ACTA STEREOL 1983; 2/1: 17-24
REVIEW

STEREOLOGICAL PROPERTIES OF POWDERS AND SINTERED ALLOYS

Kirill S. Cherniavsky

Institute for Hard Alloys

Moscow, USSR

ABSTRACT

Various stereological properties are discussed according to their applicability for studying and testing the structure of powders and sintered materials including cemented carbides. Those properties should satisfy requirements to describe adequately the spatial structure or to be its steady estimate, to be representative relative to bulk material, to be compatible when different structural states are compared. Qualitative and numerical models are considered which are most applicable to identify the structure for quality testing purposes. Practical examples are given to demonstrate the application of stereological parameters for studying the structure of powder and cemented carbides and for establishing the correlation between the structure of alloys and their strength.

Basic Principles (Cherniavsky, 1971, 1977, 1978, 1981, 1982). The main tasks of stereological analysis in material science are the following:

1) deriving the structural parameters which enable identification of the material and the state of its structure at various stages of production scheme;

2) establishing the interdependence of the structural parameters for initial, intermediate and final products;

3) founding the relations between the struc-

tural parameters and the properties of material.

The objects of stereological study in powder metallurgy, e.g. in the material science of cemented carbides, are powders and compacted materials, light microscopy (LM) and transmission (TEM) and scanning (SEM) electron microscopy being the main techniques for obtaining primary information. For a description of non-consolidated structure of powder the direct stereological reconstruction (e.g. SEM imaging) could be applied as well as the statistical reconstruction, i.e. obtaining a numerical model based on measuring at the observation plane of a monolayer of particles in transmission LM or TEM. The observation plane image are projections of particles in their maximum stability positions. The structure of the sintered material could reasonably be described in practice by means of the statistical stereological reconstruction of primary measurements at the observation plane of a polished specimen (or replica) in reflection LM, TEM and SEM. In this case the final image includes random sections of structure elements. The direct reconstruction, e.g. by means of successive sections is a very time - consuming technique, which makes it impracticable for the analysis of compacted materials.

To fulfil successfully the above mentioned tasks of stereological analysis only those quantities and means of description of structure should be used which satisfy the following requirements:

1) the adequacy of description of spatial structure or at least the possibility of attaining its biased but steady estimate;

2) the representativity of geometrical sampling relative to the actual bulk material;

3) the compatibility (i.e. the equality of physical essence and accuracy of measurements) of stereological properties of the two consequent structures.

Powder Substances (Cherniavsky, 1977, 1978, 1981, 1982; Cherniavsky et al., 1982). These requirements are satisfied by a qualitative model of a powder structure obtained with the SEM imaging. With its help it is possible to identify the powder products and derive relations between their

morphology at various stages of production scheme. Powder particles of the initial substances (Ammonium Paratungstate, H_2WO_4) and of the products at different stages of hardmetal manufacturing (WO_3, $WO_{2,9}$; $WO_{2,72}$; WO_2; W; WC, CoO_3, Co etc.) have a characteristical morphology. For this reason SEM imaging of the as-received powder sample at several magnifications allows rapid and accurate identification of powder product, it also permits to estimate characteristic particle shape (or set of shapes), size uniformity, the average size and the tendency to aggregation (Cherniavsky et al., 1982).

A numerical model of powder structure is composed of average sizes, size distributions and shape factors of maximum stability projections of powder particles. The stereological reconstruction is impossible due to lack of information about third dimension in a monolayer, so this model gives a biased but steady estimate of structure; the steadiness being provided for by the direct correspondence of a particle to its projection. The standard state of a sample can be achieved by means of a special desaggregation technique which provides complete desintegration of the aggregates without breaking the primary particles.

The size distribution could be described analytically as a Gaussian distribution of a certain diameter function $\varphi(d)$. For most powders in the cemented carbide production scheme we have found the function $\varphi(d)=\ln d$ and for some grades of WO_3, W and WC powders a different function $\varphi(d)=d^{1/3}$ has been found. The differences in particle size distributions for different batches of the same grade could be better revealed by means of empirical distribution, which could be reduced to a set of three diameter values: an average count diameter $d_n=\sum d_i \cdot n_i / \sum n_i$, a modal value d_{mod}, and a conditional maximum (e.g., for the frequency f=1%) $d_{1\%}$ (Cherniavsky, 1978, 1981b, 1982).

The average surface diameter $d_S=\sum d_i^3 n_i / \sum d_i^2 n_i$ to within the shape-dependent coefficient is essentially the same as the diameter d_{VS} which is the object of gas permeation methods. Our experi-

ments have shown that the microscopy and the gas permeation technique provided values of d_s which are practically identical within the limits of accuracy of both techniques for powders which consist of spherical particles with smooth surfaces. These values may differ from 1 to 2 orders of magnitude when a powder consists of agglomerates. Combining microscopy and Fisher "sub-sieving" permits to derive d_s for primary WO_3 particles and for hereditary agglomerates - pseudomorphs of Ammonium Paratungstate and H_2WO_4. The values of d_n for primary particles and pseudomorphs in powders of the same substance could be determined by consecutive analysis of as-received and desaggregated sample in SEM. (Cherniavsky, 1978, 1982).

The representativy of microscopic results is provided by the sufficient statistical sample volume, i.e. number of measured particles N in a monolayer. The size and shape distribution of particles in WO_2, W and WC powders with particle sizes that correspond to the LM interval (0,5-40μm) is with certainty steadily reproduced for sample volume N=1000 particles, the d_n value being stable even for smaller N. (Cherniavsky, 1978).

The demerit of a numerical model is the over-generalized description of powder structure which does not reveal the details of contours, due to geometric assumptions involved. A much more individualized description, i.e. "the passport of structure" could be obtained by means of a combined size-shape property, which is presented by Fourier (Walsh) expansion of function $\varphi(\rho)$, ρ being the radius-vector of a point at the particle surface. This technique however is very time-consuming and in its present state is impracticable. (Cherniavsky, 1981a).

Compact material (Cherniavsky, 1971, 1977, 1981, 1982). The completely adequate description of a spatial structure of compact materials is given by only those stereological properties which determination (i.e. measuring and calculation by means of stereological equations) does not require the particle shape approximation. Those are volume fractions V_V, specific surfaces S_V, mean chords L, degree of contact C, dihedral angles θ, mean

curvature H_V. Such properties also satisfy the compatibility requirement, and the methods of their representative sampling are well-known. The application of theseproperties yields the most reliable data when studying the structure development of cemented carbides and their strength - structure dependencies. The analysis of temperature and time dependencies of these properties allows to reveal the structure development scheme which is in agreement with the concept of liquid-phase sintering as a process driven by the tendency to minimize the interface energy γ. E.g., under isothermal conditions and for particles with isotropic surface energy the specific surface of carbide-binder interface $S_{V(CB)}$ progressively decreases, which is an agreement to γ decreasing due to particle growth and rounding. If prismatic facetting develops during the sintering (WC-Co) then temporary increase of $S_{V(CB)}$ could occur, provided that the surface energy decrease due to coarsening is less than its drop due to development of low-energy faces (coarse uniformly sized initial particles). For the temperature dependence of $S_{V(CB)}$ in systems with good wettability a drastic rise is characteristic which is due to molten binder flowing into the carbide particle contacts, the rise is followed by a gradual monotonous decrease due to particle growth and coalescence.

Time and temperature dependencies of $C=S_{VC-C}/(S_{VC-B} + 2S_{VC-C})$, L_C, L_B, θ_{C-C} are also in good agreement with the above mentioned structure development scheme.

The most reliable statistical data on the strength (σ)-structure dependence of cemented carbides are obtained through σ-V_{VB}, σ-L_C, σ-L_B and σ-C_{C-C} relations. (Cherniavsky and Travushkin, 1980).

The shape-invariant properties: V_V, S_V, C and L provide a generalized description of structure which in some cases may be considered a drawback as it does not reveal a difference in size and shape distributions of compared structures.

The size distribution $n_i(d_i)$ at random sections (intercepts, diameters etc.) does not reproduce true size distribution of particles

$N_i(D_i)$ because the contribution into the section size class i is made by all the particles of sizes j i. The stereological reconstruction $n_i(d_i) \longrightarrow N_i(D_i)$ is possible only if all the particles in structural system possess the same shape. In structures of most compact materials, including cemented carbides, there is a wide variety of particle shapes due to the presence of several morphological types related to one crystallographic symmetry class; and also due to the constrained growth of particles and their coalescence. Accordingly the stereological reconstruction made with an assumption of single shape for all particles results in a severely distorted distribution which could not be used even as rough estimate of $N_i(D_i)$. It is one of the reasons for obtaining unreliable data on controlling reaction of liquid phase sintering when they are derived from the analysis of distributions $n_i(d_i)$ or reconstructed $N_i(D_i)$.

The numerical models in the form of size distributions of random sections $n_i(d_i)$, average sizes d, areal numbers of sections N_A and sections shape factors φ_s are the severely biased estimates of the corresponding propertias of spatial structures, $N_i(D_i)$, D, N_V and φ_p. Some of the characteristics of particle and phase dispositions in the space of structure such as coordination number N_{p-p} and center-to-center interparticle distance L_{C-C} are also biased estimates as the shape assumption is obligatory for their statistical reconstruction. It is often difficult to estimate the steadiness of such parameters as well as their conformity to the requirements of compatibility and representativity. Though numerical models for random sections could be used to identify the known structures for routine quality testing.

But much more consistency to the concept of "fingerprint of the structure" is provided by image properties derived by means of the Mathematical Morphology (MM) technique (Serra, 1981). The interconnections and the orientations of structural constituents could be described with the covariation $C(X,h,\alpha)$. The combined size-shape property yields from the dependency of the areal

fraction A_A on the size of the "structuring element" B which is used to perform "opening" or "closing" transformations of a given phase image. With the image analysing computer based on MM-principles being available the application of MM-technique in practical material science is possible.

A special group is comprised of the stereologiclal paremeters which are representative relative to the fracture surface, i.e. areal fractions A_A and linear fractions L_L of phase and fracture modes and mean paths of a crack L through various structure constituents. These parameters were used to analyse the dependency of the strength of cemented carbides on their structure. The comparison of the linear fractions of cobalt phase $L_{L_{Co}}$ at the crack path and the areal fractions $A_{A_{Co}}$ at the fracture surface with the volume fraction $V_{V_{Co}}$ has shown that $L_{L_{Co}} > V_{V_{Co}}$ and $A_{A_{Co}} \gg V_{V_{Co}}$, the areal fraction being $A_{A_{Co}} > L_{L_{Co}}$, and probably $A_{A_{Co}} \approx L_{L_{Co}} + L_{L_{WC-Co}} + L_{L_{WC-WC}}$.

The stereological analysis helped in establishing the presence of binder portions with low fracture resistance and in revealing the crack growing through the binder layer although the fracture seemingly occur at WC-WC and WC-Co boundaries. (Cherniavsky and Travushkin, 1980).

REFERENCES

Cherniavsky K.S. - Industrial Laboratory (USSR), 1971, N 8.
Cherniavsky K.S. - Stereology in Metal Science. Moscow, Metallurgy Publishers, 1977 (In Russian).
Cherniavsky K.S. - Industrial Laboratory (USSR), 1978, N 9 and N 12.
Cherniavsky K.S. - Industrial Laboratory (USSR), 1981, N 4(a).
Cherniavsky K.S. - Contemporary Stereology. Proc. 3d European Symp. Ljubljana, 1981(b), p. 299-307.
Cherniavsky K.S. - Science of Sintering, 1982, N 1, p. 1-12.
Cherniavsky K.S., Travushkin G.G. - Problems of Strength (USSR), 1980, N 4,
Cherniavsky K.S., Usova L.A., Phalkovsky V.A., Chapiro K.Ya. - Inorganic Materials (Acad.Sci.

USSR), 1982, N 7.
Serra J. Mathematical Morphology. Clarendon Press. London, 1981.