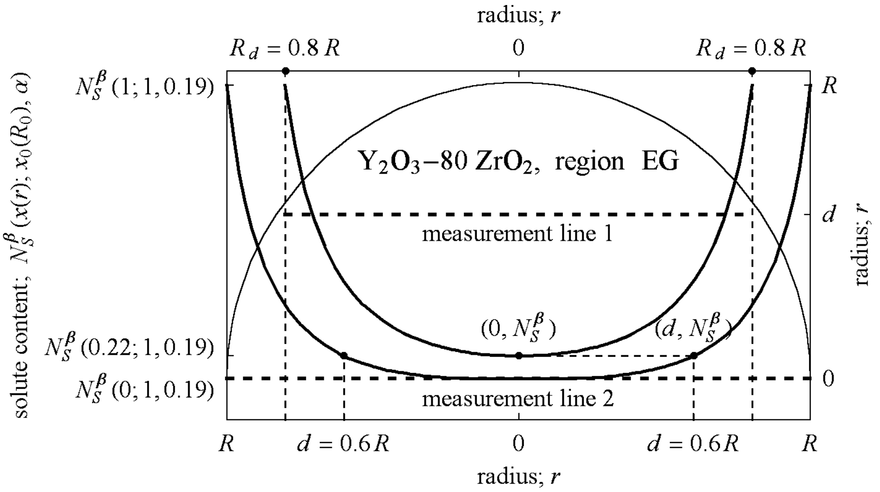

Fig. 2. Solute redistribution along diameters of two circles of equiaxed grain.
Rys. 2. Redystrybucja po średnicy dwu różnych kół ziarna równoosiowego

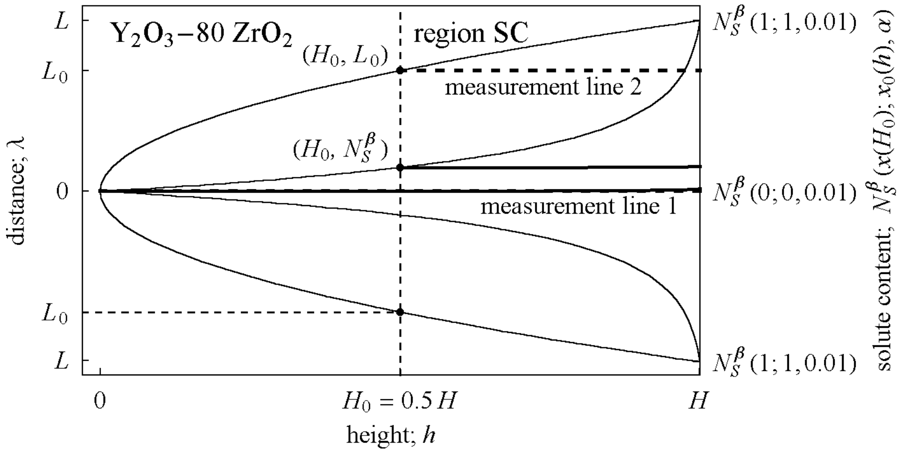

Fig. 3. Solute redistribution along cell envelope; the cell shape reproduced.
Rys. 3. Redystrybucja po obwiedni komórki oraz odtworzony jej kształt

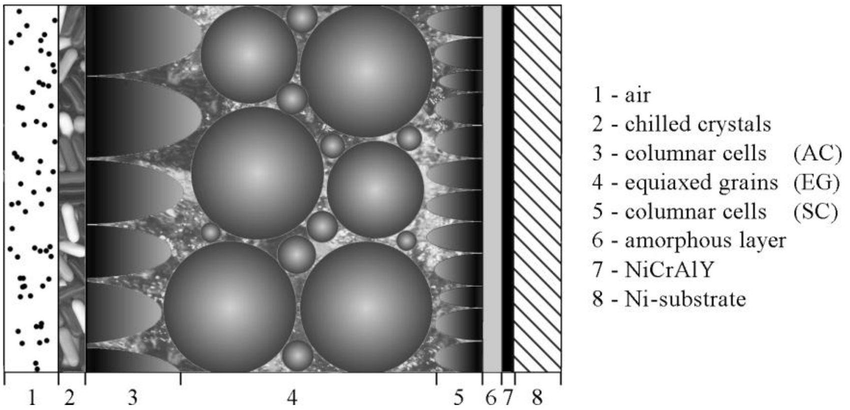

Fig. 4. Model of structure formation during solidification of $ZrO_2 - Y_2O_3$ ceramic layer on the Ni-substrate due to atmospheric plasma spraying.
Rys. 4. Model kształtowania się struktury podczas krystalizacji warstwy ceramiki $ZrO_2 - Y_2O_3$ na podłożu niklowym w trakcie natryskiwania plazmowego

Finally, a model of structure formation within the ceramic coating is worked out, Fig. 4. The proposed model presents the cells with frozen solid/liquid interface, (regions 3 (AC) and 5 (SC)).

Equiaxed fully formed (spherical) grains are supposed within region 4, (EG). This ideal structure pretends to show the mode of solidification within ceramic coating and differs more or less from the real structure, Fig. 5.

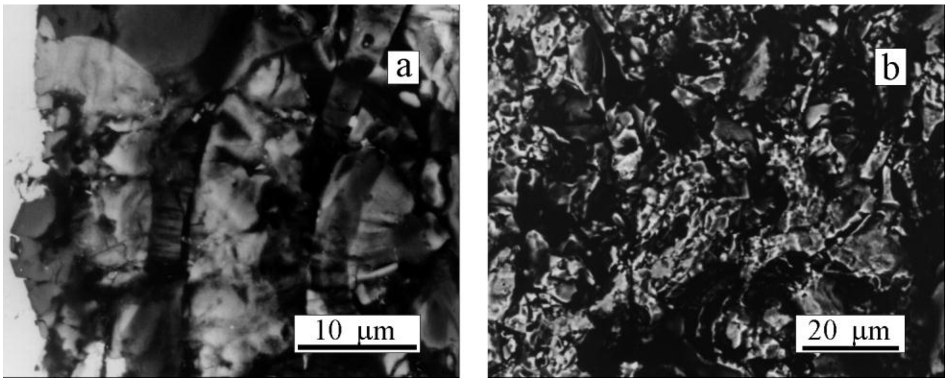

Fig. 5. $ZrO_2 – Y_2O_3$ ceramic coating onto Ni – substrate; a) sub-layers revealed within the coating (bright area on left r.h.s. – air), b) morphology of the equiaxed grains region (EG).
Rys. 5. Powłoka ceramiki ZrO_2-Y_2O_3 na podłożu Ni; a) podwarstwy ujawnione w powłoce (jasne pole z lewej strony – powietrze), b) morfologia regionu ziaren równoosiowych (EG)

REFERENCES

[1] Levin E.M., Robbins C.R., McMurdie H.F., Phase Diagrams for Ceramists, ed. American Ceramic Society, eds. M.K.Reser, Ohio 1964, 140-140.
[2] Górski L., Acta Physica Polonica A, 96 (1999) 275-281.
[3] Chraska T., King A.H., Materials Science Forum, 294-296 (1999) 779-782.
[4] Wołczyński W., Chapter 2, in: Modelling of Transport Phenomena in Crystal Growth, WIT Press, Southampton (UK) – Boston USA), 2000, 19-59.

KRYSTALIZACJA CERAMIKI ZrO_2-Y_2O_3 NA PODŁOŻU NIKLOWYM

STRESZCZENIE

Zastosowano teorię mikrosegregacji i redystrybucji w odniesieniu do rzeczywistej segregacji ZrO_2 w podwarstwach, z pomiarów EDX. Dokonano selekcji punktów pomiarowych segregacji ZrO_2, które mogą być analizowane z użyciem równań. Teoretyczne profile redystrybucji naniesiono na punkty pomiarowe po selekcji. Określono geometrię wzrostu w podwarstwach dla natryskiwania plazmowego ceramiki ZrO_2-Y_2O_3 na podłoże niklowe. Opracowano model formowania się struktury w powłoce definiując morfologię podwarstw na podstawie charakteru redystrybucji w każdej z nich. W modelu wyróżniono 2D oraz 3D rodzaje struktur i zestawiono ze strukturą rzeczywistą.

Recenzent Prof. Edward Guzik