# Solid State Sintering of Micrometric and Nanometric WC-Co Powders

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**Abstract**

*A solid stage sinterizacion model of the WC-Co is applied on this work. These results are compaired with the experimental data obtained for nanometric and micrometric sinter powder in an electric furnace and micrometric in a plasma reactor (using Abnormal Glow Discharge AGD). The correlations obtained allow the prediction of the sintering behavior in AGD for nanometric powder. The activation of the solid state sintering is shown with the decraease of the WC size and the use of AGD*

**Keywords : Sintering WC-Co, Solid state sintering, Plasma sintering, Nanopowder WC-Co**

## 1. Introduction

WC-Co is a material processed through powder metallurgy where its sintering implies several stages: initial stage when the Co that covers the WC powders spreading through surface diffusion, an intermediate stage when there is dissolution of the carbides in the Co, and a third stage where there is liquid sintering [1, 2]. For this reason, the first two stages are called solid stage sintering, for which, especially in the fist stage, the mass transportation mechanism is surface diffusion [1, 3, 4].

The surface and volumetric diffusion, vapor pressure, and the inverse of viscosity are parameters that depend on the temperature [1, 5] proporcional to the Arrhenius factor as is shown on Eq. 1 for the diffusion coefficient.

$$D = D_0 e^{-\frac{Q}{RT}} \qquad (1)$$

Q is the activation energy (sum of (i) the minimum energy that a particle must have so it can move from one space to another and of (ii) the energy that measures the possibility of the existence of a space for the particle to arrive at), R the gas constant, T the temperature, and $D_0$ the coefficient of diffusion at a predetermined temperature. Thus, *the rate at which the material flows* through diferent mechanisms will be proportional to the Arrhenius factor as presented in the initial stage by German [1].

Based on the previous reasoning and considering that a driving force (surface tension) exists, a model can be made for the initial stages of sintering that takes into account the *material's deformation* rate in time (as if it were a viscous flow). Given that each composition of WC-Co has particle and grain sizes, distributions, and distinct particle surfaces, amongst other things, a model is proposed in which with few parameters the real deformation rate of material, for the range approximately between 800 – 1100°C, can be reproduced as presented in Eq. 2 [3, 4, 6].

$$\dot{\varepsilon} = -A\rho^{2.1} d^{0.063} \frac{e^{-\frac{Q}{RT}}}{RT}\left(1-\sqrt{\frac{\rho}{3-2\rho}}\right) \qquad (2)$$

$A$ and $Q$ are constants found through linear regression of the measured deformation rate for a cylindrical piece, $\rho$ is the relative density or ratio between the density and the material's theoretical density without pores, and $d$ is the WC diameter of grain (~the initial average before sintering).

The initial stage sintering (800 – 1000°C) of micrometric and nanometric WC embedded in Co (WC-Co) was studied in this work. The WC-Co contraction model of Eq. 2 was compared with experimental results in a resistance furnace and a plasma reactor (using abnormal glow discharge -AGD). In this way, a prediction was made of what might occur when sintering nanometric WC-Co in AGD after understanding, with Bohm's criteria, that plasma generates ion impigment on the anode's surface between 1-15 eV (1eV ~ 11500°K) [7, 8], causing possibly the reduction of the activation energy (Q) in Eq. 2, explaining the results previously obtained by Escobar et al [9].

## 2. Experiments and Results

Experiments were carried out by using WC-15%Co of two different grades nano and micrometric, with the characteristcs showen in Table 1. The WC-15%Co powders were milled/mixed in ball mill in a solution of hexane (Solvent), hexanol (surfactant) and paraffin (binder). Samples were compacted at 120 MPa. in uniaxial press using floating die into cylinders.

Solid state sintering experiments were carried out at different temperatures raging from 700 to 1100 °C in Ar-$H_2$ atmosphere, by means of conventional resistance heating furnace and plasma reactor. In plasma processing (using Abnormal Glow Discharge AGD) the sample was heated by

radiation from the cathode witch was being continuously impacted with ions, neutral atoms and electrons.

The parameters A and Q were determined afterwards for the model of Eq. 2 through square minimization leaving it in a linear form. The results for each powder are also found in Table 1. A range of temperatures corresponding to the initial stage sintering between 800 – 1000°C must be chosen to perform the square minimization.

**Table 1. Powder characterization and values of Q and A for Eq. 2 model.**

| | d[nm] | $\rho_G$[%] | A[$Nm^2/s$] | Q[kJ/mol] |
|---|---|---|---|---|
| Micro 1 | 915 | 52.49 | $3.6\ 10^2$ | 56 |
| Micro 2 [9] | 2200 | 50.66 | $7.0\ 10^2$ | 56 |
| Nano | 20 | 48.99 | $3.0\ 10^5$ | 104 |

Afterwards, based on presintering results corresponding to three different materials presented by Escobar [9], a large increment in the contraction of WC-Co using AGD with respect to the resistance furnace is found for the same powder composition but with a size of 2.2µm (Micro 2-Table1). Contraction values for the resistance furnace and three combinations of electrodes for presintering in AGD are presented in Table 2

**Table 2. Linear contraction values for 2.2µm WC-Co powder (Micro 2-Table 1) in an resistance furnace and Plasma Reactor AGD for two different temperatures [9]**

| Presintering Method | 950°C | 1000°C | ΔQ/Q |
|---|---|---|---|
| Resistance Furnace | 0.4% | 0.7% | 0 |
| W cathode and graphite anode. (w-c) | 1.4% | 2.74% | 18.7% |
| Stainless steel cathode and graphite anode. (ss-c) | 2.83% | 2.9% | 21.9% |
| Stainless steel cathode and anode. (ss-ss) | 3.5% | 4.7% | 26.7% |

A change in (i) the material's sensible temperature or a (ii) reduction in the activation energy, in Arrhenious term, becomes a factor that increases the real deformation rate as presented in Eq. 3. As can be observed, if there is a decrease in the activation energy, it is represented in a factor greater than 1 ($\delta>1$) incrementing the real deformation rate in its absolute value.

$$e^{-\frac{Q-\Delta Q}{RT}} = e^{-\frac{M_Q Q}{RT}} = e^{-\frac{Q}{M_T RT}} = \delta(T) e^{-\frac{Q}{RT}} \quad (3)$$

In this way, varying the activation energy to equal the results in the plasma reactor AGD, a change in the value of the average activation energy is obtained as presented in Table 2. Fig 1 shows the lineal contraction of the resistence furnace (Table 1) introducing the parameters of Table 2 in order to find Q. This parameter is introduced on the model with the Nano parameters of A and Q (Table 1) and it allows the prediction of what is expected in the sintering on the Plasma Reactor –AGD with this nano powder, as it is shown on Fig. 2. It can be observed the enhanced of the solid stage sintering by AGD.

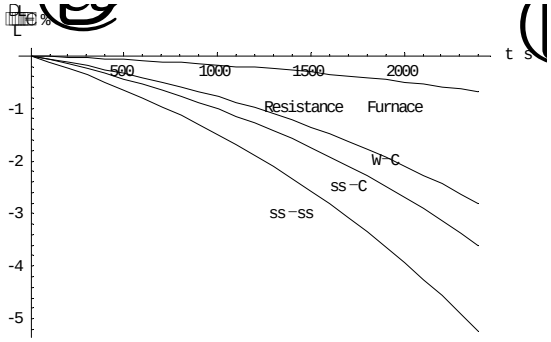


**Fig. 1. Modeling shrinkage Eq.2 and values of Table 1 changing the activation energy according to Table 2 for the powder Micro 2**

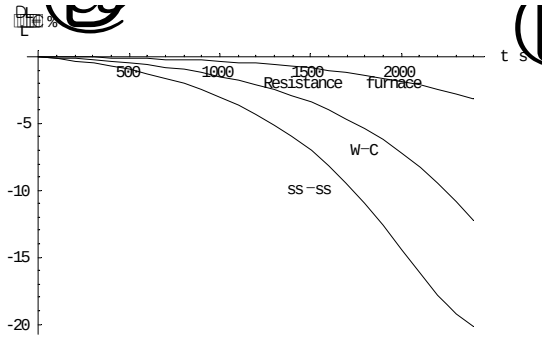


**Fig. 2. Modeling shrinkage in Plasma Reactor AGD with eq.2 and values of Table 1 changing the activation energy according to Table 2 for nanopowder Nano.**

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