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Filed May 17, 1949

2 Sheets-Sheet 1

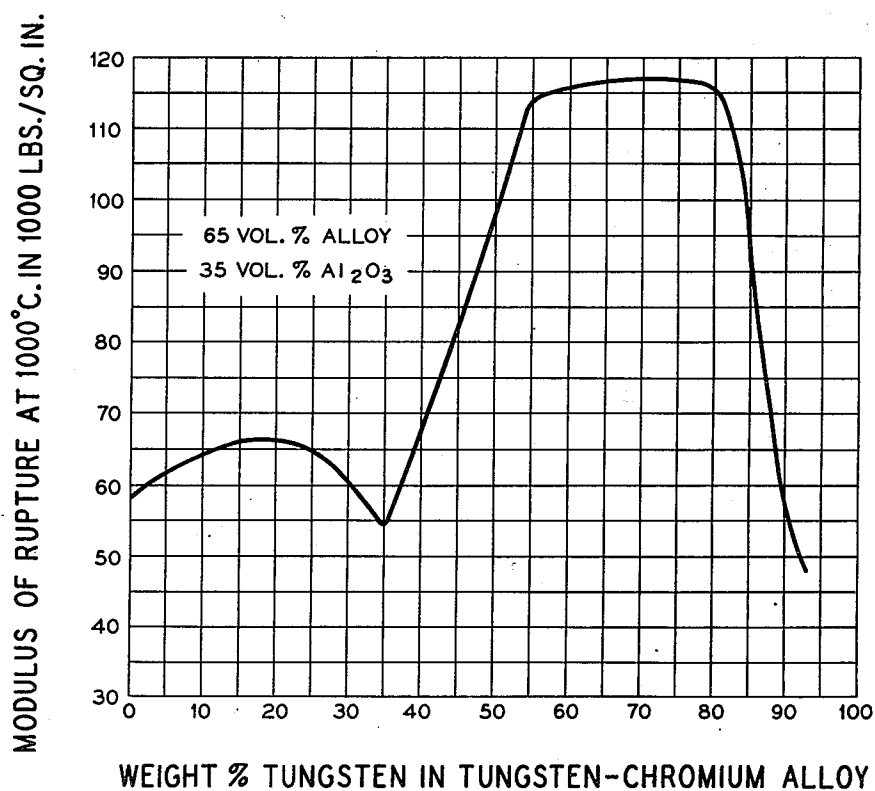


Fig. 1.

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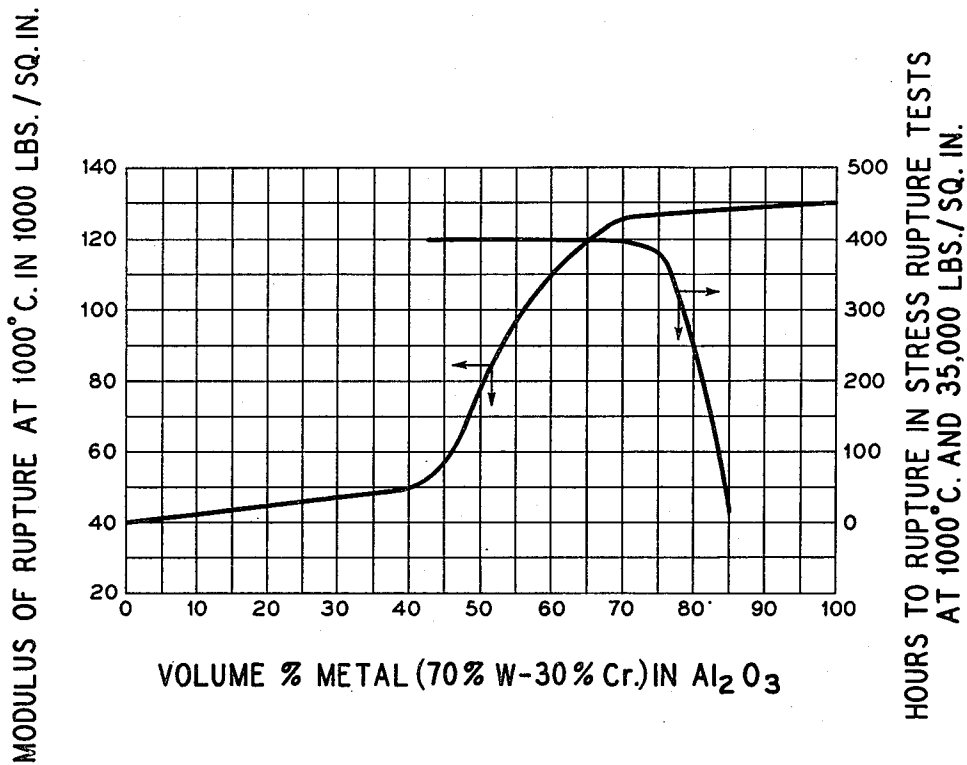


Fig. 2.

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TUNGSTEN-CHROMIUM-ALUMINA METAL CERAMICS

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4 Claims. (Cl. 29—182.5)

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The invention relates to metal ceramics and more particularly to sintered masses of comminuted chromium, tungsten and alumina.

Refractory materials having great strength and hardness coupled with resistance to oxidation at high temperatures are of increasing importance in industry. Such materials may be fabricated into many useful articles such as permanent molds for metal castings, thermocouple protection tubes, furnace parts, resistance elements, hot pressing and extrusion dies, mandrels and containers, turbine blades and other articles wherein resistance to oxidation and abrasion as well as strength at elevated temperatures are required. It is a primary object of this invention to provide such a material.

The present invention is based upon the discovery that a metal ceramic material having high oxidation resistance and superior strength at elevated temperatures may be produced when a comminuted chromium-tungsten alloy of critical chromium and tungsten content is intimately admixed and sintered with a critical volumetric amount of comminuted alumina. According to the invention the weight ratio of chromium to tungsten in the alloy must be between about 0.25 and 0.82, and the volumetric ratio of chromium-tungsten alloy to alumina must be between about 1 and 19.

Accordingly, the invention in its broadest aspect comprises a strongly cohesive, sintered metal ceramic mass composed of 5 volume percent to 50 volume percent of comminuted alumina and 95 volume percent to 50 volume percent of comminuted metal, said metal being composed of between 20% and 45% by weight of chromium and between 80% and 55% by weight of tungsten. Additions of at least 5 volume percent of alumina to the chromium-tungsten-alumina ceramics appear desirable to act as a binder in fabrication of these materials. Without alumina difficulties are experienced in fabrication. For some purposes, hereinafter described more fully, it will be desirable to maintain the volume percentage of alumina between 20% and 50% and the volume percentage of metal between 80% and 50%.

In the drawings, Figures 1 and 2 are curves showing strength properties at elevated temperatures of chromium-tungsten-alumina metal ceramics.

The data upon which the curves are based were obtained from modulus of rupture tests and stress rupture tests conducted in the following manner. A bar of the material to be tested hav-

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ing the dimensions $1\frac{1}{2}$ inches by $\frac{1}{4}$ inch by $\frac{1}{8}$ inch was placed on two cylindrical supports so as to provide a 1-inch span therebetween. In the modulus of rupture tests a load was applied to the test piece at the midpoint of the span by means of a knife edge of alumina. In the stress rupture tests the load was suspended from a point on the test piece at the center of the span. Both types of tests were conducted in an appropriate furnace at 1000° C.

Figure 1 of the drawings is a curve showing the modulus of rupture at 1000° C. for sintered material containing 65 volume percent of a chromium-tungsten alloy and 35 volume percent of alumina, wherein the weight ratio of chromium to tungsten in the alloy is varied over the full scale. From the curve it is apparent that at the volumetric proportions indicated for the alloy and alumina, the alloy phase is critically superior in strength at between 55% and 80% by weight of tungsten and 45% and 20% by weight of chromium. When the alloy contains less than 55% by weight of tungsten the modulus of rupture at 1000° C. falls off sharply and when the alloy contains more than 80% tungsten not only is there a definite loss of strength at elevated temperatures, but, in addition, there is a marked decrease in the oxidation resistance of the material.

Figure 2 shows the relationship between the composition of the metal ceramic material and the short (modulus of rupture) and long (stress rupture) time strengths. With the tungsten-chromium ratio by weight constant at 70% tungsten and 30% chromium, compositions of the metal ceramic material containing up to 45 volume percent of metal show little increase in strength over pure alumina. At 50 volume percent metal a large increase in the modulus of rupture occurs which increase continues until the volume percent of metal reaches 65 to 70, beyond which point the modulus of rupture remains fairly constant with further increases in the volume percent of metal. In the long time stress rupture tests the time in hours to rupture remains fairly constant with compositions containing up to about 75 or 80 volume percent metal. With more than 80 volume percent of metal the stress rupture or long time strength falls off sharply and excessive creep or deformation is noted. It has been observed that the thermal shock resistance of the material roughly follows the modulus of rupture curve and is poor in materials containing more than 50 volume percent alumina. It has also been observed that the

oxidation resistance roughly follows the stress rupture curve. From the curves in Figure 2, it is seen that where both long and short time strengths at elevated temperatures are desired in the material the composition is critical; the optimum properties being obtainable from materials containing from 50 to 80 volume percent of metal and from 50 to 20 volume percent of alumina.

The relation between the volume percentage of alumina and chromium-tungsten alloy required to obtain a high modulus of rupture at elevated temperatures is shown in the table below. The data from which the table was prepared were obtained from rupture tests at 1000° C. on sintered chromium-tungsten-alloy-alumina metal ceramics. The alloy constituent of the metal ceramics contained 30% by weight of chromium and 70% by weight of tungsten, which composition is approximately midpoint in the range of compositions found to be critical in the alloy constituent of the invention.

Table

Vol. Percent Alumina	Vol. Percent Alloy	Weight Percent of—			Modulus of Rupture p. s. i. 1,000° C. (average)
		W	Cr	Al ₂ O ₃	
50	50	53.6	22.5	23.9	80,000
45	55	55.5	23.8	20.7	97,000
40	60	57.7	24.8	17.5	107,000
35	65	59.8	25.6	14.6	125,000
30	70	61.7	26.4	11.9	127,000
25	75	63.3	27.2	9.5	125,000
20	80	64.9	27.8	7.3	127,000
15	85	66.1	28.3	5.6	130,000
10	90	67.6	29.0	3.4	125,000
5	95	68.9	29.5	1.6	130,000

In the manufacture of the material of the invention high purity metal powders of a minute particle size are desirable. Metal and ceramic powders having an average particle size of 10 microns and below are preferred although powders that pass through a 300 mesh screen (0.0018 inch openings) may be used. A fine "lamp grade" tungsten powder is suitable. In the chromium powder, impurities known to lower the melting point produce embrittlement should be avoided. For example, carbon is detrimental and should be kept to a minimum, preferably below 0.03%.

The constituent powders making up a particular composition may be mixed, formed and sintered, or the chromium and tungsten may be pre-alloyed before mixing with alumina. A high firing temperature of between 1700 and 1950° C. in a dry hydrogen atmosphere has been found to produce excellent results in the sintering operation. Other atmospheres such as argon, may be employed, or the materials may be pre-fired in hydrogen or in vacuum and fully fired in argon. To obtain best results it is recommended that the atmosphere be of high purity and free from oxygen.

The preparation of a typical material would comprise preparing a charge of powder containing 35 volume percent of alumina powder and 65 volume percent of metal powder of the desired composition, wet ball milling the charge in toluol, benzol or similar material for from 24 to 100 hours, drying the mixture from the ball mill, incorporating a binder such as paraffin or water, compacting the mixture at a pressure of between about 10,000 and 60,000 pounds per square inch, drying the compact overnight and then firing the compact by heating at about 1825° C. in a dry

hydrogen atmosphere for between one and five hours. Alternatively, the mixed powders, without binder, may be introduced into a graphite die and hot pressed at between 1700 and 1950° C. from 5 to 30 minutes at temperature under a pressure of from 1500 to 3000 pounds per square inch.

The chromium-tungsten-alumina metal ceramics of the invention have a metal phase of alloyed or partially alloyed chromium and tungsten, and a ceramic phase of alumina. The metal phase appears to be well-bonded to the alumina phase by surface diffusion. Within the critical composition range specified, the metal phase forms a relatively continuous network or matrix throughout the final product. This metallic continuity confers on the composite structure certain desirable properties of the metal itself to an extent which is significantly greater than that found in bodies having little or no metallic continuity.

What is claimed is:

1. A metal ceramic product characterized by its oxidation resistance and strength at elevated temperatures composed of a strongly cohesive, sintered mass of intimately dispersed minute particles of alumina and metal, said alumina being present in said mass in an amount between 5 volume percent and 50 volume percent, said metal being present in said mass in an amount between 95 volume percent and 50 volume percent, said metal being composed by weight of between 20% and 45% chromium and between 80% and 55% tungsten.

2. A metal ceramic product as claimed in claim 1 wherein the metal particles in said sintered mass are present as an alloy composed by weight of between 20% and 45% chromium and 80% and 55% tungsten.

3. A metal ceramic product characterized by its oxidation resistance and strength at elevated temperatures composed of a strongly cohesive, sintered mass of intimately dispersed minute particles of alumina and metal, said alumina being present in said mass in an amount between 20 volume percent and 50 volume percent, said metal being present in said mass in an amount between 80 volume percent and 50 volume percent, said metal being composed by weight of between 20% and 45% chromium and between 80% and 55% tungsten.

4. A metal ceramic product as claimed in claim 3 wherein the metal particles in said sintered mass are present as an alloy composed by weight of between 20% and 45% chromium and 80% and 55% tungsten.

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