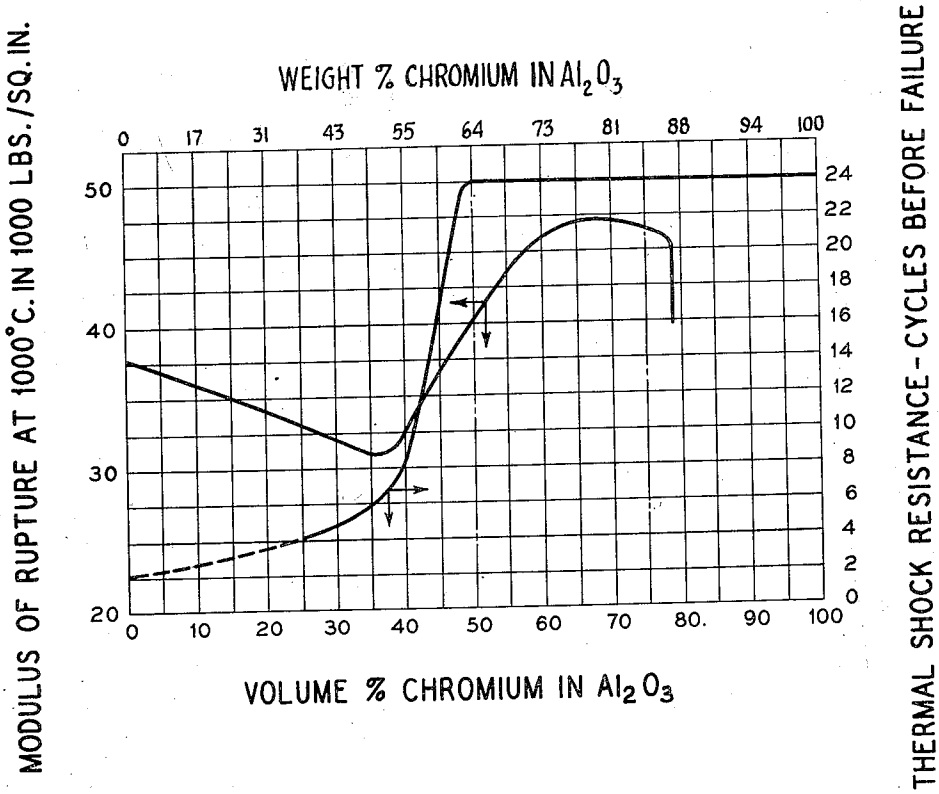
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CHROMIUM-ALUMINA METAL CERAMICS

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CHROMIUM-ALUMINA METAL CERAMICS

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

Refractory materials having great strength and hardness coupled with thermal shock resistance and 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 high temperatures are required. It is the primary object of this invention to provide such a material and a method for making such a material.

The present invention is based upon the discovery that a metal ceramic material having high oxidation resistance, excellent thermal shock resistance, and superior strength at elevated temperatures may be produced when comminuted chromium metal and comminuted alumina of designated particle size and critical proportions are intimately admixed and sintered under conditions hereinafter fully set forth.

The single figure of the drawing comprises two curves showing respectively the strength properties at elevated temperatures and the thermal shock resistance in cycles before failure of the metal ceramics of the invention.

The data upon which the high temperature strength curve is based were obtained from modulus of rupture tests conducted in the following manner. A bar of material to be tested having the dimensions 1½ inches by ¼ inch by ⅛ inch was placed on two cylindrical supports so as to provide a 1-inch span therebetween. A load was applied to the test piece at the midpoint of the span by means of a knife edge of alumina. The curve shows the modulus of rupture at 1000° C., for sintered material prepared from comminuted chromium and alumina wherein the ratio of chromium to alumina is varied over the entire scale.

The data upon which the curve illustrating the thermal shock resistance in cycles before failure is based were obtained from tests conducted in the following manner. A bar of material to be tested having the same dimensions as described in the modulus of rupture tests is mounted two inches from the flame heads of an oxy-acetylene torch. The torch is lighted at a gas flow sufficient to heat the test bar to 1400° C. in about 4 seconds. When the test bar reaches temperature, the flame is extinguished and an air blast is directed through the same nozzle at the test bar at a temperature and velocity sufficient to cool the test bar to black heat in about 4 seconds and to room temperature in about 56 seconds. The specimen is heated and cooled in this manner until it fails by cracking or spalling or otherwise, or until it has been subjected to 24 cycles If a specimen successfully passes through 24 cycles, it is then tested for mechanical strength. Test bars of metal ceramics within the ranges contemplated in the invention frequently show an increase in strength in this test. It is, of course, understood that the specimens shown as withstanding 24 cycles would also withstand an indefinite number of further cycles.

As may be seen from the two curves the thermal shock resistance falls off sharply at about 50 volume percent chromium-50 volume percent alumina and the modulus of rupture at 1000° C. falls off sharply at slightly above

about 75 volume percent chromium-25 volume percent alumina because of excessive deformation.

The invention in its broadest aspect relates to a metal ceramic product characterized by its strength at elevated temperatures and its resistance to oxidation and thermal shock comprising a strongly cohesive, sintered mass of intimately dispersed particles of alumina and chromium metal, the alumina particles being of a size between 0.1 micron and 45 microns and being present in said mass in an amount between 25 volume percent and 50 volume percent, the chromium metal particles being of a size not exceeding 45 microns and being present in said mass in an amount between 75 volume percent and 50 volume percent with the chromium metal constituting a continuous phase in said mass.

In a preferred embodiment of the invention the metal ceramic product comprises between 30 and 40 volume percent of alumina and between 70 and 60 volume percent of chromium metal. Also, in certain aspects of the invention, particularly in metal ceramic articles prepared from slip castings, it is preferred to limit the size of the alumina particles to between 0.1 micron and 10 microns.

In the manufacture of the material of the invention high purity chromium and alumina particles are desirable. In the chromium powder, impurities to be avoided are particularly those which are known to lower the melting point or cause excessive embrittlement. Carbon is especially detrimental and preferably should be kept below 0.03%. In the alumina powder a purity of 99.0% or higher is desirable for optimum high temperature properties. Impurities which lower the melting point and hot strength of alumina such as Na_2O, Fe_2O_3 and SiO_2 should be kept at a minimum.

Broadly, the method of making the chromium-alumina metal ceramics of the invention comprises mixing the requisite quantities of the minute particles of alumina and chromium metal. This operation may be done by conventional mixing methods such as dry tumbling, wet or dry ball milling, wet mixing with a paddle mixer or other conventional method. The particle size of the mixed ingredients preferably should not exceed 45 microns. The mixture so formed is then shaped and fired. The shaping operation may be done by cold pressing in steel dies; by hydraulic pressure in rubber molds; by extrusion of a plasticized mass, the plasticity being imparted through the addition of a temporary binder such as a water solution of methylcellulose; or by hot pressing. In the firing operation, a high firing temperature of between 1450° C. and 1800° C. is recommended. The firing should be done under protective conditions. For example, a dry hydrogen atmosphere has been found to produce excellent results in the firing or 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.

As an alternative to the mixing and shaping steps in the above-outlined procedure the technique of slip casting may be employed. In this procedure, it may be desired to measure the alumina and chromium metal particles on a basis of dry weight percent rather than volume percent. Table I below lists a conversion of these values for both the broad and preferred range of compositions contemplated by the invention.

Table I

Volume Percent		Weight Percent	
50 Cr	50 Al_2O_3	64 Cr	36 Al_2O_3
60 Cr	40 Al_2O_3	73 Cr	27 Al_2O_3
70 Cr	30 Al_2O_3	81 Cr	19 Al_2O_3
75 Cr	25 Al_2O_3	84 Cr	16 Al_2O_3

In the above values the true density of chromium is taken as 7.19 grams per cubic centimeter and of alumina as 4.00 grams per cubic centimeter.

The mixing and shaping steps in this alternative procedure comprise preparing a suspension of alumina particles of a size between 0.1 micron and 10 microns in water acidified to a pH of about 4.5 and adding to said suspension chromium metal particles of a size not exceeding 45 microns to form a suspension containing alumina in an amount between 16% and 36%, preferably between 19% and 27%, dry weight basis, and chromium metal in an amount between 84% and 64%, preferably between 81% and 73% dry weight basis.

In a recommended method of carrying out the above steps, the required amount of alumina is added to water acidified to the desired pH value with hydrochloric acid. The alumina powder is slowly added to the liquid in any suitable mechanical mixer until a thick slip is obtained. The acid acts as the peptizer required to suspend the alumina particles. The chromium powder is added slowly to the alumina slip with continuous agitation. Additional water is usually required to thin the slip. After the addition of the chromium powder the slip is diluted to a proper pouring consistency with more water. If desired, the alumina and chromium powders may be premixed and then added to the acidified water to form the slip. Depending on the particle size and surface area of the alumina and chromium powder from 1 ml. to 21 ml. of concentrated hydrochloric acid solution is used per kilogram of alumina for a 23.0% alumina-77.0 percent chromium, weight basis, composition.

As a specific example of the above procedure, 8520 grams of material containing 77% chromium and 23% alumina, weight basis, was prepared as follows: 830 ml. of distilled water made acid by the addition of 3.0 ml. of concentrated hydrochloric acid solution was placed in a paddle type mixer. 2000 grams of 0.2–0.25 micron size alumina particles were added to form a slip with a pH of about 4.5. 6500 grams of electrolytic chromium particles of a size below 45 microns was added, with agitation, to the alumina slip plus about 300 ml. of water for proper dilution. At this stage the chromium-alumina slip had a density of about 3.97 grams per ml. and a pH of about 4.5 to 4.6. After standing, the slip tends to settle and should be agitated and diluted to the desired consistency before casting.

The slip casting of chromium-alumina compositions may be accomplished by the use of organic surface active materials such as gum arabic, gelatin, polyethylene glycol mono-oleate, oleic acid, stearic acid, latex rubber suspensions, resins, such as silicone resins, methyl cellulose, polystyrene and polisobutylene, and other similar materials. A combination of the above type materials with electrolytes or a wetting agent such as sodium lauryl sulphate may also be used. Gum arabic has been found to be one of the best of the organic peptizers for this purpose and a slip may be prepared by mixing the constituent powders with a 2.0 to 10.0 percent solution of the gum. Hydrochloric acid is preferred as the peptizer in the invention as its use produces a slip with superior casting properties.

The slip may be cast into any suitable water absorbent mold to form a shaped article, which shaped article may then be fired in the manner already described at temperatures between 1450° C. and 1800° C.

Although chromium-alumina metal ceramics may be made by pressing or extruding as before described, slip casting, despite its more critical limitations as to particle size and somewhat lower strength characteristics, has the great advantage of enabling inexpensive, easy fabrication of relatively complex shapes and this procedure is the preferred species of the invention.

The chromium-alumina metal ceramics of the invention have a metal phase of chromium well bonded to the alumina phase by surface diffusion. Within the critical composition 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 chromium itself to an extent which is significantly greater than that found in bodies having little or no metallic continuity.

Industrial applications wherein the articles of the invention may be utilized are not limited to cast or pressed shapes alone. For example, articles prepared according to the invention may be joined by pressure welding, shrink fitting and similar techniques. An excellent joint also may be made by applying a chromium-alumina slip to adjacent surfaces of the articles to be joined, pressing the painted surfaces together and firing them.

What is claimed is:

1. Method of making a metal ceramic product characterized by its strength at elevated temperatures and its resistance to oxidation and thermal shock which method comprises preparing a suspension of alumina particles of a size between 0.1 micron and 10 microns in water acidified to a pH of about 4.5 and adding to said suspension chromium metal particles of a size not exceeding 45 microns to form a suspension consisting essentially of alumina in an amount between 16% and 36%, dry weight basis, and chromium metal in an amount between 84% and 64%, dry weight basis; adjusting the water content of said suspension to form a slip; casting said slip in a water absorbent mold to form a shaped article; and firing said shaped article at a temperature between 1450° C. and 1800° C. for a time sufficient to form a strongly cohesive, sintered mass of intimately dispersed minute particles of alumina and chromium metal with said chromium metal forming a continuous phase in said mass.

2. Method of making a metal ceramic product characterized by its strength at elevated temperatures and its resistance to oxidation and thermal shock which method comprises preparing a suspension of alumina particles of a size between 0.1 micron and 10 microns in water acidified to a pH of about 4.5 and adding to said suspension chromium metal particles of a size not exceeding 45 microns to form a suspension consisting essentially of alumina in an amount between 19% and 27%, dry weight basis, and chromium metal in an amount between 81% and 73%, dry weight basis; adjusting the water content of said suspension to form a slip; casting said slip in a water absorbent mold to form a shaped article; and firing said shaped article at a temperature between 1450° C. and 1800° C. for a time sufficient to form a strongly cohesive, sintered mass of intimately dispersed minute particles of alumina and chromium metal with said chromium metal forming a continuous phase in said mass.

3. A metal ceramic product characterized by its strength at elevated temperatures and its resistance to oxidation and thermal shock comprising a strongly cohesive, sintered mass consisting essentially of intimately dispersed minute particles of alumina and chromium metal, said alumina particles being of a size between 0.1 micron and 45 microns and being present in said mass in an amount between 16 weight percent and 36 weight percent, said chromium metal particles being of a size not exceeding 45 microns and being present in said mass in an amount between 84 weight percent and 64 weight percent with said chromium metal constituting a continuous phase in said mass.

4. A metal ceramic product as claimed in claim 3 wherein the alumina particles are of a size between 0.1 micron and 10 microns.

5. A metal ceramic product characterized by its strength at elevated temperatures and its resistance to oxidation and thermal shock comprising a strongly cohesive, sintered mass consisting essentially of intimately dispersed minute particles of alumina and chromium metal, said alumina particles being of a size between 0.1 micron and 45 microns and being present in said mass in an amount between 19 weight percent and 27 weight percent, said chromium metal particles being of a size not exceeding 45 microns and being present in said mass in an amount between 81 weight percent and 73 weight percent with said chromium metal constituting a continuous phase in said mass.

6. A metal ceramic product as claimed in claim 5 wherein the alumina particles are of a size between 0.1 micron and 10 microns.

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