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METHOD OF SINTERING CHROMIUM-ALUMINA METAL CERAMICS

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This invention relates to an improved method of sintering metal ceramics, particularly metal ceramics of the chromium-alumina type.

Metal ceramic articles, such as those of the chromium-alumina type are formed to the desired shape in the "green" (that is, unbaked) state. The shaped articles, suitably supported, are then heated to sintering temperature in an inert, reducing, or non-oxidizing atmosphere, or in a vacuum. This method is generally satisfactory for sintering most metal ceramic articles, but is impractical for elongated, slender articles over about twelve inches long. Such articles exhibit a marked tendency to fail by cracking. This is due to a decrease in strength of the article during early stages of sintering. Low thermal shock resistance of green castings is but one of the reasons for such failures. At high sintering temperatures, supporting saggers distort and thus present uneven longitudinal support for the articles. The effect of increased support-spans occasioned by this distortion of the supports becomes especially pronounced when long, thin, green castings are sintered at low strength levels, and the elongated castings are incapable of supporting their own weight over the increased support length. As a result, cracks are formed in the sintered articles before they have had a chance to gain the strength that comes with heat treatment. The prevalence of these cracks in most instances exceeds 50% of the ware charged into the furnace.

It is, therefore, a primary object of this invention to provide an improved method of sintering metal ceramic articles of a wide variety of shapes, such as rods, tubes and crucibles made from metal ceramic material, which method reduces substantially the formation of cracks during sintering.

The present invention is based on the discovery that the above defects may be minimized by preliminarily heat treating metal ceramic articles before they are sintered. By heating the metal ceramic ware preliminarily at a relatively low temperature in an oxidizing furnace atmosphere, extensive deleterious oxidizing and corrosive effects, heretofore thought to be unavoidable, are not experienced. Yet sufficient strength is imparted to the ceramic ware during this initial heat treatment to enable them to withstand more rigorous thermal treatment when later sintered to maturity. As a consequence, high temperature furnace operations may then be carried out under non-contaminating conditions without contracting the defects previously experienced in the conventional methods of sintering. The term "non-contaminating conditions," as used hereinabove, is meant to include any medium such as an inert, non-oxidizing, or reducing atmosphere, or a vacuum, which will minimze the possibility of chemical reaction occurring between the article being treated and the surrounding medium.

In carrying out the method of the invention, green castings are prepared from metal ceramic material consisting, for example, basically of a chromium-alumina composition, preferably a composition having approximately 77% chromium and 23% alumina. The cast ware are

dried and packed in undistorted supporting saggers, and are ready for preliminary firing. In the present instance the ware are preferably supported in saggers made of alumina, although other types of supports may be used.

According to this invention, control of the furnace atmosphere is not necessary in the initial phase of heat treatment of cast metal ceramic articles. In this particular instance, a low temperature heating operation may be carried out in a suitable oxidizing medium such as air. Owing to the previously described hazards of heat treatment, the temperature may well be gradually increased to a point considerably below sintering temperatures, for example, 500° C. to 1000° C., preferably 750° C.

The period over which this preliminary heating temperature is reached varies with the accuracy with which the heat can be controlled. It can take anywhere from less than an hour to as much as several hours to reach the desired tempertaure. For example, the low temperature heating operation can be effectively accomplished in less than one-half hour in an infra-red oven. On the other hand, this heat treatment may take over three hours in a gas-fired furnace.

Following the preliminary heat treatment, the chromium-alumina article is then appropriately sintered at a temperature in the range 1500° C. to 1900° C., for example, at about 1600° C. Since it is subject to oxidation at such temperature, heating should be carried out under non-contaminating conditions, i. e., in vacuo or in an inert or hydrogen gas atmosphere.

Chromium-alumina ceramics heated preliminarily in an oxidizing medium in accordance with this invention are provided with superior strength in the form of green castings, and are found to exhibit remarkably excellent thermal shock resistance at sintering temperatures. This is borne out by the sharp decrease in the occurrences of cracks, particularly in the sintering of elongated metal ceramic articles. For instance, tests employing the method of the present invention show that long, thin thermowells made from chromium-alumina material and heat-treated in accordance with the novel practice hereindescribed, had an extremely low incidence of cracking during sintering. Only 3% to 5% of them cracked during sintering, as opposed to the prior art occurrence of more than 50%. Moreover, there is a significant reduction in the number of rejects in the production of metal ceramic ware, even when the ware are supported on uneven or misaligned saggers during the sintering operation.

At radio frequencies, ware produced by the instant method exhibit increased susceptance over similar ware in the original, as-cast condition. Further, ware manufactured by the instant method experience a negligible amount of shrinkage after pre-sinter treatment, the shrinkage being of the order of less than 1%. In contrast, normal shrinkage after full sintering is approximately 15%.

From the above it will be seen that the instant method comprising initially heating the green castings in an oxidizing atmosphere at a relatively low temperature, enables the castings to become sufficiently strengthened for sintering at elevated temperatures without the formation of cracks.

It will be understood that variations and modifications may be effected without departing from the novel concepts of the present invention.

What is claimed is:

1. In a process for producing an article of substantially elongated shape from metal ceramic material consisting essentially of chromium and alumina, wherein chromium constitutes the major constituent of said metal ceramic, the process of minimizing cracking during heat hardening comprising forming the article to said elongated shape in the green state, heating the article to a temperature between 500° C. and 1000° C. in an oxidizing atmosphere

to increase the green strength of said article, and then sintering said article in a non-contaminating atmosphere until sintering of said article is complete.

2. In the process of sintering a green metal ceramic article over 12 inches in length and consisting essentially of chromium and alumina, said chromium constituting the major constituent of said metal ceramic, wherein the green article is supported on spaced supports, the combination therewith of the improvement for reducing the development of cracks during sintering due to low thermal shock resistance of said article in the green state and distortion and wide spacing of said supports during sintering, said improvement comprising heating said article prior to sintering in an oxidizing atmosphere up to a temperature between 500° C. and 1000° C. to increase the green strength of said article, and then sintering said article in a medium which is chemically inert to said article at a temperature between 1500° C. and 1900° C., whereby cracking of said article is minimized irrespective of the

distortion and misalignment of the supports for said article during the sintering operation.

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