MATHEMATICAL MODEL OF THE SINTERING PROCESS OF A MIXTURE OF MESOSCALE WC-CO POWDERS

Arif Mamedov¹, Aqil Babayev¹, Mukhtar Huseynov¹, Beture Musurzayeva¹

¹Azerbaijan Technical University

arif.memmedov@aztu.edu.az, aqil.babayev@aztu.edu.az, muxtar.huseynov@aztu.az, beture.musurzayeva@aztu.az

Abstract

The paper proposes models of the non-isothermal (solid-phase) sintering stage and isothermal (liquid-phase) sintering. When constructing the sintering process model, assumptions were made about the structure of the solid alloy, the mechanisms of its compaction and grain growth.

Based on literature data, a system of equations for the mathematical description of non-isothermal solid-phase sintering of WC-Co was constructed. The equations of the compaction kinetics at the *j*-*m* temperature stage and at the first 3.5% shrinkage, as well as the equations of the grain growth kinetics and temperature increase, are presented. The coefficients of volume grain boundary and surface diffusion were calculated.

A system of equations for the mathematical description of liquid-phase (isothermal) sintering of WC-Co under pressure in a vacuum is proposed. The proposed system considers the following equations: compaction kinetics and rheological model of a porous material, as well as the equation of the alloy grain growth kinetics. The relationships of the quality index which depends on the residual porosity, average grain size and density of the sintered hard alloy are derived.

The general equation of compaction kinetics *j*-*m* in the temperature mode, as well as the control equation of the product quality index and the characteristics of the WC-Co synthesis process with a mesostructure are obtained.

Keywords: hard alloy, mathematical model, solid-phase sintering, hot-phase sintering, rheology, compaction.

I. Introduction

In general, sintering is divided into three stages [1,2]: 1) temperature increase – heating (nonisothermal sintering); 2) holding at a constant temperature (isothermal sintering); 3) temperature decrease – cooling.

At the heating stage, sintering is carried out by a diffusion (solid-phase) mechanism. Solidphase sintering (SPS) of a powder body occurs without the formation of a liquid phase, with the following main processes occurring: volume and surface diffusion of atoms, shrinkage; recrystallization of a metal powder body (growth of some grains at the expense of others of the same phase); transfer of atoms of a substance through the gas phase due to volume and surface diffusion, viscous flow and flow caused by external loads during sintering under pressure. This type of sintering is accompanied by the effect and development of bonds between particles, the formation and growth of contacts (necks), the "healing" of pores (closing of through porosity) with their enlargement and spheroidization, compaction of the workpiece and its shrinkage, which occurs during heating mainly due to the volumetric deformation of particles, carried out by volumetric self-diffusion of atoms and adsorption of atoms (adatoms) on the surface of the substance/surface diffusion).

During liquid-phase sintering (LPS), an alloy is formed, one of the components of which is in the liquid state. Therefore, the question of the mechanism of diffusion displacement, or interaction, of the solid and liquid phases is of fundamental importance. The diffusion of atoms from the liquid phase to the solid at the first stage of their interaction should cause an increase in the volume of the component particles forming the basis of the powder body, the movement of their geometric centers and, consequently, an increase in the dimensions of the entire body. The subsequent dissolution of the solid phase particles in the liquid should be accompanied by a decrease in their volume, the convergence of their centers as a result of the action of capillary forces and, as a consequence, shrinkage of the powder body. Thus, after the formation of the liquid phase, the powder body during sintering should, in general, first exhibit growth and then shrinkage [1].

However, it should be borne in mind that the indicated successive stages of growth and shrinkage of the powder body must take place with low solubility of the liquid phase component in the solid or significant content of the liquid phase. Otherwise, the liquid phase quickly disappears, since due to the finely dispersed solid phase, the area of its surface through which diffusion occurs becomes very large and the powder body will only experience growth.

Since the solubility of tungsten carbide in cobalt in the solid state is about 10%, the dissolution process must be completed before the appearance of a eutectic liquid with a melting point below the melting point of cobalt. Therefore, sintering of the WC - Co alloy is characterized by significant compaction even before reaching the temperatures of the liquid phase appearance and rapid (within a few minutes) almost complete compaction after the liquid phase appears. Compaction before the liquid phase appears is carried out in solid phases (Co and WC) and is accompanied by diffusion of WC into Co, with the formation of solid solutions (intermetallics) [3]. The process of "liquid-viscous" flow leads to almost complete compaction of the sintered body, which is true in the presence of liquid of at least 20 ... 35% (of the total volume); liquid cobalt melt flows into the pores and pulls together the WC grains.

At a sintering temperature exceeding the melting point of the eutectic in the WC-Co system, a density close to the theoretical one is achieved in a very short time (1...4 min); during sintering in the absence of a liquid phase (below 1300°C), the final density is lower than the theoretical one even with a sintering duration of 30 min and its value depends on the temperature. As the results of experimental studies show, the degree of shrinkage for fine-grained powder is higher both during sintering in the solid phase and in the presence of a liquid one. The mechanism of WC grain growth during sintering of the WC-Co alloy has several variants [3]. Firstly, due to the precipitation of WC during cooling from the Co \odot solid solution. An examination of the data on the interaction of tungsten carbide with cobalt shows that during sintering, significant amounts of tungsten are first dissolved and the resulting liquid phase contains about 40% WC. Saturation of the liquid occurs due to the dissolution of some of the grains. When cooling, almost all of the WC contained in the liquid precipitates on undissolved tungsten carbide crystals as crystallization centers. However, as a result of this process, one cannot expect a significant increase in the size of the WC crystals.

If the content of Co in the WC-Co alloy is, for example, 10%, the latter is capable of dissolving about 6% of the WC present in the alloy during sintering. With uniform distribution of this amount of WC (when it precipitates from the liquid) on the remaining undissolved WC crystals, the size of the latter may increase slightly. Secondly, the growth of WC grains occurs due to recrystallization through the liquid phase. This is the main mechanism of WC phase growth. With an increase in the

cobalt content in the alloy, a more noticeable increase in the size of WC grains is observed, their maximum growth is achieved with an increase in the cobalt content from 1 to 6%, and with a large amount of cobalt, the growth becomes less due to an increase in the path of crystal transfer through the liquid due to an increase in the thickness of the interlayers. Some growth of the WC phase is also possible due to the coalescence mechanism, similar to the collective recrystallization of grains.

II. Mathematical model of the sintering process and quality control of WC-Co hard alloy from a mixture of meso-sized powders

As stated above, the sintering process is divided into three stages. Let us construct mathematical models of the first two stages: non-isothermal (solid-phase) sintering (i=1) and isothermal (liquid-phase) sintering (i=2). For solid-phase sintering (SPS), we will use the general equation (1) as the differential equation for porosity, which is valid throughout the entire solid-phase sintering stage, and for the first 3.5% of shrinkage at this stage, we can use equation (2).

$$\frac{dP_c}{dt} = \frac{3(1-P_c)}{1-P_0} \frac{d_y}{dt}$$
(1)

$$\frac{dP_c}{dt} = \frac{3(1-P_c)^2}{1-P_0} \cdot \frac{1}{\left[\frac{P_0 - P_c}{3(1-P_c)}\right]^{2,1}} \quad \left\{\frac{2\sigma\Omega D_v}{RTr_g^2} \cdot \frac{P_0 - P_c}{3(1-P_c)} + \frac{\varphi\Omega bD_b}{2KTr_g^a}\right\}$$
(2)

For liquid-phase sintering (LPS), the kinetics of compaction will be analyzed based on the rheological description of the deformation of the porous structure, considering the diffusion-viscous flow and compaction of a porous body under a uniform stress state under conditions of all-round compression [4]. This formulation of the problem is directly related to the sintering process under the simultaneous action of both the Laplace (capillary) pressure N_k and the hydrostatic pressure N_g applied from the outside (which is summed with the Laplace:

N=Nk+Ng

Dimensionless volumetric deformation under all-round compression is described by the relation [5]:

$$\Delta V/V = \varepsilon_{ii} = -N/\chi \tag{3}$$

where V- is the volume of the sintered porous body; \mathcal{E}_{ii} - is the volume of the body after sintering; \mathcal{X} - is the sum of the diagonal terms of the strain tensor; is the coefficient of bulk viscosity. Based on the hydrodynamic analogy of the theory of elasticity (it is on this analogy that the modern version of the rheological theory of sintering is based [6]), the following equation for the viscous flow of a compressible body can be written [4]:

$$V = \varepsilon_{ii} = 3\varepsilon_{rr} = -N/\chi \tag{4}$$

since in the above formulation of the problem the strain rate tensor is spherically symmetric and is reduced to one radial component $\dot{\varepsilon}_{rr}$. Taking into account the obvious connection $V = V_b(1-P)$ between the volume of a porous body and the volume of the substance enclosed in it (without pores) V_b , we obtain:

$$\dot{V} = \dot{p}(1-p) \tag{5}$$

where p - is the porosity of the body (dimensionless quantity).

The hydrodynamic analogy of the theory of elasticity gives grounds to believe that, when applied to an isotropic medium, the viscosity tensor has two components: χ – the coefficient of bulk viscosity and η – the coefficient of shear viscosity; they are analogous to the modulus of uniform compression and shear, respectively.

In the rheological description of the porous structure (χ, η) , the Mackenzie-Shuttleworth model is adopted [7,8], according to which the void phase can be represented as localized in an ensemble of non-interacting pores of equal size, spaced so far apart that it is possible to introduce into consideration an element of the porous body consisting of a pore of radius R, surrounded by a layer of an incompressible body with radius R° , while $p = (R/R^\circ)^3$.

By hydrodynamic analogy, the relationship between χ and η has the form

$$\chi = 4\eta \ (1-p)/3p \tag{6}$$

Taking into account the dependence of the shear viscosity coefficient η on porosity, studied in works [6,8]

$$\eta = \eta_0 \left(1 - p \right)^{5/3} \left[p a \cdot c \right] \tag{7}$$

and using the relation (6), (7), assuming $(1-p)^{5/3} \approx 1-(5/3) \cdot p$, we obtain the following law of compaction of a porous body:

$$\frac{dP}{dT} = \frac{1}{(1 - 5p/3) \cdot p} \cdot \frac{3(N_k + N_g)}{4\eta_0}$$
(8)

When constructing a model of the sintering process, we will accept the following assumptions from [9] about the structure of the material, the mechanisms of its compaction and grain growth:

1) the grains of the material are single-crystal and the structural parameter of the material is the average grain size (L);

2) compaction of the material at the sintering stage in a vacuum is carried out by the mechanism of diffusion-viscous flow, accompanied by thermally activated (with activation energy Q_b) slip along grain boundaries with a decrease in pore volume due to the absorption of voids by vacancy sinks, where the role of sinks is played by intergranular boundaries;

3) compaction (ρ) at the sintering stage under the pressure of uniform compression is carried out by the mechanism of viscous flow with volume (χ) and shear (η) viscosities;

4) the Mackenzie - Shuttleworth model is used for the rheological description of the porous structure ($\chi \cdot \eta$);

5) the growth of grains of the material occurs due to thermally activated (with activation

energy Q_s) diffusion coalescence of dispersed particles, consisting in the redistribution of the substance of small particles over the surface of large ones under the action of surface self-diffusion with the coefficient D_s;

6) the temperatures T_j at the j-stages (j=1,...n) of surface sintering (SSS) and the temperatures T_c of liquid-phase sintering (LPS) do not change over the volume of the furnace space;

7) the temperature of the material and the furnace space are equal.

Let us denote by time $\Delta_{1,j} = (t_{1,j=1}, t_{1,j}] - j - e(j = 1, ..., n \text{ intervals of non-isothermal})$

sintering with temperature $T_{1,j}$ maintained over an interval $\Delta_{1,j}$ of duration $\tau_{1,j}$;

$$t_{1,j} = \sum_{i=1}^{J} \tau_{1,i} (j = 1,...n); \ \tau_1 = t_{1,n}$$

Through we denote $\Delta_2 = (\tau_1, \tau_1 + \tau_2]$ the time interval of isothermal sintering of duration τ_2 , during which a constant temperature is maintained. We denote the porosity and grain sizes $\Delta_{1,j}$ (j = 1,...n) on through $p_{1,j}$ and L1, j, and Δ_2 on through p_2 and L_2 .

The system of equations for the mathematical description of non-isothermal solid-phase sintering includes:

- the equation for the kinetics of compaction at the j-m temperature stage (see equation (2)):

$$\frac{dp_{1,j}}{dt} = -\frac{3(1-p_{1,j})^2}{1-p_0} \frac{1}{\left[\frac{p_0 - p_{1,j}}{3(1-p_{1,j})}\right]^{2,1}} \times \left\{\frac{2\sigma\Omega D_{V,j}}{kT_{1,\nu}r_g^3} \frac{p_0 - p_{1,j}}{3(1-p_{1,j})} + \frac{\sigma\Omega bD_{b,j}}{2kT_{1,\nu}r_g^4}\right\}, \ t\epsilon \Delta_{j,j} = I \ (9,a)$$

for the first 3.5% of shrinkage, the equation of compaction kinetics is written as:

$$\frac{dp_{1,j}}{dt} = -\frac{3(1-p_{1,j})^2}{1-p_0} \frac{1}{\left[\frac{p_0 - p_{1,j}}{3(1-p_{1,j})}\right]^{2,06}} \times \left\{\frac{2,63\sigma\Omega D_{V,j}}{kT_{1,\nu}r_g^3} \left[\frac{p_0 - p_{1,j}}{3(1-p_{1,j})}\right]^{1,03} + \frac{0,70\sigma\Omega bD_{b,j}}{kT_{1,\nu}r_g^4}\right\} t \in \Delta j, = 1, \dots, n (9,b)$$

- the equation of the kinetics of grain growth of the material (from equation (10)):

$$\frac{dL}{dt} = \frac{B_1 \sigma D_s}{4L^3} \frac{\delta^4}{kT}$$
(10)

will

$$\frac{dL_{1,j}}{dt} = \frac{B_1 \sigma D_{s,j} \delta^4}{4L_{1,j}^3 \cdot kT_{1,j}}$$
(11)

- temperature increase equation

$$\frac{dT_{1,j}}{dt} = w_{T,j}, w_{T,j} = (T_{1,j} - T_{1,j-1}) / \tau_{1,j}, \ t \epsilon \Delta j.$$
(12)

The coefficients of volume grain boundary and surface diffusion are calculated using form (13):

$$D = D_0 \cdot \exp\left(-\frac{Q}{kT}\right) \tag{13}$$

$$D_{V,j} = D_{V,0} \cdot \exp\left(-\frac{Q_V}{kT_{1,j}}\right), \qquad D_{b,j} = D_{b,0} \cdot \exp\left(-\frac{Q_b}{kT_{1,j}}\right), \qquad D_{s,j} = D_{s,0} \cdot \exp\left(-\frac{Q_s}{kT_{1,j}}\right)$$
(14)

- initial conditions:

$$p_{1,1}\Big|_{t=0} = p_0, \ L_{1,1}\Big|_{t=0} = L_0, \ T_{1,1}\Big|_{t=0} = T_0$$
 (15)

- conditions for conjugation of temperature stages in time:

$$p_{1,j}\Big|_{t=t_{1-j}} = p_{1,j-1}, \ L_{1,j}\Big|_{t=0} = L_0, \ T_{1,1}\Big|_{t=0} = T_0$$
 (16)

The system of equations for the mathematical description of the stage of isothermal (liquid-phase) sintering under pressure includes:

- the equation of the kinetics of compaction of the material (see equation (8)):

$$\frac{dp_2}{dt} = \frac{1}{\left(1 - \frac{5}{3}p_2\right)} \cdot \frac{3(N_k + N_g)}{4\eta_0}, \ t\epsilon\Delta 2, \qquad (17)$$

- rheological model of a porous material (see equations (6) and (7)):

$$\chi = \frac{4\eta(1-p_2)}{3p_2}, \qquad \eta = \eta_0 (1-p_2)^{5/3}$$
(18)

- equation of the kinetics of grain growth of the material:

$$\frac{dL_2}{dt} = \frac{B_1 \sigma D_{s,n} \delta^4}{4L_2^3 \cdot kTc}, \ t \epsilon \Delta 2 \tag{19}$$

where

$$D_{S,n} = D_{S,0} \cdot \exp\left(-\frac{Q_S}{kT_S}\right)$$
(20)

The capillary pressure Pk applied to the pore surface and the current pore radius Rp are determined by the equations [9]:

$$P_{k} = 2p_{2} \cdot \sigma / R_{p}, \qquad R_{p} = R_{p} \left\{ \frac{\left[1 - p_{1,n}\right]}{p_{1,n}(1 - p_{2})} \right\}^{1/3}$$
(21)

- initial conditions:

$$p_2|_{t=t_n} = p_{1,n}, \ L_2|_{t=t_n} = L_{1,n}, \ T_c = T_{1,n}$$
 (22)

The density of the material at the stages of the process is calculated depending on its current porosity using the equations

$$\rho_{1,j} = (1 - p_{1,j})\rho_0, \quad j = 1,...,n, \qquad \rho_2 = (1 - p_{1,n})\rho_0$$
(23)

Volume shrinkage at stages is calculated using the equations:

$$\frac{\Delta V_{1,j}}{V_0} = \left(V_0 - \frac{m}{\rho_{1,j}} \right) / V_0, \ (j = 1, ..., n); \\ \frac{\Delta V_2}{V\Delta_0} = \left(V_0 - \frac{m}{\rho_2} \right) / V_0,$$
(24)

where $\Delta V_{1,j} = V_0 - V_{1,j}$, $\Delta V_2 = V_0 - V_2$, *m* - sample mass.

The quality index (residual porosity $p\rho$ and average grain size $L\rho$ and density $\rho\rho$) of a hard alloy is determined by the following relationships:

$$p_p = p_2 \Big|_{t=\tau_1+\tau_2}; \qquad L_p = L_2 \Big|_{t=\tau_1+\tau_2}; \qquad \rho_\rho = \rho_2 \Big|_{t=\tau_1+\tau_2}$$
 (25)

Discussion. Since at low and medium annealing temperatures used in non-isothermal sintering, $D_b \gg D_V$, namely $D_b / D_b = 10^3 \dots 10^5$, then in approximate calculations using formulas (9) we can assume $D_V \approx 10^{-4} D_b$. Instead of such an approximation, we can use the kinetic equation of linear shrinkage, applicable in the case of dominance of grain-boundary diffusion with respect to volume diffusion. This leads to the following equation of compaction kinetics in the j-m temperature regime instead of equation (9a):

$$\frac{dp_{1,j}}{dt} = \frac{-3(1-p_{1,j})^2}{1-p_0} \cdot 0.33 \left(\frac{2.14 \cdot \sigma \Omega b D_V}{kT_{1,j}r_g^4}\right)^{0.33} \cdot t^{-0.67}$$

which can be applied to all $t \in \Delta j$, starting from j=2 to j=n.

Let us denote by and the volume shrinkages at the end of the TFS stage (i=1) and at the end of the LFS stage (i=2) and the corresponding rates $W_i = \frac{d\gamma_i}{dt}$ (*i* = 1,2), where $\Delta V_{1,j} = V_0 - V_{1,n}$, $\Delta V_2 = V_0 - V_2$.

The indicators Y_1 and Y_2 are calculated using the equation

$$Y_1 = \left(V_0 - \frac{m}{\rho_{1,n}}\right) / V_0, \quad Y_2 = \left(V_0 - \frac{m}{\rho_2}\right) / V_0$$

Product quality management consists of selecting such control actions $U_1 = \{T_{1,j}, \tau_{1,j}, j = 1,...,n\}, U_2 = \{T_C, \tau_2\}$ with elements that satisfy the constraints

 $U_{k,i}^{\min} \leq U_{k,i} \leq U_{k,i}^{\max}$ that ensure the specified (desired) values of the quality indicators of the obtained material

$$p_{\rho} \leq p_{\rho}^{\max}$$
, $L_{\rho} \leq L_{\rho}^{\max}$, p_{ρ}^{\min}

and characteristics of the synthesis process

$$Y_i^{\min} \leq Y_i \leq Y_i^{\max}, \quad W_i^{\min} \leq W_i \leq W_i^{\max} \quad (i = 1, 2)$$

Where p_{ρ}^{\max} , L_{ρ}^{\max} , p_{ρ}^{\min} , – ultimate residual porosity, average grain size and alloy density, Y_i^{\min} , Y_i^{\min} , F_i^{\max} – hreshold values of volume shrinkage at the stage i, W_i^{\min} , W_i^{\max} – threshold values of shrinkage rate of the synthesized material, $U_{k,i}^{\min}$, $U_{k,i}^{\max}$ – regulatory values of control actions from the set Ui, depending on the equipment and material.

III. Conclusions: 1

1. A mathematical model of the non-isothermal stage of sintering of a WC-Co hard alloy from a mixture of meso-sized powders has been obtained. It consists of the equation of compaction kinetics at the j-m temperature stage, at the first 3.5% shrinkage, and the equation of grain growth kinetics and temperature increase. The coefficients of volume grain boundary and surface diffusion have been calculated.

2. Equations for the mathematical description of isothermal sintering of a WC-Co hard alloy under pressure in a vacuum have been proposed. They consider the following equations: compaction kinetics equations, a rheological model, and a grain growth equation in the alloy structure. These equations allow one to control the product quality indicator and the characteristics of the WC-Co synthesis process with a meso structure.

IV. Conflict of interest

The authors declare that they have no conflict on interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper

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