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Example of Application of Probabilistic Models: Determination of the Kinetics Parameters during Liquid Phase Sintering

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Résumé. — Le but de cet article est de montrer comment les modèles probabilistes peuvent être un moyen utile pour estimer certains paramètres d'ordre physique à l'aide de paramètres purement mathématiques. Le cas de la croissance des grains pendant le frittage en phase liquide des cermets WC-Co a été étudié ici ; trois différents modèles ont été testés pour décrire ce processus physique : un schéma booléen, un modèle de feuilles mortes et une mosaïque bicolore de Poisson. Le modèle donnant les meilleurs résultats est le schéma booléen avec des grains primaires de Poisson. La modélisation a permis ensuite d'obtenir des estimations des constantes de vitesse, de l'exposant cinétique ainsi que de l'énergie d'activation de ce processus de croissance. Nous avons pu aussi estimer la valeur du nombre de connexité dans l'espace $\mathbb{R}^3$, paramètre qui est difficilement mesurable expérimentalement.

Abstract. — The purpose of this paper is to present how the probabilistic models, which lead to the obtention of mathematical parameters, allow to estimate physical parameters. The application presented here deals with the determination of kinetics parameters of cermets materials during the coarsening of particles in liquid phase sintering: the growth rate and the kinetics exponent. The materials used are WC-Co cermets and three models were tested: a Boolean scheme, a dead leaves model and a mosaic model. The model which gives the best result is the Boolean model with Poisson primary grains. It allows also to estimate a topological parameter, the number of connectivity in $\mathbb{R}^3$, which is in strong connection with the number of grains present at each time during the sintering; this parameter is then also a good indicator of the kinetics in the sintering process.

Introduction

Sintering [1] is an industrial process which allows to obtain dense products from several powders by heating the mixture: applications are particularly common in metallurgical sciences. While the sintering temperature is over the melting point of one of the powders of the mix, a liquid phase

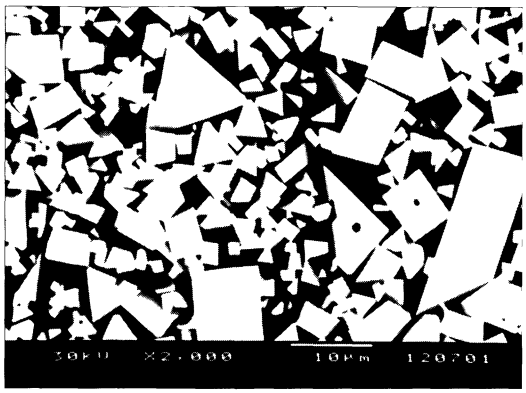

Fig. 1.

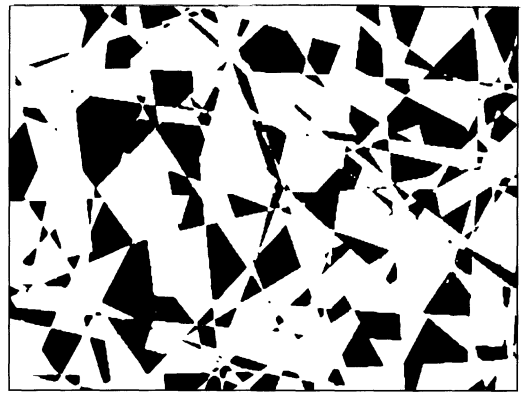

Fig. 2.

Fig. 1. — Micrograph of WC-15 wt.% Co, sintered at 1450 °C for 7 hours. WC particles are white and the cobalt matrix is black.

Fig. 2. — Simulation of a two-colored mosaic with Poisson primary grains in $\mathbb{R}^2$.

appears; the process is then called liquid phase sintering and the materials obtained consist in a matrix, which was the liquid phase, involving grains of the refractory phase. The size of the refractory grains depends on several sintering parameters: the size of the green powders is evidently a major parameter of the final size, but it is generally known; the sintering temperature and the duration of the coarsening at this temperature are essential. Moreover, it is well known that the properties of a material are related to its microstructure, and especially to the size distribution of the grains. In order to estimate at best the final properties of a material, it is then essential to control the size of the microstructure and so to determine the kinetics parameters which govern its evolution.

Usually, these kinetics exponents are estimated by classical grains coarsening experiments: samples are heated at different temperatures for several times and the measurement of diameters of the grains allows to estimate the kinetics parameters. But this classical method cannot be used in the case of sintered materials in which the volume fraction of refractory phase (grains) is high and does not allow to estimate the size of grains because of non spherical shape and large contacts between particles: for example, Figure 1 presents a WC-Co sintered material with 15 wt.% of cobalt. Another method has then to be used in order to determine the kinetics parameters and it will be shown that probabilistic models are of some help in this aim.

1. The Probabilistic Models

Probabilistic models were first introduced by Matheron [2] in the seventies, and afterwards subsequently used and developed in many disciplines [3, 4 for instance], essentially by the School of Mines at Fontainebleau, in France. The theoretical aspect of these models are developed in [2, 4 or 5] and will not appear in this paper. It can be briefly said that, from a mathematical point of view, these models are random closed sets (RACS) and they follow the classical laws of the probabilistic theory. They are defined by very few parameters which can be estimated on real microstructures by using image analysis and mathematical morphology. Moreover, the stereological

properties of these probabilistic models allow to test a model defined in $\mathbb{R}^3$ from plane sections observed in $\mathbb{R}^2$.
The RACS are characterized by a functional called the Choquet's capacity. This function, $T(\mathrm{K})$, defines the probability P that a given compact K hits the RACS X:

$$T(\mathrm{K}) = P(\mathrm{K} \cap \mathrm{X} \neq \emptyset) = 1 - P(\mathrm{K} \subset \mathrm{X}^{\mathrm{C}}) \tag{1}$$

where X^{C} is the complementary set of X. Using the classical morphological operations, the Choquet's capacity of set X can be estimated for the compact K by:

$$T(\mathrm{K}) = 1 - A_{\mathrm{A}}(\varepsilon^{\mathrm{K}}(\mathrm{X}^{\mathrm{C}})) \tag{2}$$

where ε^{K} is the erosion operation by the structuring element K and A_{A} the area fraction of the eroded set. The analytical expressions of $T(\mathrm{K})$ depend on the parameters of the models and are known for some of them. Therefore, the comparison between the theoretical Choquet's capacities and the experimental ones, obtained from erosions of the complementary phase by the considered compact K, is possible for several different compact sets and that is this comparison which allows to estimate the ability of a model to describe the microstructure of a given material.
In the case of WC-Co cermets, we have used two-component models with Poisson primary grains because of the microstructure and the hexagonal symmetry of WC grains (see Fig. 1); the three models tested are: a Boolean model, a bicolor mosaic and a two-phased dead leaves model. The main characteristics of these models are presented below.

1.1 THE POISSON MOSAIC. — This first model is very important because it allows also to build the Poisson primary grains which are necessary in both other models.
This two-colored Poisson mosaic [4] is built from a Poisson plane tessellation. Straight lines Δ are randomly oriented in the space and a Poisson point process of uniform parameter λ is implanted on these lines. At each point, a plane Π perpendicular to the line Δ is allocated. The space is then divided in a Poisson polyhedra network, which faces are the Poisson planes. This method is used to build the Poisson polyhedra which are used to build specific Boolean and dead leaves models. The two-colored Poisson mosaic is itself built from the whole tessellation attributing each polyhedron randomly and independently to one or another phase. Figure 2 presents a simulation of mosaic model in $\mathbb{R}^2$. This model is described by two parameters which are λ, the Poisson polyhedra parameter and q, the volume fraction of one of both phases. The particularity of this model, except for its stereological properties, is that it is a symmetrical model which implies that the parameters may be estimated by measurements on one or the other phase.
The analytical expressions of $T(\mathrm{K})$ allow to obtain estimations of λ while K is the segment ℓ, the bipoint h and the equilateral triplet of points T(h); they are given in Table I, where $\overline{C}(\mathrm{h})$ is the centered covariance and $W(\mathrm{h})$ the third order centered moment [6].
Moreover, the expression for the specific connectivity number in $\mathbb{R}^2$ is given in the hexagonal grid by the equation [6]:

$$N_{\mathrm{A}}(\mathrm{X}) = \frac{\sqrt{3}}{2}\pi^2\lambda^2 q(1-q)(1-2q). \tag{3}$$

1.2 THE BOOLEAN MODEL. — The Boolean model is often used [3, 5-7]. To build it, a Poisson point process of density θ is generated in space $\mathbb{R}^n$. Then, at each point, a primary grain is implanted (Fig. 3). To generate Poisson grains, we used the Poisson mosaic model defined above. Then, two parameters define the model: θ and λ, the parameter of Poisson grains.

Table I. — *Analytical expressions of the Choquet's capacities used in order to validate the three different models tested.*

Compact	Mosaic model	Boolean model
Point P		$Q(\mathrm{P}) = q \exp\left(-\frac{6\theta}{\pi^4 \lambda^3}\right)$
Segment ℓ	$Q(\ell) = q \exp(-\pi\lambda(1-q)\ell)$	$Q(\ell) = q \exp\left(-\frac{6\theta\ell}{\pi^3\lambda^2}\right)$
Bipoint h	$\overline{C}(\mathrm{h}) = q(1-q)\exp(-\pi\lambda h)$	$K(\mathrm{h}) = K(0)\exp(-\pi\lambda h)$
Hexagon H(r)		$\frac{1}{r}\mathrm{Ln}\left[\frac{Q(\mathrm{H}(r))}{q}\right] = \frac{-18\theta}{\pi^3\lambda^2} - \frac{9\sqrt{3}}{2}\frac{\theta r}{\pi\lambda}$
Triplet T(h)	$W(\mathrm{h}) = q(1-q)(1-2q)\exp\left(-\frac{3}{2}\pi\lambda h\right)$	$\mathrm{Ln}\left[\frac{q^3 Q(\mathrm{T}(\mathrm{h}))}{Q(\mathrm{h})^3}\right] = q\exp\left(-\frac{3}{2}\pi\lambda h\right)$

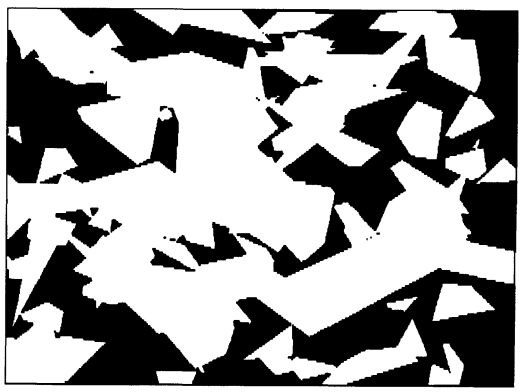

Fig. 3.

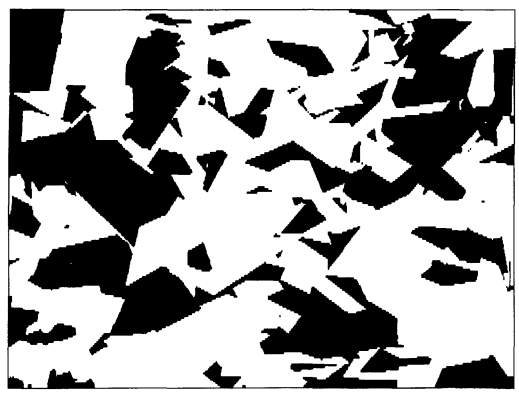

Fig. 4.

Fig. 3. — Simulation of Boolean model with Poisson primary grains in $\mathbb{R}^2$.

Fig. 4. — Simulation of dead leaves model with Poisson grains.

The different compact sets used in order to estimate the validity of the Boolean model are the following: the point P, the segment ℓ, the bipoint h, the hexagon of size r, H(r) and the equilateral triplet of points T(h). The analytical expressions of the Choquet capacity for these compacts are given in Table I, [6].

In Table I, K(h) is the mean geometrical covariogram of a primary grain X′ and q the volume fraction of the Boolean set X^{C}. In the case of a bipoint, K(h) is related to the Choquet's capacity

$Q(\mathrm{h})$, the covariance, by the expression:

$$K(\mathrm{h})/K(0) = 2 - \mathrm{Log}\, Q(\mathrm{h})/\mathrm{Log}\, q. \tag{4}$$

The parameters of the Boolean model allow also to estimate the specific connectivity numbers, $N_{\mathrm{A}}(\mathrm{X})$ in $\mathbb{R}^2$ and $N_{\mathrm{V}}(\mathrm{X})$ in $\mathbb{R}^3$ [6]:

$$N_{\mathrm{A}}(\mathrm{X}) = q\theta\left[\frac{\overline{M}(\mathrm{X}')}{2\pi} - \theta\frac{\sqrt{3}}{2}\frac{\overline{S}(\mathrm{X}')^2}{16}\right] \tag{5}$$

$$N_{\mathrm{V}}(\mathrm{X}) = q\left[\theta - \frac{\theta\overline{M}(\mathrm{X}')\theta\overline{S}(\mathrm{X}')}{4\pi} + \frac{\pi}{6}\left[\frac{\theta\overline{S}(\mathrm{X}')}{4}\right]^3\right]. \tag{6}$$

The last relation is quite important because it is almost the onely solution to estimate $N_{\mathrm{V}}(\mathrm{X})$. The classical method consists indeed in a serial sectioning which is a long and tedious operation. An estimation of $N_{\mathrm{V}}(\mathrm{X})$ using the Boolean model parameters is then of great interest.

1.3 UNIFORM DEAD LEAVES MODEL . — This model introduced by Matheron [2] and developed by Jeulin [6] is built as follows: for both phases, Poisson primary grains of parameters λ_1 and λ_2 are implanted randomly between t and $t+\mathrm{d}t$ with the constant density θ_1 and θ_2. The grains implanted may overlap the former grains and the process is performed to stability when the support of the specimen is fully recovered by the grains ($t = \infty$). Figure 4 presents for instance a simulation of dead leaves model with Poisson grains. Finally, this model is defined with three parameters: $\theta = \theta_1/\theta_2$, λ_1 and λ_2.
In this model, only the covariance $C(\mathrm{h})$ is used to test the model. If the volume fraction of the phase X is called p (volume fraction of X^{C}: $q = 1 - p$), we obtain an expression giving $C(\mathrm{h})$ as a function of geometric covariogram of both primary grains $K_1(\mathrm{h})$ and $K_2(\mathrm{h})$ according to the following equation:

$$C_1(\mathrm{h}) = \frac{p(1-2p)r_1(\mathrm{h}) + 2p^2}{2 - pr_1(\mathrm{h}) - (1-p)r_2(\mathrm{h})} \tag{7}$$

with $r_1(\mathrm{h}) = K_1(\mathrm{h})/K_1(0)$ and $r_2(\mathrm{h}) = K_2(\mathrm{h})/K_2(0)$. Practically, the function $\Phi(\mathrm{h})$ is used:

$$\Phi(\mathrm{h}) = \frac{2 - r_1(\mathrm{h}) - r_2(\mathrm{h})}{2 - pr_1(\mathrm{h}) - (1-p)r_2(\mathrm{h})}. \tag{8}$$

2. Experiment

WC-Co samples were furnished by UGICARB society. Different compositions with WC grains (mean size of grains obtained by Fisher granulometry: 5 μm) and cobalt powder with contents ranging from 10 to 25 wt.% were provided. These hardmetals were annealed in a graphite resistance furnace at low pressure (approximately 10^{-4} Pa) between 1 350 and 1 650 °C. After sintering, samples were polished and observed with a scanning electron microscope in back-scattering electron mode. The micrographs obtained were analyzed by means of an image processor using an hexagonal digitization grid (NS-1500, Nachet).

3. Results

3.1 WC-CO MICROSTRUCTURES MODELING. — The first model tested was the dead leaves tessellation. Although the simulations of the model present many similarity with the structure of

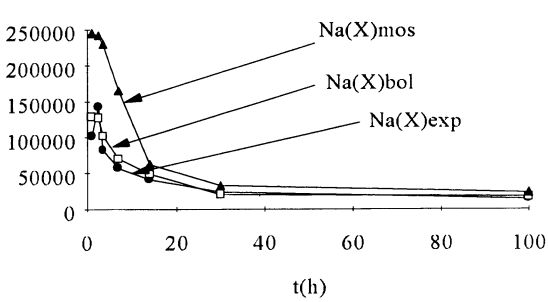

Fig. 5.

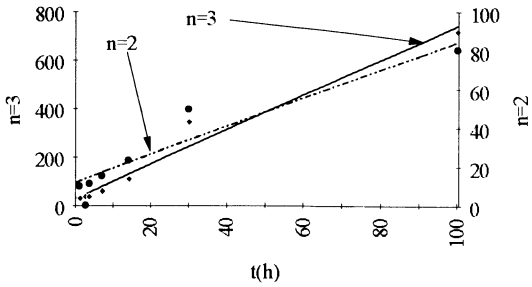

Fig. 6.

Fig. 5. — Comparison between experimental number of connectivity in $\mathbb{R}^2$, $N_A(X)_{exp}$, and theoretical for the mosaic model, $N_A(X)_{mos}$, and for the Boolean model, $N_A(X)_{bol.}$.

Fig. 6. — Variation of $\lambda^{n/-1}$ with the sintering time for both values of n, 2 (•, μm^{-2}) and 3 (♦, μm^{-3}).

the cermets, it was rapidly stated that this model did not describe WC-Co microstructure. Many tests were performed using more and more wide hypothesis, so that all cases were studied [8]: same primary grains for both phases ($\lambda_1 = \lambda_2$), one primary grain much larger than the other ($\lambda_1 \gg \lambda_2$) and approximations on the values of λ_1 and λ_2 using a least square minimum, knowing the sum $\lambda_1 + \lambda_2$. None of these approximations gave good results. Moreover, simulations show also inclusions of one phase into the other, which is physically impossible (a WC grain cannot include cobalt); the presence of large isolated grains is also not compatible with the existence of a rigid continuous skeleton of WC grains. For all these reasons this first model was dropped.
The second model is the two-colored mosaic model. The value of the first parameter is attained measuring the surface area of the cobalt phase and estimations of the second parameter λ, from the three compacts considered in Table I, are obtained. As this model is a symmetric one, λ parameter was estimated from measurements on both phases. The comparison between the two series of values did not allow to validate the model. So, the next step was to estimate the theoretical number of connectivity and to compare it with the experimental one measured on the samples. Results are presented in Figure 5 and revealed a bad fit between the two curves. This second model was then discarded.

Finally the Boolean model was tested. Five different estimations of the parameter λ were obtained using the five different compact sets tested. The different values obtained are quite similar but the comparison between the experimental and the theoretical number of connectivity in $\mathbb{R}^2$ was also performed (Fig. 5). The relatively good results obtained let us to conclude that a Boolean model with Poisson primary grains was correct to describe the microstructure of WC-Co cermets. The parameters of this model allow afterwards to estimate the physical kinetics constants. Finally images obtained from simulations (Fig. 3) look qualitatively very similar to images of the microstructure (Fig. 1).

3.2 DETERMINATION OF KINETICS PARAMETERS. — The kinetics parameters are determined from the parameters of Boolean model and coarsening laws:

$$X^{n/d}(t) - X^{n/d}(0) = kt \tag{9}$$

in which $X(t)$ is the parameter at time t and d the dimension of its unit. Generally these relations are used with the mean diameter or mean radius of the grains instead of a probabilistic model's parameter but we demonstrated that the obtained kinetics exponent and growth rate were in the same range as values found in the literature. Figure 6 presents the variation of $\lambda^{n/-1}$ with the sintering time for both values of n, 2 and 3 which are the only possible values in sintering [1]. The coefficient of variation is lower for $n = 3$ than for $n = 2$. This result agrees with previous one obtained by several authors from other methods using segmentation of WC phase and estimation of a mean diameter of grains [9, 10]. The values of the growth rate, k, are also determined from the slope of the curves. Their order of magnitude is 10^{-18}, 10^{-19} m^3 s^{-1}, for $n = 3$. The different authors who leaded experiences comparable to ours [9-11] obtained values between 10^{-22} and 10^{-21} m^3 s^{-1}. Finally, the activation energy of the coarsening for temperatures between 1 350 and 1 600 °C was also estimated, using Arrhenius laws with λ parameter for samples with 20 wt.% Co [8]. The slopes of the curves gave values of about 240 kJ mol^{-1}. The results obtained by the probabilistic method are weaker but compatible with those found in the literature: 380 kJ mol^{-1} by Coster [9] for samples to be compared with ours. This variation between our results and the literature proceeds surely from differences in the method: measurements were carried out on phases and not on segmented particles. And moreover, the variations in experimental conditions (vacuum, temperature, nature of furnace...) may also induce differences in the results. So, the validity of this method using probabilistic models is not put in defect.

3.3 DETERMINATION OF $N_V(X)$. — From the parameters of the Boolean model, it is also possible to estimate easily, without serial sectioning, the number of connectivity in $\mathbb{R}^3$, $N_V(X)$ [7], using relation (6). $N_V(X)$ allows to obtain information about the topology of the structure in $\mathbb{R}^3$. The values of $N_V(X)$ obtained are between -2×10^8 mm^{-3} for sample annealed 1 hour to -1×10^7 mm^{-3} (100 hours) [8]. These results put in evidence a very strong interconnection of WC grains which is in agreement with the presence of the WC skeleton observed on micrographs.

4. Conclusion

The aim of this study was to point out how the probabilistic models could be useful to material scientists to obtain information about physical properties in the studied system, for instance the coarsening parameters during annealing of WC grains in liquid phase sintering of WC-Co cermets. It was established that a modeling of WC phase by a Boolean scheme with Poisson primary grains can best describe the microstructure of these cermets. Then, the estimated parameters of the Boolean model, calculated using erosions of images of metallographical sections, allow to evaluate the kinetics parameters. The values of kinetics exponent, growth rate and activation energy of the coarsening process agree with the previous values found in the literature and obtained by classical ways. Moreover, the great advantage of Boolean model is that it gives estimations of the connectivity number in $\mathbb{R}^3$, which is difficult to obtain by classical methods. As a conclusion, the probabilistic models are valuable tools to determine with a good accuracy physical parameters, as far as the observed structure can be modeled by random sets.

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