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APPLICATION OF PROBABILISTIC MODELS TO THE DESCRIPTION OF THE GROWTH OF TITANIUM CARBIDES DURING LIQUID PHASE SINTERING

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ABSTRACT

The growth of several cemented carbides was analysed by means of probabilistic models. These models are mathematical models and do not depend on physical parameters. Then, they could allow to describe primary grains and to follow their evolution during sintering without any experimental assumptions. Nevertheless, probabilistic models do not apply easily to the coarsening of carbides with spherical grains such as TiC-Ni and TiC-Co.

Keywords : *probabilistic models, Boolean model, dead leaves model, liquid phase sintering, carbides, coarsening.*

INTRODUCTION

In a previous paper (Quenec'h et al, 1992), an investigation on the growth of WC grains in WC-Co alloys was made using probabilistic models. Two different models were used : a Boolean scheme with poissonian grains and a mosaic model. Using their properties, it has been shown that the coarsening of the WC grains may be modelled by the Boolean scheme. The parameters of the model allow the estimation of the kinetics parameters (kinetics exponent and activation energy). In this paper, the same approach is used for two other liquid phase sintered cermets, TiC-Co and TiC-Ni (Figures 1 and 2). Because of the morphology of these alloys, only multiphased models with spherical primary grains are used.

THE PROBABILISTIC MODELS

The probabilistic models were first introduced by Matheron (1967) and were afterwards used and developed in many disciplines (Serra, 1982; Stoyan and al., 1987; Jeulin, 1991). They follow the classical laws of the probabilistic theory, have stereological properties and are characterized by a function T(K) which represents the probability that a given compact K hits the set X :

$$T(K) = \mathcal{P}(K \cap X \neq \varnothing) = 1 - \mathcal{P}(K \subset X^c) \qquad (1)$$

where X^c is the complementary set of X.

The classical methods of image analysis (Serra, 1982; Coster and Chermant, 1989) allow to estimate T(K) from polished sections :

$$\mathcal{P}(K \subset X^c) = A_A(X^c \ominus K) \qquad (2)$$

where $\ominus$ represents the erosion operation in image analysis and A_A is the area fraction.

In order to acceed to the parameters of the model, the experimental curves of T(K) are compared with their analytical expressions which are known for some compacts and some models (Jeulin, 1991) and depend on the parameters of the chosen model.

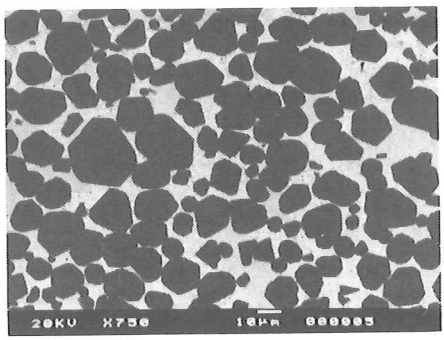

Fig.1. Micrograph of TiC-Co sample sintered 16 hours at 1450°C.

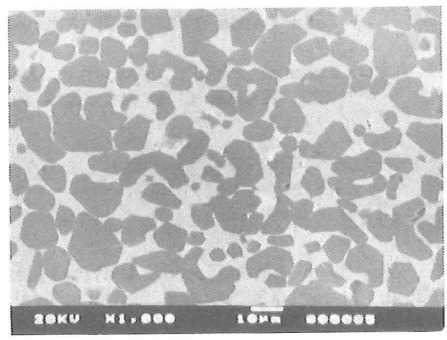

Fig.2. Micrograph of TiC-Ni sample sintered 16 hours at 1400°C.

The Boolean model

The Boolean scheme is built from a Poisson point process of intensity θ. In each point a primary grain is implanted. The hypothesis are the following : the primary grains are convex and they have a spherical shape, according to the microstructure of the material. Several grain size distributions are tested : single size, uniform, exponential or linear distributions, of parameter a (Jeulin, 1979), in which a is the maximum diameter of the grain. The linear distribution depends also on another parameter, k : we have :

$$\begin{cases} f(x) = 2x/ka^2 & \text{for } 0 \le x \le ka \\ f(x) = 2(a-x)/(1-k)a^2 & \text{for } ka \le x \le a \\ f(x) = 0 & \text{for } x > a \text{ and } x < 0 \end{cases} \qquad (3)$$

The Boolean model depends therefore on two parameters : θ, the parameter of the Poisson point process and a, the parameter of the primary grain. Figure 3 represents a simulation of a Boolean scheme in $\mathbb{R}^2$ with circular grains.

The dead leaves model

The homogeneous dead leaves tesselation model was also used. It was introduced by Matheron (1968) and developed by Serra (1982) and Jeulin (1979, 1991).

This tesselation is built as follows : for both phases, primary grains of parameters a1 and a2, which are the maximum particle size of both phases, are implemented randomly with constant density, respectively $\theta 1dt$ and $\theta 2dt$. The grains appeared between t and t + dt may hide a portion of the former grains. If the generation continues up to stability, a random tesselation of space is obtained. We used consequently a two-phased dead leaves model with three para-

meters : a1, a2 and θ, in which θ is the ratio of θ1 and θ2. Figure 4 shows a simulation of a dead leaves model in $\mathbb{R}^2$ with circular grains.

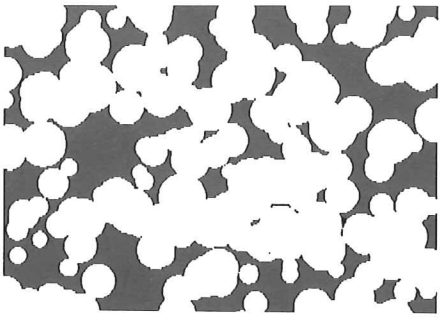

Fig.3. Simulation of a Boolean model in $\mathbb{R}^2$ with circular grains.

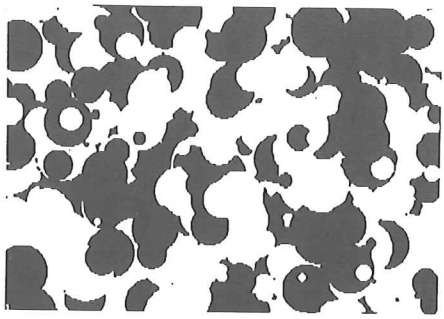

Fig.4. Simulation of a dead leaves model in $\mathbb{R}^2$ with circular grains.

FITTING OF THE MODELS

The Boolean model

The primary grain X' is defined by its average volume, $\overline{V}(X')$, its surface area, $\overline{S}(X')$ and its integral of mean curvature, $\overline{M}(X')$. These mean values are shown in Table I and depend on the parameter a of the model (Jeulin, 1979).

Table I : $\overline{V}(X')$, $\overline{S}(X')$ and $\overline{M}(X')$ for several distribution laws.

Distribution law	$\overline{M}(X')$	$\overline{S}(X')$	$\overline{V}(X')$
Single size	$2\pi a$	πa^2	$\pi a^3/6$
Uniform	πa	$\pi a^2/3$	$\pi a^3/24$
Exponential	$2\pi a$	$2\pi a^2$	πa^3
Linear $(0 \le k \le 1)$	$\frac{2\pi a}{3}(1+k)$	$\frac{\pi a^2}{6}(1+k+k^2)$	$\frac{\pi a^3}{60}(1+k+k^2+k^3)$

The parameter a of the Boolean model is estimated from the range of the experimental mean geometric covariogram K(h) which is deduced from the experimental covariance Q(h) :

$$K(h)/K(0) = (2 - \text{Ln } Q(h)/\text{Ln } q) \qquad (4)$$

where q is the surface area of the phase X^c.

The second parameter θ is estimated using the analytical expressions of the Choquet's capacity for several compacts K ; for example :

-if K is a point P :

$$Q(P) = q = \exp(-\theta\, \overline{V}(X')) \qquad (5)$$

-if K is a segment ℓ of size ℓ :

$$Q(\ell) = q \exp(-\theta \ell \frac{\overline{S}(X')}{4}) \qquad (6)$$

The expressions for a bipoint h or an hexagon of size r may be also used (Jeulin, 1979 ; Quenec'h and al., 1992).

The number of connectivity in $\mathbb{R}^2$, $N_A(X)$ for an hexagonal grid and theoretical mean geometric covariogram , may be also estimated when the parameters and the distribution f(x) of the grains of the model are known (Jeulin, 1979) :

$$N_A(X) = q\theta \left[\frac{\overline{M}(X')}{2\pi} - \theta \frac{\sqrt{3}}{2} \frac{\overline{S}(X')^2}{16} \right] \quad (7)$$

$$K(h) = \frac{\pi}{6} \left[\int_h^\infty a^3 f(a)da - \frac{3}{2}h\int_h^\infty a^2 f(a)da + \frac{1}{2}h^3\int_h^\infty f(a)da \right] \quad (8)$$

These two theoretical values are compared to the experimental ones and allow to test the good fit of the model.
The relative complexity of relation (8) explains the fact that we have used only simple distribution functions for this study. The normal and lognormal distributions, which will be also tested, are more difficult to use.

The dead leaves model

The good fit of the crossed covariance, $\gamma(h)$, is used to test the model ; $\gamma(h)$ is obtained from the experimental covariance C(h) :

$$\gamma(h) = p - C(h) \quad (9)$$

$$C(h) = \frac{p(1-2p)\, r1(h) + 2p^2}{2 - p\, r1(h) - q\, r2(h)} \quad (10)$$

with $r1(h) = K_1(h)/K_1(0)$ and $r2(h) = K_2(h)/K_2(0)$.

Then we pose : $\Phi(h) = \dfrac{\gamma(h)}{p(1-p)}$ (11)

$$= \frac{2 - (r1(h) + r2(h))}{2 - p(r1(h)) - q(r2(h))} \quad (12)$$

$\Phi(h)$ may be experimentally determined using the covariance C(h) and relations (9) and (11). The function Φ depends only on the two covariograms of both phases. As these covariograms are known for several distribution functions of the diameters of the primary grains, the validity of this model can be tested comparing the experimental $\Phi(h)$ functions and the different theoretical functions calculated.
The simplest hypothesis which was used was to assume that both phases have the same grain parameter and the same distribution function of the diameters. So :

$$r(h) = r1(h) = r2(h) \quad (13)$$

and

$$\Phi(h) = \frac{2\,(1 - r(h))}{2 - r(h)} \quad (14)$$

But many other hypothesis for a1, a2 and r1(h) and r2(h) can also be tested.

RESULTS

The samples, which have a TiC volume fraction of about 0.6, were made using infiltration of TiC by Co or Ni. They were heat treated in a graphite resistance furnace at 1450°C for Co and 1500°C for Ni for a time varying between 1 and 100 hours. After polishing and observations with a SEM (JEOL JSM T330A), 20 micrographs for each sample were analysed using an image processor NS-1500 (Nachet Micro-contrôle) with an hexagonal grid.

The dead leaves model

The hypothesis of similarity of the parameters and of the distribution func-

tions of the grains was tested. The parameter of the grain was taken as the range of the experimental covariance and the same distribution laws as for the Boolean model were used. Both phases of the two materials were tested using relation (14). For all samples, we saw that the theoretical $\Phi(h)$ functions used do not fit with the experimental one (Figure 5) and so we can conclude that the dead leaves model does not apply to these materials.

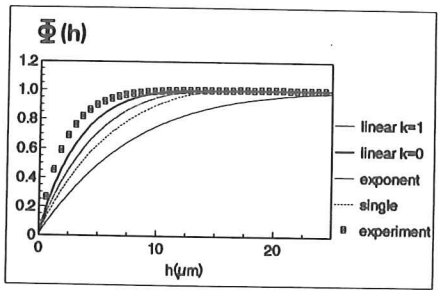

Fig.5. Comparison between $\Phi(h)$ experimentally determined and calculated with several distributions laws for a TiC-Co sample sintered 16 h at 1450°C .

This conclusion may be explained by the fact that the building of this model does not fit at all to describe such microstructures obtained by liquid phase sintering ; the growth of the grains is indeed essentially caused by dissolution precipitation phenomena (Ostwald ripening), giving usually convexe structures without the possibility of inclusions of the binder in the hard phase, which is seen in the simulations of the dead leaves model.

The Boolean model

TiC-Ni

The observations of the TiC-Ni samples showed that no theoretical mean geometric covariogram fits with the experimental curves. Moreover, the values of $N_A(X)$ calculated for the different distributions laws are far from the experimental values. We concluded consequently that a Boolean model does not describe the TiC grains in TiC-Ni cermets although the Ln $Q(\ell)$ functions are always linear.

TiC-Co

The variations of Ln $Q(\ell)$ as a function of ℓ are linear for all samples. Moreover, the experimental mean geometric covariograms fit for some samples with one of the theoretical distributions tested. The figure 6 shows experimental points with theoretical K(h)/K(0) functions for a sample sintered 4 hours at 1450°C. A very good fit is found between the points and a linear distribution with k=1 of the TiC particles. For the sample sintered 8 hours at the same temperature, there is a good agreement with a linear distribution with k=0; in the case of longer sintering times, the experimental K(h) differs totally from the theoretical laws. Values of θ were calculated from relations (5) and (6) and give very closed results for the right law. The numbers of connectivity calculated from relation (7) deviate from the experimental one. But this last result can be minimized because these values are very sensitive in this range of values when a small variation of volume fraction occurs.

It can be said that the grains in TiC-Co alloys may be described by a Boolean model with spherical primary grains which distribution law varies with sintering time. But the distribution should theoretically be stationary and the grains should be represented by a lonely theoretical law of the Boolean scheme. An influence of the coalescence during the coarsening may perhaps explain this change in the distribution.

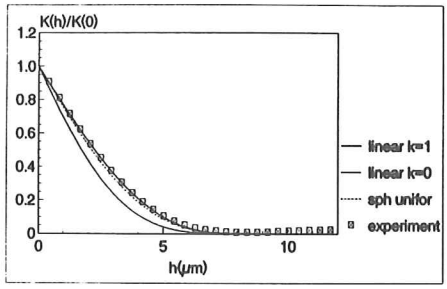

Fig.6. Variations of experimental and theoretical K(h) functions for TiC-Co sample sintered 4 hours at 1450°C.

CONCLUSION

An attempt to model the growth of TiC grains in TiC-Co and TiC-Ni carbides during liquid phase sintering was made. The dead leaves model does not fit at all to model this kind of structures and the Boolean scheme does not apply to TiC grains in TiC-Ni alloys. For TiC-Co alloys, the particles are approximatively described by a Boolean model with a linear distribution law of spherical grains. This study should be detailed testing other distribution laws, particularly the log-normal law which represents in the most cases the experimental particle size distribution.

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