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SUMMARY

The effect of 10-volume-percent additions of chromium, molybdenum, tungsten, nickel, titanium, boron nitride, and zirconium diboride on the grain growth of alumina, hafnia, magnesia, and zirconia was investigated by vacuum-heat-treating specimens made from bars of the same material previously vacuum-hot-pressed at lower temperatures. These vacuum-hot-pressed bars contained a layer of the pure oxide to allow comparison of grain-growth effects. A study of the grain size of the pure oxide layer adjacent to the oxide-metal composition led to the unexpected discovery of exaggerated grain growth of the pure oxide at the interface with some of the oxide-metal layers.

The results of this investigation show that (1) most of the metals and compounds added inhibit the grain growth in varying degrees of the four oxides studied; (2) some metals and compounds enhance grain growth, which appears to be related to the effect of impurities from the addition; and (3) no correlation could be found between reactivity, melting point, and volatility of the metal addition and grain growth of the matrix oxide. The effect of each metal appears to be specific.

The results of this study indicate that additional work on the effect of amount of metal addition, temperature, and time on the grain growth of selected system should yield fruitful results.

INTRODUCTION

AUTHOR

The strength of ceramics decreases with increasing grain size (refs. 1 to 3). Since grain size is a function of temperature and time, and one of the main uses of ceramics

*This report is a summary of a Master of Science thesis submitted to Case Institute of Technology in June 1964.

is as a high-temperature refractory, it is clear that grain growth may limit the usefulness of these materials in load-bearing high-temperature applications. In addition, theoretical considerations indicate that the smaller the grain size, the better the thermal shock resistance of a ceramic material (ref. 4). On the other hand, there are certain applications of ceramics where grain-size control to a specific value during sintering or hot-pressing is more important than small grain size per se. Such is the case, for instance, in the manufacture of certain types of magnetic ceramics in which a grain size of the same order of magnitude as the size of a magnetic domain is required (ref. 5).

The role played by second-phase particles in controlling grain growth has received increased attention in recent years, but most of the investigations were concerned with the effects in metals and alloys (ref. 6). In the case of ceramics, most of the studies were concerned with the effects of relatively large amounts of metal additions (in excess of 50 percent by weight in some cases) on mechanical properties or sinterability (refs. 7 to 9) rather than on grain growth. Little work on the effects of metal additions on the grain growth of oxide ceramics appears to have been performed previously. [1]

In view of the probable importance of second-phase additions in controlling grain growth in ceramics, the present investigation on the effects of metal additions in oxide ceramics was undertaken. In this preliminary work, 10 volume percent of six metal additions - chromium (Cr), manganese (Mn), molybdenum (Mo), nickel (Ni), titanium (Ti), and tungsten (W) - were studied to determine the effects of different chemical and physical properties of the metallic addition on the grain growth of four oxides - alumina (Al_2O_3), hafnia (HfO_2), magnesia (MgO), and zirconia (ZrO_2). The metals used in this investigation covered a wide range of chemical reactivity, melting points, and volatility at the temperature used. For comparison purposes, two ceramic compounds - boron nitride (BN) and zirconium diboride (ZrB_2) - were also used as additions to the oxide ceramics.

MATERIALS AND EXPERIMENTAL PROCEDURES

Raw Material Processing

The choice of oxide ceramics used in this investigation was based on their availability in pure form and fine particle size, ease of metallographic preparation of sintered

[1]After the original submission of the report on the work summarized herein, a short study in this area of research was found in the literature (R. D. Carnahan: Mechanical Behavior of Hot-Pressed MgO Containing a Dispersed Phase, J. Am. Ceram. Soc., vol. 47, no. 6, June 1964, pp. 305-306).

TABLE I. - SOURCE, COMPOSITION, TREATMENT, AND

PARTICLE SIZE OF RAW MATERIALS

Material	Supplier (a)	Composition	Milling time, hr	Average particle size, μ	Method
Alumina	A	99.98 alumina	0	0.3	Electron microscopy
Hafnia	B	0.45 iron, 1.0 zirconium, 0.1 titanium, 0.1 silicon, 0.07 aluminum, 1.25 sulfate	0	.027	BET[b]
Magnesia	C	98.5 magnesia, 0.5 sodium	0	.46	
Zirconia	D	98.8 zirconia (includes hafnia) 0.33 silicon, 0.1 titania, 0.1 calcia	48	.26	
Chromium	E	99 chromium		.52	
Manganese	F	Not available		.05	
Molybdenum	G	99.9 molybdenum, 0.1 oxygen		.19	
Nickel	H	0.003 iron, 0.1 oxygen	0	2.0	
Titanium	I	98 titanium, 1.1 nitrogen	48	1.8	
Tungsten	G	99.9 tungsten, 0.13 oxygen	2	.24	
Boron nitride	J	99.5 boron nitride	0	15	Optical microscopy
Zirconium diboride	K	Not available	24	.14	BET

[a]Qualified requesters may obtain a key to this column.

[b]Determination of surface area by adsorption of gas.

bodies, amount of previous knowledge, or possible use as high-temperature structural materials. The materials used, along with the manufacturer's analysis, designations, and sources, are given in table I.

Some of the as-received powders had too large a particle size to allow densification at low hot-pressing temperatures, others formed agglomerates that would hinder mixing, and still others had original particle sizes that differed too much from those of other materials with which they were to be compared. In such cases the powders were milled before use for specimen preparation. All milling was carried out in 2-liter-capacity, 12.5-centimeter inside-diameter, tungsten carbide mills with 4.3 kilograms of tungsten carbide balls (104 balls, 3/8 in. diameter; 328 balls, 1/4 in. diameter; and 134 balls, 5/32 in. diameter) and 1 liter of acetone as the grinding medium. The powder charges were about 200 grams for high-density materials, like W and Mo, and about 100 grams

for less dense materials, like Ti and ZrB_2. All milling was carried out at 80 rpm. The milling time for the various materials is given in table I.

Although it was realized at the outset that the particle size of the addition can have a pronounced effect on the grain growth of the matrix oxides, this variable was not studied in detail here, since, in this initial investigation, only gross effects were sought.

After completion of milling, the powder-acetone slurry was dried in a stream of warm air, and the dried powders were passed through a 100-mesh sieve and stored in a vacuum desiccator.

The particle size of the materials was determined by a surface area technique using the BET method (ref. 10), except in the few cases where suppliers reported the particle size of their materials. These particle sizes are included in table I. Those determined by the BET method are based on the assumption that the particles are spherical in shape.

Experimental Procedures

The following general procedure was observed in preparing the test specimens of the various compositions. The ceramic and metal powders were weighed, wet-mixed, dried, cold-pressed, and then vacuum-hot-pressed to obtain a relatively dense compact of small grain size. The specimens were then cut into smaller test pieces and vacuum-heat-treated at temperatures higher than those used for hot-pressing to obtain grain growth. One surface of each heat-treated specimen was polished, etched, and photomicrographed for grain-size determination. The details of the various procedures are given in the following paragraphs.

All materials were dried in a vacuum desiccator immediately before weighing. The major components of the mixtures (matrix oxides) were weighed to the nearest 0.01 gram and the additions to the nearest 0.001 gram. All cermets described in this investigation contained 10 volume percent of the addition.

The weighed powders were mixed in the same tungsten carbide mills used for milling some of the raw materials. All mixing runs were carried out with 40 to 100 grams of powder and 1 liter of acetone at 80 rpm for 1 hour. The acetone was removed by evaporation in a stream of warm air with constant stirring of the mixture to obtain an even distribution of the metal particles in the ceramic matrix.

Fabrication

Hot-pressing was performed in an induction-heated vacuum-hot-pressing furnace specially designed (ref. 11) to operate in conjunction with a 20 000-pound maximum-

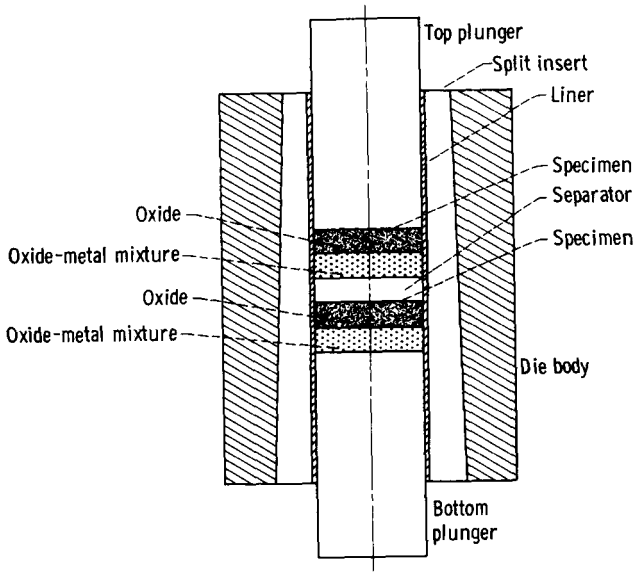

Figure 1. - Graphite hot-pressing die.

capacity tensile machine.

The double-acting graphite die designed for hot-pressing the compacts is shown in figure 1. The die has a split conical insert to facilitate removal of the fragile cermets without fracturing them. The powders were cold-pressed in the same die to about 3000 pounds per square inch before loading in the hot-pressing furnace, so that the assembly was held in place by friction. Two specimens were hot-pressed at the same time, as shown in figure 1, provided the metal in the cermet was the same in both specimens.

The amount of powder used for each hot-pressing composition was that required for making hot-pressed bars with a nominal size of $2\frac{1}{4}$ by $\frac{1}{2}$ by $\frac{1}{2}$ inch after hot-pressing. Each cermet composition was hot-pressed together with a layer of pure oxide (of about the same volume as the cermet) bonded to it so that each cermet specimen would have a built-in "standard" for comparing grain growth. The two-layer-specimen procedure was used to ensure the same hot-pressing and heat-treating conditions for the cermet and the standard.

After loading the die in the hot-pressing furnace, the chamber was evacuated to less than 10^{-3} torr and a force of about 500 pounds applied to the die to prevent it from collapsing while being heated to the hot-pressing temperature. When the desired hot-pressing temperature was reached, a load of 2500 pounds per square inch was applied in all cases. This load was monitored and maintained constant throughout the hot-pressing run by an automatic load holder incorporated in the tensile machine. At the end of the hot-pressing run, the load was released and the specimens were allowed to cool to room temperature without load. All compositions were vacuum-hot-pressed at 1375° C for 15 minutes. The temperature and time were chosen in an attempt to obtain maximum density while minimizing grain growth and contamination (by reaction with the graphite die, ref. 12). Maximum density is desirable because experimental evidence (ref. 13) indicates that pores can act similarly to inclusions in their effect on grain growth in some ceramics.

Spectrographic chemical analysis of some of the as-hot-pressed cermets indicated a qualitative estimate for tungsten pickup (from milling of metal powders and from mixing of the cermets) ranging from 0.04 to 0.3 volume percent. It should be noted that the

pure oxide layer used as a standard was treated by the same procedure as the oxide in the cermet so that the effect of the pickup on grain growth should be about the same in both the cermet and the standard.

The furnace pressure, as measured with a discharge vacuum gage, varied from a maximum of about 10^{-2} torr during the heating cycle to less than about 3×10^{-4} torr at the end of the hot-pressing run. In no case was gas evolution (as would occur during reaction of graphite with an oxide) noted. The furnace temperature was determined by means of a disappearing-filament optical pyrometer.

To remove the dark coating of graphite or carbide formed on the surface of the compacts during hot-pressing, a layer about 0.040 inch thick was removed by surface grinding all compact faces with a diamond grinding wheel. The ground bars were then cut with a diamond wheel into smaller specimens about 1/2 inch long to be used for heat-treating.

The density of representative bars was determined from the dimensions and the weight of the dry bar. When the percent theoretical density of the matrix material was calculated, the weight and volume of the bar were corrected for the amount of metal in the mixture.

Heat Treatment

To heat treat the specimens obtained by hot-pressing, they were loaded into 3/4-inch-diameter by 1-inch-high tungsten boats with covers. These boats were loaded three at a time in a 3-inch-diameter by 4-inch-high tungsten boat that was then heated to temperature in an induction-heated vacuum furnace. Furnace pressures, as measured with an ionization gage, were less than 4×10^{-4} torr during heat-treating. All aluminum-oxide- and magnesium-oxide-base compositions were vacuum-heat-treated at 1620° C for 1 hour. Zirconia- and hafnia-base compositions were vacuum-heat-treated at 1875° C for 1 hour.

The grain size of the hot-pressed and heat-treated specimens were measured in the following manner: The specimens were mounted in a thermosetting plastic and were polished and etched by standard ceramographic techniques (ref. 14). Photomicrographs for grain-size determination were taken with a metallograph at linear magnifications between 50 and 1000, depending on the grain size involved.

The grain size was determined by lineal analysis (refs. 15 and 16). In these computations, the "average intercept grain size" contribution of second-phase particles was corrected for by subtracting the (calculated) length of the line falling on second-phase particles from the total length of the lines. Since the volume fraction of a second phase is equal to the area fraction in a plane through the sample and is also equal to the linear

TABLE II. - EFFECT OF 10-VOLUME-PERCENT ADDITION ON GRAIN SIZE OF FOUR OXIDES IN MIXTURE AND AT INTERFACE

[All compositions were vacuum-hot-pressed at 1375° C and 2500 psi for 15 min. MgO and Al_2O_3 base compositions were further vacuum-heat-treated at 1620° C for 1 hr. ZrO_2 and HfO_2 base compositions were further vacuum-heat-treated at 1875° C for 1 hr.]

Addition	Oxide							
	Magnesia		Alumina		Zirconia		Hafnia	
	Grain size of pure oxide, μ							
	23.5		4.4		11.3		13.2	
	Grain size, μ							
	In mixture	At interface	In mixture	At interface	In mixture	At interface	In mixture	At interface
Chromium	[a]7.4	26.2	3	5.5	5.8	20.2	[a]4.7	13
Molybdenum	9.6	25	4.3	6	10	17	8	13
Tungsten	11.7	24.5	2.2	4.5	8	18	8	13
Manganese	28.2	64	[a]23	86	15	(b)	[a]23	(b)
Nickel	14	25	3.2	6	3.8	(b)	3.2	(b)
Titanium	5.3	24	[a]8.4	(b)	3.6	44	6.3	25
Boron nitride	[a]9.5	70	[a]3.0	13	[a]2.5	12	[a]3	[b]18
Zirconium diboride	[a]9.6	73	[a]3.0	6	6	13	[a]21	(b)

[a]Indicates reaction between the addition and the oxide matrix.

[b]Grain-size determination not possible or doubtful either because the pure oxide separated from the mixture on heat-treating or for other causes (cracks, etching problems, reactions, etc.).

fraction of the second phase intercepting a random line in this plane (ref. 15), it follows that the presence of the second phase can be corrected for by multiplying the uncorrected average intercept grain size by the volume fraction of the continuous phase. This procedure does not take into account material that may have evaporated during hot-pressing or heat-treating or the presence of reaction products. In the great majority of cases, however, these processes are of minor importance.

Since the purpose of the present investigation is to compare the relative effects of the various additions, only the average intercept grain size as defined is used here.

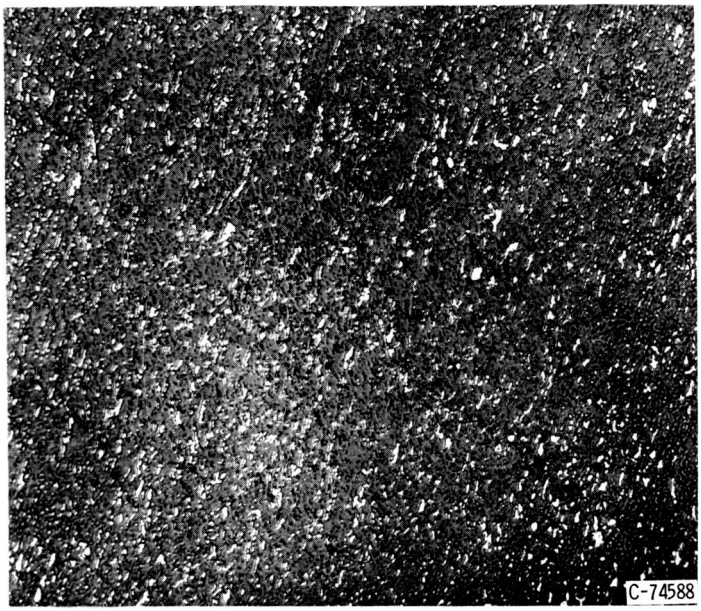

Figure 2. - Photomicrograph of aluminum oxide with 10-volume-percent tungsten after heat-treating at 1620° C for 1 hour. Unetched. X250.

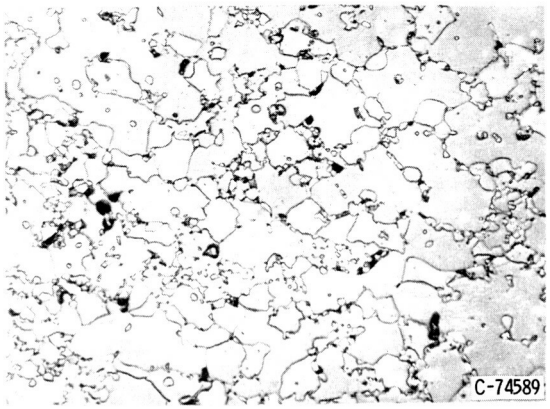

Figure 3. - Photomicrograph of aluminum oxide with 10-volume-percent manganese after heat-treating at 1620° C for 1 hour showing phases resulting from reaction. Unetched. X250.

RESULTS

The matrix oxide grain sizes in the various cermets studied in this investigation are shown in table II. The grain sizes in the bulk of the corresponding pure oxides treated under the same conditions are also included in this table for comparison. In the determination of these grain sizes in the cermets and in the bulk of the pure oxides, usually upwards of 80 intersections were counted, giving a standard deviation of less than 7 percent (ref. 16). This number of intersections was readily obtainable at moderate magnifications in the ceramics examined.

A typical microstructure of the type of cermet studied in this investigation is shown in figure 2. In this photomicrograph the white spots are metal particles, the fine dark spots are either pores or pull outs, and the gray background is the oxide matrix. This photomicrograph shows that the mixing techniques used are satisfactory, as evidenced by the apparently uniform dispersion of the metal in the oxide.

In some mixtures, the oxide and the metal or compound addition reacted to form additional phases. A typical microstructure of this type of cermet is shown in figure 3. It should be noted by comparison with figure 2 that there are fewer metal particles in this type of structure due to the reaction. The cermets in which reaction is evident from an examination of the photomicrographs are denoted with the letter "a" in table II.

It will be recalled that each cermet was hot-pressed together with a layer of the corresponding pure oxide bonded to it to use the latter as a standard for comparison of grain

(a) As-hot-pressed.

(b) After heat-treating at 1405° C for 1 hour.

(c) After heat-treating at 1620° C for 1 hour.

Figure 4. - Microstructure of magnesium oxide at interface with mixture of magnesium oxide plus 10-volume-percent molybdenum vacuum-hot-pressed at 1375° C, 2500 pounds per square inch for 15 minutes followed by vacuum heat-treating. Etchant, hydrochloric acid. X250.

growth. Microscopic examination of the interface between the cermet and the pure oxide led to the discovery that, in the majority of cases, there was an exaggerated grain growth in the pure oxide side of the interface compared with the bulk grain size in the same pure oxide. These pure oxide interface grain sizes are given in table II. A typical microstructure of an interface is shown in figure 4. This grain-growth enhancement at the interface will be termed the "interface effect".

In determining the grain size of the pure oxide at the interface with the cermet, usually only one line parallel to the interface could be traced, because the grain-growth effects at the interface decrease rapidly with distance from it. Since fewer intersections were counted at the interface, the results have a standard deviation usually no better than 17 percent. In addition, some of the ZrO_2 cermets showed columnar grain growth in the pure oxide at the interface and only the intersections corresponding to the smaller dimension of these columnar grains could be counted. In a few cases, cracks appeared at the interface due to the difference in thermal expansion of the two structures, and a meaningful interface grain size could not be determined. Compositions in which, for these or other reasons, no grain size could be determined are indicated in table II with the letter "b".

In an attempt to gain a better

understanding of the interface effect described previously, specimens of MgO with 10 volume percent Mo were hot-pressed under the same conditions already stated. The hot-pressed specimens were then heat-treated at two different temperatures (1405° and 1620° C) for 1 hour. Photomicrographs of the heat-treated and of the as-hot-pressed specimens are shown in figure 4. As shown in these photomicrographs, the depth of the zone of exaggerated grain growth is a function of temperature at constant time.

The approximate values of percent of theoretical densities obtained for the oxide were 95 for MgO, 92 for Al_2O_3, 95 for ZrO_2, and 98 for HfO_2.

After hot-pressing and after heat-treating, the pure MgO and pure Al_2O_3 layers were white, the pure ZrO_2 layers were yellowish, and the pure HfO_2 layers (originally salmon pink) were black. The same color was obtained by vacuum-sintering the HfO_2 at temperatures as low as 1000° C. It is concluded that this black color is due either to reduction of HfO_2 in vacuum or the reduction of some impurity in the oxide. This effect was not studied any further, since it was outside the main scope of this study. The cermet layers were either dark gray or black in all the mixtures, both after hot-pressing and after vacuum-heat-treating.

DISCUSSION

The results presented in table II show for the experimental conditions studied that

(1) Grain growth in magnesium-oxide-base cermets is inhibited in varying degrees by the metals Cr, Mo, Ni, Ti, and W, and by the compounds BN and ZrB_2. In contrast, Mn may have enhanced grain growth.

(2) Grain growth in aluminum-oxide-base cermets is inhibited only by the metals Cr, Ni, and W and the compounds BN and ZrB_2. In contrast, Ti and Mn enhance grain growth. The ratio of (inhibited) grain size to grain size of pure Al_2O_3 is larger than for MgO.

(3) In zirconium-oxide-base cermets, all the metals (except perhaps Mo and Mn) and compounds used in this investigation inhibit grain growth.

(4) In hafnium-oxide-base cermets, additions of Cr, Mo, W, Ti, Ni, and BN inhibit, while additions of Mn and ZrB_2 enhance grain growth. Many of these additions react with HfO_2.

(5) The metals Cr, Ni, and W inhibit the grain growth of all four oxides, but the other metals and compounds are specific in their effects.

(6) The grain size of the pure oxide phase at the interface with the cermet or mixture is usually not the same as that of the pure oxide far away from the interface. As a general rule, this interface grain size is larger, even in systems where the addition actually inhibits grain growth.

(7) Some of the systems with BN, ZrB_2, Cr, Mn, Ni, and Ti show phases other than the original oxide and the addition because of reaction. (These systems are denoted with the letter "a" in table II.)

As stated in the INTRODUCTION, the experiments described in the preceding sections were carried out to study mainly gross effects of reactivity, vapor pressure of the metal, and melting point of the metal addition on grain growth. With some oxide additions, the as-milled particle size of the addition appears to be inversely related to the final oxide grain size. Due to the agglomeration that is known to occur during processing, however, such a correlation cannot be made without a thorough electron microscopy study. It is anticipated that such a study would give no definite correlation between the as-milled particle size and the final size of the addition.

If the free energy of formation of the corresponding oxide is taken as a measure of reactivity, the effect of this factor on grain growth can be shown to be inconclusive. Thus, for instance, the free energies of formation of chromic oxide, nickel oxide, and manganese oxide at 1600° C are -98 000, -37 000, and -117 000 calories per mole of oxygen, respectively (ref. 16), whereas the grain sizes of MgO specimens with 10 volume percent of these additions are 7.4 microns for chromium, 14 microns for nickel, and 28.2 microns for manganese. It appears from these and similar data for other compositions that reactivity alone does not explain grain growth in all systems.

If the metal in the cermet evaporates and is adsorbed on the surface of the oxide particles before the cermet has had a chance to consolidate, it can be surmised that the adsorbed metal can influence grain growth and that this adsorption (if any) will depend (partly) on the vapor pressure of the metal addition. The vapor pressures of Mn, Cr, Ni, Ti, Mo, and W at 1620° C are approximately 3×10^{-2}, 10^{-2}, 5×10^{-4}, 3×10^{-6}, 10^{-10}, and 10^{-15} atmosphere, respectively (ref. 16), whereas the grain sizes of specimens of MgO with these metals are 28.2, 7.4, 14, 5.3, 9.6, and 11.7 microns, respectively. However, Mn and Ni are molten at the heat-treating temperature (1620° C), and if the data for these two metals are disregarded, it appears that high-vapor-pressure metals like Cr and Ti restrict the grain growth of MgO (and ZrO_2) more strongly than low-vapor-pressure metals like W and Mo. This, however, does not apply for Al_2O_3 (and HfO_2), and for this reason no generalization can be drawn regarding the effect of the vapor pressure of the metal addition on grain growth.

The degree of interdiffusion appears to depend on the melting points of the materials in contact, at least for metals (ref. 17). It was, therefore, pertinent to correlate the melting point of the addition with grain size, since diffusion of the addition in the matrix oxide can be expected to affect grain-boundary energy and, hence, grain growth (ref. 6). The melting points of Mn, Ni, Ti, Cr, Mo, and W are 1244°, 1455°, 1660°, 1850°, 2600°, and 3380° C, respectively (ref. 18). An examination of table II will readily show that there is no apparent relation between melting point and grain size.

As suggested by the interface effect, grain growth is affected by diffusion or evaporation of the metal addition or some impurity from it. Considering the relatively small amounts of material involved in diffusion in this investigation, it can be surmised that even minute amounts of ions from the addition, from the heat-treating boats, or already present in the raw materials can greatly enhance grain growth in oxide ceramics. Judging from the grain size of the cermet compositions studied here, this grain-growth enhancement is, in most cases, offset by the grain-growth-inhibiting properties of the metallic inclusions. Thus it appears that, at least qualitatively, inclusions inhibit grain growth in oxides just as they do in metals and alloys (ref. 6).

CONCLUSIONS

Although no definite generalizations of the effects of reactivity, vapor pressure, or melting point of the addition on the grain growth of the matrix oxide can be derived from the results of the present investigation, the following conclusions can be drawn:

1. Most of the metal additions studied inhibit the grain growth of magnesia, alumina, zirconia, and hafnia. It is surmised that the same may be true for other oxides.
2. Some compounds can also be effective grain-growth inhibitors for oxides.
3. Diffusion or evaporation of either the addition or an impurity from it (its oxide, for instance) can also influence (enhance) grain growth of the matrix oxide in the oxide-metal or oxide-compound mixtures, as indicated by the "interface effect". Hence, grain growth should also depend on amount of addition and this variable should be studied in selected systems.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 1, 1965.

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