Microstructural Development and Evolution of Liquid Phase Sintered Cr-Cu Composites

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Abstract:
Features of the microstructure formation of Cr-Cu composites under impregnation followed by liquid phase sintering of reduced and electrolytic chromium powders at 1200°C in a vacuum of \((2-4) \times 10^{-3} \text{ Pa}\) have been studied. The refractory component particle size distribution in the microstructure of samples with reduced chromium sintered for 60 min is shown to obey a normal logarithmic law; with distribution parameters being sensitive to the volume fraction of the refractory particles. The calculated values of the dihedral angle are close to the value of one of the modes in the experimental dihedral angle distribution for the microstructure of electrolytic chromium based samples \((115^\circ)\). The interfacial and interparticle surface energies ratio \(\sigma_{sl}/\sigma_{ss}\) > 0.5 is shown to correspond to theory for the Cr-S-Cu system in equilibrium, which indicates the presence of skeleton structure elements in the course of composition formation under liquid phase sintering (including the case of excess liquid phase). Experimentally determined interparticle and interfacial surface areas, solid particle contiguity and continuity are discussed in terms of concurrent diffusion-controlled particle coarsening (in Lifshitz, Slyozov and Wagner theory) and particle coalescence (in German’s model). The kinetics of shrinkage for the composites with 50...55 % solid-phase volume-fractions at heating and isothermal sintering in a vacuum at a temperature of 1200°C in terms of linearly viscous rheological theory are discussed.

Keywords: Liquid-phase sintering, Composite, Chromium, Copper, Microstructure.

Introduction

Cr-Cu composites are widely used as contact materials for medium-voltage and high-current interrupters. A variety of their properties (abrasive, erosion-resistant, specific resistant and others) are produced by the liquid phase sintering process. The properties of these depend largely on the microstructure developed during sintering. Liquid-phase sintered microstructures are characterized in terms of the solid phase volume fraction, \(V_p\), scale (average solid particles radius), \(R\), the surface-to-volume ratio, \(S_v\). Solid phase morphology is conditioned on interfacial and interparticle surface energies ratio \(\sigma_{sl}/\sigma_{ss}\) and can be quantified by the dihedral angle \(\psi\), (between two particles on the boundary with liquid phase), contiguity, \(C_c\) (interparticle surface area as a fraction of the total surface area), and continuity, \(C_p\) (the number of solid-solid particle contacts per particle).

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This paper is concerned with an experimental study relating the scale and morphology of liquid phase sintered Cr-Cu composites and features of densification of these under isothermal and nonisothermal sintering conditions in a vacuum.

Experimental procedure

Electrolytic and reduced by hydride calcium powders of chromium (99.93 and 99.3 % purity respectively) as well as copper melted in a vacuum and electrolytic (99.999 and 99.3 % purity respectively) are used. The specimens were produced by impregnation of freely poured chromium with copper at 1200°C in a vacuum of (2-4)⋅10^{-3} Pa (of excess liquid phase or equal chromium and copper mass) and subsequent isothermal liquid sintering for 3-90 min. Other specimens were produced by blending powders of reduced chromium and electrolytic copper with subsequent compacting (pressure of 200 MPa) into 10 mm diameter and 10 mm high cylindrical powder compacts with a green theoretical density of about 70 %. The compacts were sintered in a vacuum of 10^{-5} Pa with a heating rate up from 2 to 33 K/min at 1200 °C and isothermal sintering at this temperature for 1 hour. Quantitative metallography was performed on suitably prepared metallographic samples. The average solid particles size - \( \bar{R} \), the interfacial surface to-volume ratio, \( S_{s-l} \) (between solid and liquid phases) and interfacial surface to-volume ratio, \( S_{s-s} \) (between two or three solid particles), were determined using the line intercept method [1], and the volume fraction - \( V_p \) was determined as a check on composition. The contiguity, \( C_c \), was defined by the ratio [1]:

\[
C_c = \frac{2S_{s-s}}{2S_{s-s} + S_{s-l}}
\]

The continuity, \( C_p \), was determined using the Gurland method [2], by counting the number of interparticle contact particles, \( M_{s-s} \), and total number of particles, \( N_{total} \), on a two-dimensional plane of polish (per unit area), by the ratio:

\[
C_p = \frac{8}{\pi^2} \left( \frac{M_{s-s}}{N_{total}} \right)^2 \frac{2}{C_c}
\]

It was also necessary to define at what stage of particle fusion «two» particles should be considered as «one». In this regard, it was postulated that if the neck diameter was at least two-thirds of the diameter of the smaller of the contacting particles, the particles were considered as having fused into one. Computer automated analysis of the images was carried out. Measurement of at least 2000-3000 particles-matrix and 300-400 interparticle line intercepts were necessary to obtain accurate values for \( S_{s-s} \), \( C_c \), and \( C_p \).

Experimental results

Solid-phase volume-fractions in the specimens after impregnation of freely poured chromium with copper were estimated as \( V_p=37...40 \) % vol. (in the case of excess liquid phase) and as \( V_p=50...55 \) % (in the case of equal chromium and copper mass). Fig.1 shows that in the composites formed from reduced chromium the number of interparticle contacts and the average particle size increase with increasing sintering time and solid phase volume fraction. Coalescence occurs in the composites studied even at an excess of liquid phase. Particle size distribution parameters appear sensitive to the solid-phase volume-fraction (fig. 2). With an increase in the volume fraction of the solid phase, the shift of the distribution curve in a region of great significance occurs as well as an increase in the degree of the
inhomogeneity of particles according to size (broadened histogram peak). The distribution obeys a normal logarithmic law for 60 min under sintering.

The results of studies show that particle size growth kinetics obey the law of $\overline{R}^3 \sim t$ (fig.3), by the mechanism of diffusion-controlled coarsening theory developed by Lifshitz, Slyosov and Wagner (LSW-theory, [3]) described by the relation:

$$\overline{R}^3 = \overline{R}_0^3 + kt,$$

where: $\overline{R}_0$ is the average initial solid particle radius; $k$ is the coarsening rate constant; $t$ is the sintering time.

The experimentally determined coarsening rate constants are:

- $K_{\text{exp}} = (0.265 \pm 0.004) \cdot 10^{-18} m^3 / s$ - for $V_p = 37...40$ % vol.
- $K_{\text{exp}} = (0.34 \pm 0.03) \cdot 10^{-18} m^3 / s$ - for $V_p = 50...55$ % vol.

LSW-theory modified by Ardell [4] predicts that while the basic $t^{1/3}$ kinetics are maintained the coarsening rate increases with increasing solid volume fraction. The theoretical rate constant can be determined by the relationship:

$$K_{\text{theor}} = \frac{8}{9} \sigma_{s-l} \cdot \Omega \cdot \frac{D_s \cdot C_e}{k \cdot T} f(v),$$

where: $\sigma_{s-l}$ is the surface energy solid-liquid; $\Omega$ is the atomic volume of solid phase; $D_{s-l}$ is the diffusion coefficient of solid phase into the liquid; $C_e$ is the equilibrium solubility of solid phase in the liquid; $k$ is Boltzmann's constant, $T$ is the absolute temperature; $f(v) = K_{\text{exp}} / K_{\text{theor}}$ is a function which depends on the solid volume fraction.
An estimate of the diffusion coefficient of chromium in copper at 1200 °C by formula (4) using the experimentally determined coarsening rate constant and calculated $f(v)$ by Ardell (13.2 and 17.8 for 37-40 and 50-55% vol. of solid phase respectively, [4]) showed that

$$D_{Cr-Cu} = 6.4 \cdot 10^{-9} \text{m}^2/\text{s}.$$  

The time of initial stage of diffusion-controlled coarsening, while asymptotic particle size distribution (which is characterized by ratio $\frac{R_{\text{max}}}{R}$ = 2.25, [4]) has not yet been established, is equal: $t_{\text{ini}} = \frac{R_v}{D_{\alpha} \cdot \alpha}$ (where $\alpha$ is a thermodynamic characteristic of system, 

$$\alpha = \frac{2\sigma_{\text{c-l}} \cdot \Omega \cdot D_{\text{eq}} \cdot C_m}{\kappa \cdot T,}$$

The calculated time of initial stage sintering $t_{\text{ini}} = 30$ min, is in very good quantitative agreement with experimental data (tab. I).
Tab. I. Experimental ratio \( \frac{R_{\text{max}}}{R} \) in relation to the sintering time

<table>
<thead>
<tr>
<th>Solid-phase volume fraction, %</th>
<th>Sintering time (min)</th>
<th>3</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>37-40</td>
<td></td>
<td>4.5</td>
<td>3.8</td>
<td>2.6</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>50-55</td>
<td></td>
<td>3.4</td>
<td>3.2</td>
<td>2.9</td>
<td>2.9</td>
<td>3.4</td>
</tr>
</tbody>
</table>

The value of the equilibrium dihedral angle, \( \psi \), between the adjacent equiform particles of solid phase on the boundary with liquid:

\[
\frac{\sigma_{s-s}}{\sigma_{s-l}} = 2 \cos \frac{\psi}{2}
\]  \hspace{1cm} (5)

where: \( \sigma_{s-s} \) and \( \sigma_{s-v} \) – are surface energy on solid-solid and solid-liquid boundaries respectively.

The equilibrium dihedral angle can be estimated by the equation:

\[
\psi = 2 \arccos \frac{\sigma_{s-s}}{2(\sigma_{s-g} - \sigma_{l-g} \cos \Theta)}
\]  \hspace{1cm} (6)

The equation (6) is obtained via substitution into expression (5) using the Young–Neumann relation-ship: \( \cos \Theta = (\sigma_{s-g} - \sigma_{s-l})/\sigma_{l-g} \) (where: \( \sigma_{s-g} \), \( \sigma_{l-g} \) – surface energies on solid-gas and liquid-gas boundaries respectively).

Fig. 3 Plot of average solid particle size \( \bar{R} \) in relation to the sintering time in the microstructure of composites. Curves (1) and (2) – \( V_p = 37-40 \% \) and \( V_p = 50-55 \% \) vol. respectively.

The dihedral angle in the Cr-Cu system in equilibrium, calculated by formula (6) is equal \( \psi = 128-140^\circ \) (used following data: \( \sigma_{s-g} = 1300 \text{ mJ/m}^2 \) for copper and \( \sigma_{s-g} = 1631 \text{ mJ/m}^2 \) for chromium [5]; \( \sigma_{s-s} = 0.4 \sigma_{s-g} \) is the averaged value for polycrystalline chromium [6], \( \sigma_{s-g} = 2400 \text{ mJ/m}^2 \) as determined by the zero creep method [6] or \( \sigma_{s-g} = 1876 \text{ mJ/m}^2 \) calculated
from $\sigma_{s-g} = 1.15\sigma_{l-g}$ [7], and $\Theta = 39^\circ$ under the experimental conditions [8]). The calculated $\psi$ is close to the value of one of the modes in the experimental planar dihedral angle distribution in the microstructure of electrolytic chromium based samples (115°) (fig. 4, a, b).

![Fig. 4 Microstructure of specimen formed by electrolytic chromium (a) and histogram for planar dihedral angle $\psi$ distribution in the microstructure (b).](image)

Average values for the dihedral angles in the microstructure of the composites, formed by reduced chromium, are already stable during the first minutes of isothermal sintering and are kept constant throughout 90 min of sintering at a level of 88±10°. The evaluation of the thermodynamic ratio of solid skeleton formation for system in equilibrium (which $\frac{\sigma_{v-1}}{\sigma_{v-1}} \geq 0.5$, [9]) shows that in Cr$_s$-Cu$_l$ system this ratio is realized:

$$\frac{\sigma_{Cr-Cr}}{\sigma_{Cr-Cr}} = 0.9-1.3$$

(we used data given above).

![Fig. 5 Effect of sintering time and solid-phase volume-fraction on microstructure geometric characteristics of composites: (a) - contiguity, C$_c$ and (b) - member contacts per unit particle, C$_p$. Curves (1) and (2) - $V_p=37-40$ and $V_p=50-55$ % vol. respectively.](image)

It is established that in the microstructure of composites formed reduced chromium contiguity, C$_c$, attains values 0.30 and 0.35 and the number of solid-solid particle contacts per particle, C$_p$, established over 0.4 and 2 for $V_p=37-40$ and $V_p=50-55$ % vol. respectively, at
90 min sintering time (fig. 5, a, b). According to the Gurland’s criteria (C_p > 1.5, [2]) for composites with V_p = 50...55 % vol. a rigid skeleton is formed. The area of the interparticle surface-to-volume ratio S_s-s remains the essentially constant (within error-margin of experiments) up to 60 and 90 min sintering for V_p = 37...40 and V_p = 50...55 % vol. respectively (fig. 5, a, b). The absence of changes in S_s-s in the initial stage of sintering (fig. 6, a) can be explained by the low speed of increase in the interparticle contacts, limited by solid diffusion.

German’s model [10], which connects the surface area reduction rate of particles with mechanism neck radius growth (in the Kuczynski model) at the initial stage of the sintering is used for analysis of the kinetics of changes in the interphase surface-to-volume ratio S_s-s in the microstructure of the Cr-Cu composites formed reduced chromium. German's model predicts the surface area reduction by relationship:

$$\frac{\Delta S_v}{S_v^o} = \gamma$$

where:

$$S_v = \gamma$$

and

$$C$$

is the kinetic constant.

Since

$$\Delta S_v = 1 - \frac{S_v}{S_v^o}$$

and

$$S_v \geq S_v^o$$

whence it follows that

$$\frac{\Delta S_v}{S_v^o} = S_v^{-1}.$$  It is known that in the system of the isometric spherical particles

$$S_v = \frac{4\pi R^3}{(4/3)\pi R^3} = \frac{3}{R},$$

and if

$$R \sim t$$

then

$$\left(\frac{\Delta S_v}{S_v^o}\right) = Ct.$$  

Taking into account that at the first stage of liquid phase sintering of Cr-Cu composites changes S_s-s are still sufficiently small, and also that a volume of refractory particles remains constant, than for Cr-Cu composites

$$\frac{\Delta S_v}{S_v^o} \approx \frac{\Delta S_{s-s}}{S_{s-s}^o}$$

(where

$$S_{s-s}^o$$

initial and instantaneous interphase surface-to-volume ratio).

The estimate of \(\gamma\) of from experimental data of surface area reduction kinetics showed that (fig. 6, b):

Fig. 6 The interparticle surface-to-volume ratio, \(S_{s-s}\), for different sintering times (a) and surface area reduction kinetics in the logarithmic coordinates (b). Curves (1) and (2) – \(V_p = 37-40\) and \(V_p = 50-55\) % vol. respectively.
The features of the shrinkage kinetics of composite with $V_p=50\ldots55\%$ at heating and isothermal sintering (at 1200 °C) are studied.

**Tab. II.** Porosity change after sintering in vacuum $10^{-5}$ Pa of composite with $V_p=55\%$ vol. against heating rate

<table>
<thead>
<tr>
<th>Heating rate, K/min</th>
<th>Maximum temperature of heating, °C</th>
<th>Initial porosity, %</th>
<th>Finite porosity, %</th>
<th>Volume change $\Delta V/V^*$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid phase sintering</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1050</td>
<td>32</td>
<td>26</td>
<td>-7.9±1.2</td>
</tr>
<tr>
<td>8</td>
<td>1050</td>
<td>32</td>
<td>36</td>
<td>+6.6±1</td>
</tr>
<tr>
<td>33</td>
<td>1050</td>
<td>32</td>
<td>33</td>
<td>+4.4±1.5</td>
</tr>
<tr>
<td><strong>Liquid phase sintering</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1200</td>
<td>32</td>
<td>19</td>
<td>-15.3±2.3</td>
</tr>
<tr>
<td>8</td>
<td>1200</td>
<td>32</td>
<td>29</td>
<td>-5.2±0.8</td>
</tr>
<tr>
<td>33</td>
<td>1200</td>
<td>33</td>
<td>31</td>
<td>-3.7±0.5</td>
</tr>
<tr>
<td>33**</td>
<td>1200</td>
<td>33</td>
<td>22</td>
<td>-17.7±1.2</td>
</tr>
</tbody>
</table>

* "+" and "−" increasing and decreasing of volume specimens respectively;
** Isothermal sintering for 1 hour.

The heating of specimens is accompanied by "increase of the specimens", which continues up to temperatures of 900-900 °C at all heating rates (fig. 7, a), the finite volume changes of specimens at nonisothermic sintering depend on the heating rate and maximum temperature (tab. II). The effect of "increase" more strongly appears with an increase of heating rate, probably, because of the development of the process of local non-uniform densification in different zones of specimens.

The evaluation of kinetics during isothermal sintering at 1200 °C was carried out. The densification kinetics under isothermal hold can be estimated in the framework of a
phenomenological sintering theory, accounting for rates of change in porosity controlled by the particle accommodation mechanism (the Ashby model), by ratio \[9]\):

$$\theta = \theta_0 \left(1 + \frac{B \cdot K}{R^3} \right)^{-\frac{q}{K}}$$

(6)

where: \(K\) – rate coarsening constant; \(q\) – constant, \(q = \frac{A \cdot \sigma_{slv} \cdot D_{slv} \cdot C_{\infty} \cdot v \cdot \Omega}{B \cdot k \cdot T}\), \(A = 100\), \(B = 10\).

The theoretical estimation of densification kinetics of Cr-Cu composite with \(V_p = 55\%\) vol. carried out using experimentally determined data \(D_{Cr-Cu} = 6.4 \cdot 10^{-9} m^2/s\) and \(K_{exp}(\approx 0.34 \pm 0.03 \cdot 10^{-9} m^2/s\), is different from experimentally observed volume changes of specimens (fig.7, b). The difference between the experimental data and theoretical estimation of densification probably, may be explained by anomalous porous growth because of local non-uniform densification and the rigid skeleton solid phase formation under sintering. The features of shrinkage kinetics of the Cr-Cu composites are in need of further studied.

Conclusions

A rigid skeleton structure is formed in the liquid phase sintered Cr-Cu composites. It is confirmed by: calculated thermodynamic ratio \(\sigma_{sl}/\sigma_{ss}\); agreement of theoretical estimation and experimental data of the dihedral angles; presence of skeleton elements in the microstructure of composites and number of contacts per unit particle more than 1.5. Experimentally determined solid particle growth kinetics follows a cubic law \(R^3 = t\), that indicates domination of diffusion-controlled particle coarsening mechanism (by Lifshitz and Slyosov and Wagner theory).

Coarsening rate constants for composition with 37-40 and 50-55\% solid-phase volume-fractions are determined. Evaluation of the diffusion coefficient of chromium in copper at 1200°C is carried out. Stationary particle size distribution is established for 30 min sintering.

German’s model connected the surface area reduction kinetics with neck growth mechanisms (in the Kuczynski model) and it can be used for determination of coarsening structure mechanism during liquid phase sintering. The difference between the experimental data and theoretical estimation of densification of composites, probably, may be explained by anomalous porous growth because of local non-uniform densification and the rigid skeleton solid phase formation during sintering.

References


Садржај: Проучене су особености формирања микроструктуре композита Cr-Cu добијених импрегнацијом и синтеровањем у присуству течне фазе редукованих и електролитичких прахова хрома на 1200°Ц у вакуму од (2-4)⋅10⁻³ Па. Расподела честица праха рефракторне компоненте у микроструктурама узорака са редукованим хромом синтерованим 60 минута прати нормалну логаритамску законитост, при чему су параметри расподеле осењиви на запреминску фракцију рефракторних честица. Израчунате вредности дихедралног угла су близу вредности за један од модова у експерименталној дихедралној расподели за микроструктуру електролитичких узорака на бази хрома (115°C). Показано је да однос површинске енергије на граници и између честица σ_sl/σ_ss>0,5 одговара теорији Cr₅-Cu₁ система у равнотежи, што указује на присуство скелетних структурних елемената током формирања састава током синтеровања у присуству течне фазе (укључујући случај вишка течне фазе). Експериментално одређене површине између честица и на границима, континуалност и додир између чврстих честица су дискутовани у смислу конкурентног дифузијом контролисаним згушивањем честица (коришћеном теорије Лифшица, Слизова и Вагнера) и коалесценције честица (Џерманов модел). Размотрена је кинетика скупљања за композите са 50-55% черсте фазе запреминских фракција током загревања и изотермског синтеровања у вакуму на температури од 1200°C у односу на линеарно вискоznу реолошку теорију.

Кључне речи: Синтеровање у присуству течне фазе, композит, хром, бакар, микроструктура.