MICROSTRUCTURE OF HOT-PRESSED MOLYBDENUM CARBIDE

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The hot pressing of refractory compounds results in structural changes, which depend on the temperature, applied pressure, and process duration [1]. Since the properties of hot-pressed parts made from powders of these materials are largely determined by their structure, considerable theoretical and practical interest must attach to studies of structure formation in the course of hot pressing. Changes in the structure of materials may be roughly represented by changes in their mean grain size, while for full characterization it is necessary to introduce also changes in the density and type of grain size distribution. The type of distribution determines the confidence of estimates of its parameters. In studies of these characteristics, use may be made of the techniques of mathematical statistics.

In the present work, the effects were investigated of hot-pressing temperature on the mean grain size and the type and parameters of grain size distribution of molybdenum carbide. The starting material was a powder of commercially pure molybdenum carbide containing 6.0% combined C and 0.1% free C. A laboratory hot-pressing press [1] with graphite die sets of 8-mm inner diameter was used. The process was performed for 5 min under a pressure of 240 kg/cm^2 at 100°C intervals in the range 1900-2200°C. Pressing was followed by cooling for 15 min without the application of external pressure. The heating-up time was 3 min. The sintering temperature was measured with an optical pyrometer. To characterize the starting powder, 400 powder particles were measured under an MBR-1 microscope at a magnification of 1000 diameters; the grain size of hot-pressed specimens was determined under an MIM-8 microscope at a magnification of 400 diameters on 100 grains located within a certain microsection area. The maximum grain size was recorded.

Sufficiently large volumes of measurements (samples) make it possible to employ the "grouped data" method — division of n available values (grain sizes) into m classes (m $\approx \sqrt{n}$). For each such class, the absolute frequency n_i of the sizes covered by it is determined. The character of the empirical distributions obtained in this work provides a basis for testing their conformity to the normal distribution. When only a group of measurements is available, the mean values and variabilities of the results obtained are used as the parameters of theoretical distribution,

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{m} n_i x_i; \ S^2 = \frac{1}{n-1} \left[\sum_{i=1}^{m} n_i x_i^2 - \frac{\left(\sum_{i=1}^{m} n_i x_i \right)^2}{n} \right]. \tag{1}$$

The normal distribution is fully determined by the parameters $\bar{x}$ and S, with the aid of which it is possible to calculate theoretically all the remaining distribution parameters. A comparison of such calculated parameters with the corresponding parameters obtained from experimental data provides quantitative estimates of the degree to which the empirical distribution approximates to the normal distribution.

The first group of such parameters is given by moments of the third and fourth order [2], which constitute integral characteristics of distribution and determine, respectively, the degree of symmetry (asymmetry A) and steepness (excess E) of the distribution density curve.

For the normal distribution, these moments are equal to zero, although random values of A and E even for the normal distribution may differ from zero; these are calculated with the transformed formulas

$$A = \frac{1}{S^3} \left[\frac{\sum\limits_{i=1}^{m} n_i x_i^3}{n} - \frac{3 \sum\limits_{i=1}^{m} n_i x_i^2 \cdot \sum\limits_{i=1}^{m} n_i x_i}{n^2} + \frac{2 \left(\sum\limits_{i=1}^{m} n_i x_i \right)^3}{n^3} \right], \tag{2}$$

$$E = \frac{1}{S^4} \left[\frac{\sum\limits_{i=1}^{m} n_i x_i^4}{n} - \frac{4 \sum\limits_{i=1}^{m} n_i x_i^3 \sum\limits_{i=1}^{m} n_i x_i}{n^2} + \frac{6 \sum\limits_{i=1}^{m} n_i x_i^2 \left(\sum\limits_{i=1}^{m} n_i x_i \right)^2}{n^3} \right.$$

$$\left. - \frac{3 \left(\sum\limits_{i=1}^{m} n_i x_i \right)^4}{n^4} \right] - 3. \tag{3}$$

Here conformity factors are provided by the inequalities

$$|A| \leqslant 3\sqrt{D(A)}, \quad |E| \leqslant 5\sqrt{D(E)}. \tag{4}$$

D(A) and D(E), the variabilities of these magnitudes, are determined with the formulas

$$D(A) = \frac{6(n-1)}{(n+1)(n+3)}, \quad D(E) = \frac{24 \cdot n (n-2)(n-3)}{(n+1)^2 (n+3)(n+5)}, \tag{5}$$

where n is the volume of the sample under investigation.

The most rigorous and reliable is the χ^2 factor, which enables all sample elements to be utilized. Here a comparison is made of theoretically expected frequencies n_t of grains falling into any given class and experimentally found frequencies n_i:

$$\chi^2 = \sum_{i=1}^{m} \frac{(n_i - n_t)^2}{n_t}. \tag{6}$$

The difference between the theoretical and empirical distributions is negligible when $\chi^2 < \chi^2_{0.95}(f)$, i.e., when the theoretical value is greater at the usually employed 5% significance level.

As an example, let us analyze the grain size distribution of molybdenum carbide specimens pressed at 1900°C. The results obtained have been grouped into 11 classes, each class being 5 μ wide. These data are presented in the first three columns of Table 1. The data in the remaining columns are helpful in calculations of the mean size, variability, A, and E from Eqs. (1)-(3). Calculations with Eqs. (1)-(3), using the sums in the last line of the table, give $\bar{x} \approx 42$, S ≈ 12, A = 0.34, and E = -0.41. When the values of A and E are compared with their variabilities calculated from Eq. (5) ($3\sqrt{D(A)} = 0.72$; $5\sqrt{D(E)} = 2.3$), it is seen that they satisfy the inequality (4), and it can therefore be concluded that the empirical distribution does not conflict normality.

Let us verify this conclusion with the aid of the χ^2 factor, using the scheme presented in Table 2. To calculate the theoretical frequency, it is first of all necessary to normalize the class width according to $(x_i - \bar{x})S$. For these values, tabulated ordinates are found (Table 12.1 [3]), after which, for the available n measurements at a class width of b and a root-mean-square deviation of s, theoretically expected frequencies n_t are calculated.

When the first two and the last three classes are combined (n_t should be not less than five), the number of classes becomes m = 8 and the number of degrees of freedom f = m -3 = 5. The calculated value χ^2 factor is the sum of the values in the last column of Table 2, i.e., 7.73. From Table 12.4 [3], we find χ^2 (at P = 0.95 and f = 5) to be equal to 11.1. Hence, this factor must also be regarded as a normality criterion. The remaining calculations demonstrated (Table 3) that all the distributions investigated corresponded to the normal distribution. In mean size evaluations, this made it possible to utilize quantities of the standard normal distribution (for example, Table 11 [2]), by employing the usual confidence probability of 0.95. Here the random variability was equated to the general variability.

TABLE 1. Starting Data for Determination of $\bar{x}$, S, A, and E

No.	x_i	n_i	$n_i x_i$	$n_i x_i^2$	$n_i x_i^3$	$n_i x_i^4$
1	20	4	80	1600	3200	640 000
2	25	5	125	3125	78 125	1 953 125
3	30	15	450	13 500	405 000	22 150 000
4	35	13	455	15 925	557 375	19 508 125
5	40	20	800	32 000	1 280 000	51 200 000
6	45	10	450	20 250	911 250	41 006 250
7	50	16	800	40 000	2 000 000	100 000 000
8	55	6	330	18 150	998 250	54 903 750
9	60	5	300	18 000	1 080 000	64 800 000
10	65	3	195	12 675	823 875	53 551 875
11	70	3	210	14 700	1 029 000	72 030 000
		100	4195	189 925	9 194 875	471 743 125

TABLE 2. Scheme for Calculating χ^2 Factor

Class No.	x_i	n_i	$u=\dfrac{x_i-\bar{x}}{s}$	$\varphi(u)$ (Table 12.1 [3])	$n_t=\dfrac{n \cdot b}{s}\varphi(u)$	$\dfrac{(n_i-n_t)^2}{n_t}$
1	20	4⎫9	1,83	0,07477	3,1154⎫9,1803	0,0035
2	25	5⎭	1,42	0,14556	6,0649⎭	
3	30	15	1,00	0,24197	10,0819	2,3967
4	35	13	0,58	0,33718	14,0489	0,0783
5	40	20	0,17	0,39322	16,3839	0,7981
6	45	10	0,25	0,38667	16,1110	2,3179
7	50	16	0,67	0,31874	13,2806	0,5568
8	55	6	1,08	0,22265	9,2769	1,1937
9	60	5⎫	1,50	0,12952	5,3966⎫	
10	65	3⎬11	1,92	0,06316	2,6316⎬9,1294	0,3833
11	70	3⎭	2,33	0,02643	1,1012⎭	
		100			97,4929	7,7283

TABLE 3. Results of Statistical Processing of Data on Changes in Grain Size Distribution of Mo_2C during Hot Pressing

Characteristic	Starting Mo_2C powder	Hot-pressing temperature, °C			
		1900	2000	2100	2200
$\bar{x}$, μ	10±1,3	42±2,4	47±4	84±6	94±7,4
S, μ	6,70	12	20	30	38
A	1,00	0,34	0,47	0,36	0,16
$3\sqrt{D(A)}$	0,42	0,72	0,72	0,72	0,72
E	0,84	—0,32	—0,32	—0,8	—0,64
$5\sqrt{D(E)}$	4,35	2,3	2,3	2,3	2,3
χ^2_{calc}	14,64	7,73	4,72	7,33	4,73
$\chi^2_{0.95}(f)$	15,5 ($f=8$)	11,1 ($f=5$)	11,1 ($f=5$)	15,5 ($f=8$)	16,9 ($f=9$)

From Table 3 it follows that the degree of approximation to the normal distribution is not constant, but increases on passing from the starting powder to hot-pressed specimens and also with rise in hot-pressing temperature. This is accompanied by an appreciable growth of Mo_2C grains (increase of $\bar{x}$) and, judging from the root-mean-square deviation, by an increase in the scatter of grain size values. At the same time, there is a relative shift of the peak toward larger grain sizes, which increases the symmetry of grain size distribution (A).

The steepness of grain size distribution shows a general downward tendency. While for the starting Mo_2C powder the degree of steepness exceeded theoretical (E > 0), for the grain size distribution of hot-pressed specimens it was less than the theoretically expected value (E < 0) and decreased with rise in pressing temperature. Thus, raising the temperature in the hot pressing of molybdenum carbide powder is accompanied by a substantial growth of the mean grain size and a simultaneous increase of the particle size spectrum.

Typical microstructures of hot-pressed specimens are illustrated in Fig. 1. It is interesting that the porosity of specimens pressed at various temperatures was approximately identical, namely, 8-12%.
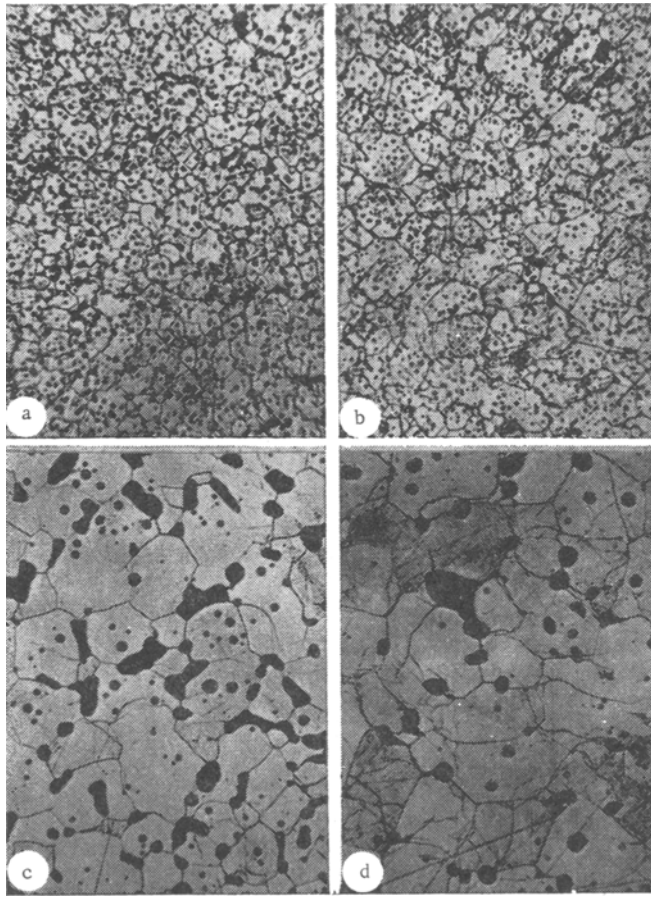
Fig. 1. Microstructures of molybdenum carbide pressed at
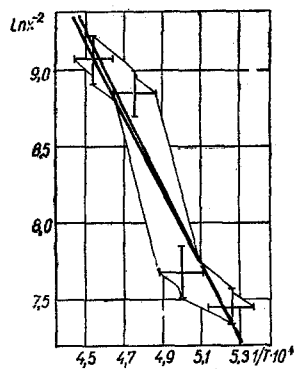temperatures of: a) 1900; b) 2000; c) 2100; d) 2200°C.

Fig. 2. Effect of temperature
on grain size of hot-pressed
Mo_2C specimens.

The pores were located both in the grains and at their boundaries. In
view of the marked difference in particle size between hot-pressed
specimens and the starting powder, the presence of pores in the car-
bide grains can probably be attributed to the grain coalescence process.
When the hot-pressing temperature is raised, fine pores merge to form
large ones, the proportions of pores located in the grains and at the
grain boundaries remaining more or less unchanged. It may be con-
cluded that the choice of an optimum temperature for the hot pressing
of molybdenum carbide should be dictated by structural considerations.

Grain growth is controlled by the diffusional mobility of bounda-
ries and is due to the action of surface tension at grain boundaries. A
general increase in size of all grains reduces the length of boundaries
per unit volume $(S \approx 1/\bar{x}^2)$, thereby lowering their total energy. For
this reason, grain growth in a short-time process is governed by a par-
abolic law [4],

$$\bar{x}^2 = c(t - \text{const}) \cdot e^{-U/kT}, \tag{7}$$

where t is the time (in our work, t = const). In plotting the function $\ln \bar{x}^2 = f(1/T)$ (Fig. 2), use was made
of a confidence region determined by the confidence of estimates for the mean grain size of Mo_2C and the
accuracy of the pyrometric temperature determinations. The two straight lines drawn in this region are
boundaries of the possible values of the energy of activation for Mo_2C grain growth, which are equal to
49 ± 3 kcal/mole.

Similar estimates performed for TiC (63.0 kcal/mole [5]) and $NbC_{0.8}$ (65.5 kcal/mole [6]), and also for the growth of Mo_2C grains in the loose sintering of powders (67.0 kcal/mole [7]) indicate that the value obtained in this work is a reasonable one. It has been shown [8] that external pressure accelerates the process of collective recrystallization by, inter alia, reducing the total number of pores, which may inhibit recrystallization-induced boundary migrations. For refractory compounds, grain growth resulting from rise in pressure has been established in the hot pressing of chromium carbide [9]. It would appear, therefore, that the estimate of the energy of activation for grain growth refers to the hot-pressing conditions selected.

CONCLUSIONS

1. A study was made of the effect of temperature on the mean size and the density and type of distribution of grains in the hot pressing of molybdenum carbide.

2. Raising the hot-pressing temperature in the range 1900-2200°C at constant process pressure and time is accompanied by an appreciable growth in the mean size of Mo_2C grains. At the same time, both the symmetry of grain size distribution and the grain size spectrum increase.

3. The energy of activation for the growth of Mo_2C grains, which has been found to be 49 ± 3 kcal/mole, characterizes collective recrystallization for pressing under the conditions employed.

LITERATURE CITED

1. G. V. Samsonov and M. S. Koval'chenko, Hot Pressing [in Russian], Gostekhizdat USSR, Kiev (1962).
2. E. I. Pustyl'nik, Statistical Methods of Analysis and Processing of Observations [in Russian], Nauka, Moscow (1968), p. 99.
3. K. Doerfel, Statistics in Analytical Chemistry [Russian translation], Mir, Moscow (1969).
4. J. Friedel, Les Dislocations, Gauthier-Villars, Paris (1956).
5. M. S. Koval'chenko and N. N. Sereda, Transactions of the Second Conference on Powder Metallurgy, Part 2, Karkow (1967), p. 495.
6. S. S. Ordan'yan and A. I. Avgustinik, Poroshkovaya Met., No. 9, 50 (1966).
7. I. P. Kushtalova, Recrystallization Processes of Refractory Compounds, Candidate's Dissertation, Kiev (1967).
8. Ya. E. Geguzin, Physics of Sintering [in Russian], Nauka, Moscow (1967), p. 317.
9. I. M. Fedorchenko and V. K. Mai, Poroshkovaya Met., No. 2, 70 (1961).