THEORY AND TECHNOLOGY OF SINTERING, THERMAL, AND CHEMICOTHERMAL TREATMENT PROCESSES

EFFECT OF OXYGEN ON THE LIQUID-PHASE SINTERING OF VERY FINE TUNGSTEN-COPPER POWDER MIXTURES

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The process of liquid-phase sintering (LPS) of tungsten-copper powder mixtures containing* less than 33% Cu can be intensified by increasing the degree of dispersion of the W phase, i.e., by decreasing the tungsten powder particles to micron and submicron sizes [1]. The main contribution to the densification of such mixtures comes from a regrouping of their particles, which continues virtually up to the instant of complete shrinkage of blanks. With a very fine tungsten powder, even a small solubility of tungsten in copper is sufficient to bring about some changes in the shape of the particles during their migration in the liquid copper phase under the action of the compressive capillary pressure. For the regrouping, therefore, full wetting of the solid phase by the liquid is necessary.

In practice the LPS of very fine powder mixtures is accompanied by sweating-out of copper and its redistribution inside the part being sintered. As a result, maximum densification is not attained. In the authors’ opinion, these phenomena are attributable to the conditions of wetting of tungsten by liquid copper being disturbed by incomplete reduction of surface oxides on the particles, insufficient purification of copper from oxygen, and the retention of water vapor forming inside the part.

In the present work a study was made of the processes of oxygen removal accompanying the sintering of blanks from W-30% Cu (TC) powder mixtures and of the effect of this refinement on their densification. TC powder mixtures contain up to 0.5% of oxygen, a large part of which is combined in surface oxides and a smaller part dissolved in copper. It has been established that at 1100-1200°C oxygen-saturated copper does not wet tungsten. With rising temperature the angle of contact decreases, but, when oxygen on the W/Cu interface is in the form of WO₃, complete wetting is not achieved even with oxygen-free copper [2]. When substances active with respect to oxygen are added to copper, they react with surface oxides in an inert atmosphere and sharply decrease the angle of contact of copper on a partly oxidized tungsten base. Similar processes can, of course, be expected to take place in hydrogen.

With rise in temperature from 800 to 1000°C the solubility of hydrogen in copper increases threefold, and its diffusion coefficient at 1030°C is equal to 3·10⁻⁴ cm²/sec [3]. At the same temperature the coefficient of diffusion of oxygen in copper is slightly smaller, 1·10⁻⁵ cm²/sec. Liquid copper dissolves some oxygen and at 1065°C forms a eutectic with Cu₂O. To the eutectic point there corresponds a concentration of 0.39% O₂ or 3.5% Cu₂O. In solid copper oxygen is present mainly in the form of Cu₂O inclusions, and hydrogen, on reducing them, gives rise to the appearance of swellings ("hydrogen disease"). It is only at oxygen contents of less than 0.06% (or less than 0.54% Cu₂O) that this phenomenon does not occur [4]. Thus, to ensure good wetting, it is advisable, before the melting of copper, to purify both it and tungsten from oxygen, aiming to lower its total content to 0.06% or less.

Refining will be more rapid and fuller with TC compacts of high gas permeability. Yet it is known that specimens from fine powders begin to experience densification at low temperatures and that a coarsening of their porous structure as a result of local densification can occur in them even during the heating stage. As a characteristic of porous structure, in our work we adopted the mean pore size (dₚ) determined from the minimum pressure required for forcing a gas bubble through a porous specimen [6].

The pore size was found to depend on the initial porosity, and above 600°C it grew, particularly in specimens of lower initial porosity (Fig. 1). Gas permeability was a maximum at 900-950°C, since at these temp-

*All contents are expressed in volume percentages.

Data on the effect of annealing in hydrogen (dew point \(-55^\circ C\)) on the oxygen contents of blanks from TC mixtures of different degrees of fineness (the specific surfaces of mixtures I and II were 0.3 and 1.1 m\(^2/g\), respectively) are given below.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>950</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O_2) %</td>
<td>I</td>
<td>0.1</td>
<td>0.10</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.11</td>
<td>0.11</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Notes. Exposure time at each temperature was 4 h. The starting oxygen contents of mixtures I and II were 0.11 and 0.20%, respectively.

It will be seen that in both cases it proved impossible to lower in the solid phase the oxygen content to 0.06% in an acceptable time, and that it was only above 1083°C that it fell appreciably. Prior refining of blanks from the powder of specific surface 1.1 m\(^2/g\) at 950°C had a beneficial effect on densification (Fig. 2): Its maximum was attained already at 1200°C, and no case of sweating-out of copper was ever observed. Clearly, when the amount of oxygen does not exceed 0.1%, its rate of combining and the rate of water vapor removal above the melting point of copper are higher. There are two reasons for this: a fivefold increase in the solubility of hydrogen in copper at the latter's melting point and the retention of porosity in specimens at 1100°C.

Absence of sweating-out of copper is evidence for the formation of tungsten/liquid copper contacts, as a result of which the energy of the system diminishes. When there is no wetting, copper trapped in pores is not retained in them by surface tension forces, but tends to form spherical drops either on the surface of the part or in its inner voids. In these circumstances energy is gained as a consequence of a decrease in surface area when a cylinder becomes transformed into a sphere. For example, for a 1-mm-long, 1-μm-diameter capillary the surface area ratio at constant volume is equal to five.

Thus, in the LPS of very fine tungsten-copper powder mixtures maximum densification takes place under conditions of full wetting of tungsten by liquid copper, for which its purification from oxygen is required. A reduction in oxygen content to 0.03% in the sintering in hydrogen of parts of wall thickness greater than 10 mm takes place only after the copper has melted.