COLLECTIVE RECRYSTALLIZATION IN LOOSELY Poured ZIRCONIUM CARBIDE POWDERS

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An earlier investigation into the collective recrystallization processes (grain growth at high temperatures in undeformed metal) in loosely poured titanium and niobium carbide powders [1] demonstrated that, already at 1600°C, recrystallization grain growth begins in nonstoichiometric phases of these carbides, the magnitude of the energy of activation for this process depending on the imperfection of the carbon sublattice of the carbides.

In the present work, a study was made of collective recrystallization in zirconium carbide powders representing the homogeneity region of this compound.

ZrC powders were obtained by synthesis from metallic zirconium and calcined acetylene black in a vacuum resistance furnace at an initial pressure of 10^{-3} mm Hg, the process consisting of the following operations: heating to 1400°C and holding for 30 min, followed by heating to 1850°C and holding for 1.5 h. The resultant carbide was comminuted to a mean particle size of 3.5 μ.

Powder batches weighing 0.25 g each were heated in a vacuum resistance furnace at temperatures of 1600, 1800, and 2000°C for periods of 1, 2, 4, and 6 h. Heating to the desired temperature was performed in 1 h. The chemical compositions of the zirconium carbide phases obtained are presented in Table 1.

The techniques for the preparation of microsections and calculation of the mean grain size were the same as those employed earlier [1].

The effect of holding time on the mean linear grain size of zirconium carbide at various temperatures is illustrated in Fig. 1. It has been demonstrated that the rate of growth is related to the linear grain size by the expression [1]:

\[
\frac{dl}{dτ} = K \left( \frac{1}{T} - \frac{1}{l_∞} \right),
\]

where K is the rate constant of collective recrystallization, l is the instantaneous grain size, and l_∞ is the limiting grain size at a given temperature.

<table>
<thead>
<tr>
<th>Carbon content, wt.%</th>
<th>Resulting compound</th>
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<tbody>
<tr>
<td>before sintering</td>
<td>after sintering</td>
</tr>
<tr>
<td>total C free C combined C</td>
<td>total C free C combined C</td>
</tr>
<tr>
<td>7.74  0.4  7.36</td>
<td>8.11   0.35  7.8   ZrC_{0.65}</td>
</tr>
<tr>
<td>8.77  0.3  8.5</td>
<td>9.09   0.35  8.8   ZrC_{0.73}</td>
</tr>
<tr>
<td>9.32  0.16 9.17</td>
<td>9.68   0.20  9.5   ZrC_{0.97}</td>
</tr>
<tr>
<td>11.68 0.35 11.28</td>
<td>11.68  0.35 11.28</td>
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</tbody>
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Fig. 1. Grain growth during sintering of loosely poured zirconium carbide powders: a) ZrC$_{0.85}$; b) ZrC$_{0.73}$; c) ZrC$_{0.8}$; d) ZrC$_{0.97}$. 1) 1600; 2) 1800; 3) 2000°C.

Graphic differentiation of the curves in Fig. 1 yields straight lines the tangent of whose angle to the axis of abscissas gives the rate constant of collective recrystallization, $K$, for the given temperature (Fig. 2). As the rate constant of collective recrystallization is proportional to the diffusion coefficient, its temperature dependence would be expected to be described by the equation:

$$K = K_0 \exp\left(-\frac{E}{RT}\right).$$  \hspace{1cm} (2)

Figure 3 shows ln K vs 1/T curves for all the zirconium carbide compositions investigated. Using graphic extrapolation, determinations were made, by means of the least squares technique, of energies of activation $E$ and coefficients $K_0$ for loosely poured zirconium carbide powders of the four compositions (Table 2).

Figure 4 shows the dependence of the energy of activation for collective recrystallization in loosely poured zirconium carbide powders on the imperfection of their carbon sublattice. For comparison, corresponding data obtained earlier [1] for titanium and niobium carbides have also been included. For each of these three carbides, the energy of activation for collective recrystallization increases as the stoichiometric composition is approached. Characteristically, at a given number of carbon vacancies, the energy of activation for zirconium carbide can be seen to be higher than that for titanium or niobium carbides.

The driving force during collective recrystallization is excess surface energy. To explain the migration mechanism of grain boundaries, it is necessary to know their atomic structure. At the present time, diversity of opinion exists as regards the structure of large-angle boundaries. The most common is a dislocational model of grain boundary structure [2]. This model, however, has not yet been rigorously calculated because, at disorientation angles greater than 10-15 deg, dislocations lie very close to one another and their nuclei merge together. Adopting this model and considering, to a first approximation, that the role of perturbances predomnates over the role of impurity atom segregations, it may be assumed that the energy of activation for collective recrystallization will diminish with increasing density of dislocational perturbances at grain boundaries.

It has been demonstrated [3] that a decrease in the statistical weight of atoms with the stable sp$^3$ configurations and an increase in the fraction of delocalized electrons in nonstoichiometric titanium carbide