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# Carbide grain growth in cemented carbides

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**Abstract**

Abnormal grain growth is often observed in cemented carbides during sintering, but cannot be understood in terms of the classical LSW theory. In this work the grain growth behavior during sintering at 1430 °C is studied both experimentally and by means of computer simulations. A model based on several processes—2-D nucleation of growth ledges, mass transfer across the interface and long-range diffusion coupled in series—is formulated and the equations are solved numerically. Both computer simulations and experimental studies reveal that the grain growth behavior is strongly influenced by the initial size distribution.


*Keywords:* Carbides; Grain growth; Abnormal grain growth; Sintering; Modeling

## 1. Introduction

Cemented carbides consist of WC grains in a ductile Co matrix and are made by liquid-phase sintering. During sintering the average carbide grain size increases by means of coarsening or Ostwald ripening, i.e. large grains grow and small grains dissolve, leading to an increase in average grain size. In principle, two rate-limiting mechanisms are possible, i.e. long-range diffusion or interfacial reactions. These two limiting cases were considered in the classical analysis presented by Lifshits, Slyozov and Wagner (LSW) [1,2]. In both cases the analysis leads to a stationary particle size distribution with an average size that increases with time.

Such behavior is often observed experimentally. Nevertheless, it is well known that so-called abnormal grain growth may occur, i.e. a few large grains consume all small grains, leading to an abnormally large grain size. In cemented carbides, where normal WC grain size is of the order of μm or less, abnormal grain growth can sometimes lead to grain sizes of several hundred μm. In this paper an abnormal grain is defined to be around seven times larger than the average grain size, since this seems reasonable according to the microstructures. This phenomenon cannot be understood from the classical LSW theory.

In the case of cemented carbides the diffusion distances are very short and the common faceted shape of the WC particles indicates that the difficulty in forming new atomic layers rather than long-range diffusion is the rate-controlling mechanism. Different growth behavior may be interpreted in terms of difference in the interface mobility [3–6].

When grains are faceted, one expects a significant energy barrier for atom attachment on the particle surface. Therefore two-dimensional nucleation of atomic planes or surface defects are necessary for the growth of faceted grains [7–10]. In this paper the growth of individual grains is described by a model based on the nucleation of new atomic layers, a "pill-box" mechanism, as the major rate-controlling step [6–9]. The two processes—interface friction and long-range diffusion—are assumed to be coupled in series and will also consume part of the driving force.

On the other hand, dissolution may proceed more easily because atoms can dissolve without any barrier at the crystal corners. In that case the dissolution would proceed more or less at a rate controlled by mass transfer across the interface and by how rapidly atoms diffuse away from the crystal. It is also possible that the conditions may

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change in such a way that even the growth becomes controlled by diffusion. A reasonable model would thus need to account for both long-range diffusion and nucleation of new atomic layers.

It should be emphasized that the present model suggests an asymmetry between growth and shrinkage behavior. Consider a particle of critical size and suppose it has a partly filled atomic layer. If a fluctuation made it supercritical, it would grow by filling the atomic layer. The growth would then stop and could not continue until a new layer is nucleated, which requires that an activation barrier is bypassed. On the other hand, if a fluctuation made the particle hypocritical, it would shrink by removing atoms until the whole layer is removed. However, the removal of atoms from the next layer does not require any thermal activation because it can always start from corners.

In the present paper we will present a tentative model and analyze experimental data on grain growth during sintering at various times at a constant temperature. The tendency for abnormal grain growth is of particular interest.

## 2. The driving force for coarsening

Coarsening of $\beta$ phase grains in an $\alpha$ matrix is accompanied by a decrease in the $\alpha/\beta$ interfacial energy which provides the driving force for the process. It may be tempting to apply the method based on Onsager's extremum principle in order to derive the set of model equations. That method was applied recently to grain growth in one-phase materials by Svoboda and Fischer [11]. However, the method is based on a linear relation between rate and force which makes the dissipation a quadratic function of the rate. Unfortunately the pill-box nucleation model gives a highly non-linear relation that cannot even be linearized. Here we shall thus take a different and more intuitive approach which will include the traditional LSW theory as a special case. In the present work we use the term grain growth instead of coarsening since that is the term commonly used for cemented carbides.

In this first work the geometry of the $\beta$ grains is simplified as spherical and fully characterized by their radius $r$ and average interfacial energy $\sigma_p$. Of course WC, $\beta$ in the present case, is highly anisotropic and non-spherical, but for the sake of simplicity we neglect that complication for now; it will be taken into account at a later stage. Based on the traditional mean-field approximation, the driving force $F(r)$ for a grain with radius $r$, positive for growth and negative for shrinkage, is given by:

$$F(r) = 2\sigma_p\left(\frac{1}{r_c} - \frac{1}{r}\right) \tag{1}$$

The driving force is thus expressed per volume as a pressure. Of course, it may be expressed per mole by multiplying by the molar volume. Here $r_c$ is a critical radius, i.e. larger grains will grow and smaller shrink. As usual, grains with a critical size are in unstable equilibrium with the matrix. In the mean-field approximation the matrix composition is represented by its content of element $j$, $c_j^\alpha$, where $\alpha$ denotes the matrix, i.e. the Co-rich binder in the present case. An approximate relation between $r_c$ and $c_j^\alpha$ in a binary system is obtained from the well-known Gibbs–Thomson relation:

$$c_j^\alpha - c_j^{\alpha\infty} = \frac{c_j^{\alpha\infty}}{RT\left(c_j^\beta - c_j^\alpha\right)}\frac{2\sigma_p}{r_c} \tag{2}$$

where $c_j^{\alpha\infty}$ represents the normal solubility which is given by the phase diagram. In the classical LSW theory $r_c$ is very close to, and may be approximated as, the average radius. In the general case the critical size may be calculated from a thermodynamic calculation where the quantity $2\sigma_p V_m/r_c$ is added to the molar Gibbs energy of the $\beta$ phase, where $V_m$ is the molar volume (see Section 4).

The growth or shrinkage of a given grain may depend on several processes which all consume a part of the available driving force. In the next section these processes will be discussed in detail.

## 3. Growth and shrinkage of individual particles

The faceted character of the grains indicates that the growth rate is controlled by nucleation of new atomic layers rather than by long-range diffusion or mass transfer across the interface. Nevertheless we shall here consider nucleation of new atomic layers, mass transfer across the interface and long-range diffusion as coupled in series, i.e. all three processes must occur for a grain to grow.

### 3.1. Nucleation of new atomic layers during growth

The nucleation of new atomic layers is expressed in terms of the so-called pill-box model (see Refs. [7–9]). The rate of nucleation of new layers per area on particle $i$ is given by:

$$\dot{N}_i \propto exp\left(\frac{-\sigma_d^2\pi h}{F^n(r)kT}\right) \tag{3}$$

where $h$ is the height of the layer and $\sigma_d$ the interfacial energy of the cylindrical sides. $F^n(r)$ is the part of $F(r)$ that is used for nucleation of new atomic layers. The barrier for nucleation of new layers will thus depend on the quantity $\sigma_d^2 h$, which we shall evaluate from experimental information (see Sections 7 and 8).

Taking the particle growth rate as proportional to the nucleation rate, the thickness of a plane and the area of the particle, one may write:

$$\dot{r} = Ah4\pi r^2 exp\left(\frac{-\sigma_d^2\pi h}{F^n(r)kT}\right) \tag{4}$$

where $A$ is a kinetic coefficient.