OXIDIZED CHROMIUM-ALUMINA METAL CERAMIC PROTECTIVE TUBE

Fig. 1.

Fig. 2.

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This invention relates to a thermocouple protective tube for immersion in molten metals, especially in liquid brass, and more particularly to an object to prolong the life of a metal ceramic coating of the sort made from a chromium-alumina type metal ceramic.

Metal ceramic protective tubes have been constructed of the chromium-alumina type metal ceramic of the prior application of L. A. Comant et al., Serial No. 140,442, filed January 25, 1930 and issued on January 11, 1935 as U. S. Patent No. 2,698,990. Such were found to be better than ceramic tubes for some purposes. However these chromium-alumina metal ceramic protective tubes were found to have a comparatively short life in liquid brass.

According to this invention the chromium-alumina protective tube has been given a longer life of several hundred percent by forming a metal oxide coating on both the inner and outer surfaces of such tube at an elevated temperature in an oxidizing atmosphere. To accomplish the essentials of this invention it is necessary that at least the outer surface of the protective tube receive a continuous oxide coating.

Referring to the drawing:
Fig. 1 is a section on the line 1—1 of Fig. 2.
Fig. 2 is a longitudinal view partly in section through an embodiment of this invention.

A protective tube 10 is an oxidized chromium-alumina metal ceramic to contain a thermocouple 11 for immersion in liquid brass. This protective tube contains a body portion 12 preferably formed by slip casting the closed end tube in a mold. After the tube has shrunk slightly to facilitate its removal from the mold it is sintered. After firing the tube to a sintering temperature in the manner pointed out in the aforementioned United States Patent and in a non-oxidizing atmosphere which is inert to the metal ceramic, the same is then heated to between about 1000° C. and 1400° C. in an oxidizing atmosphere. An oxidizing atmosphere is an atmosphere which will promote the formation of metal oxides. Air is a good example of such an atmosphere and has been used herein. A continuous, adherent, oxide coating is thereby formed on the surface of the metal ceramic.

A test of the adequacy of the oxide coating for the purpose of this invention is its electrical resistance. The coating 13 on the inside of the tube and the coating 14 on the outside should each have an electrical resistance of at least about 100 megohms if they are to be considered as being continuous. These coatings are shown much thicker than they are because they average perhaps less than a thousandth of an inch. The quality of the coating, as determined by electrical resistance, appears to depend on the temperature and the time of exposure in the oxidizing atmosphere. With the higher temperature mentioned above only a short duration of exposure is needed to form a suitable oxide coating while with the lower temperature of 1000° C. about five to twenty-four hours exposure in an oxidizing atmosphere is needed. At about 1200° C. it is found approximately a two hour exposure is needed. The satisfactory metal oxide coating can also be formed with the aid of an oxidizing blowpipe flame when after heating the work to about 1400° C. an exposure of only about ten minutes to an oxidizing atmosphere was found sufficient.

To obtain a more uniform oxide coating on the metal ceramic, it was found that cleaning the surface by sand blasting or wire brushing prior to exposure to the oxidizing atmosphere was desirable. This treatment, while desirable, is not essential to this invention. The tube may be oxidized by simply immersing it in a suitable ceramic support and thus exposing the inner metal ceramic to the oxidizing atmosphere as mentioned above in order to obtain the desired coating. One appropriate size of tube was found to be 8" long, 4" outside diameter and .24" inside diameter. Of course, other sizes may be formed. The composition tested was the 77% chromium and 23% by weight of alumina of the abovementioned United States Patent, the combined chromium and alumina content being 100 percent. Another tube tested contained 76.9% chromium, 21.9% alumina and 1.2% titania, the combined chromium and alumina content being 98.8 percent. A third tube contained chromium, 35.1% molybdenum, 18.7% alumina, and 2.1% titania, the combined chromium and alumina content being 62.8 percent. When tubes of any of the foregoing compositions were immersed in molten cartridge brass at a temperature of 1050° C. to 1180° C. it was found that the average life of those protective tubes oxidized according to this invention was longer than that of corresponding untreated tubes by 500% to 3000%. While an unoxidized tube of the chromium-alumina metal ceramic was penetrated by molten brass, those of the present invention were not. The bonding strength of the unoxidized chromium-alumina metal ceramic was lowered due to penetration by the liquid brass from about 40,000 pounds per square inch to about 20,000 pounds per square inch, whereas tubes of the present invention were not penetrated by the liquid brass nor was their strength weakened. As mentioned above, a criterion of a good coating is its electrical resistance. In testing for the electrical resistance the oxidized tube may be immersed in mercury and mercury then placed within the tube and the electrical resistance between the two bodies of mercury measured in some customary manner.

This invention offers other benefits besides the improved service from a thermocouple tube in molten brass. Thermocouple tubes for use in other molten metals, such as aluminum and zinc, are similarly improved. Protective tubes for other than thermocouples and for use in corrosive media in general may thus be produced. The chromium-alumina metal ceramic is thought to be permeable to the entry of molten metal and the entry of metal into the structure weakens it, perhaps by the different coefficients of expansion. In the present invention the metal phase in the metal ceramic is believed to be coated by a substantially continuous layer of metal oxide. This oxide layer is believed to be in substantial part, the oxide of chromium, Cr₂O₃.

The aforementioned U. S. Patent 2,698,990 discloses the sintering temperature of the chromium-alumina metal ceramic to be preferably between about 1450° C. to 1800° C. The temperatures mentioned herein for oxidation of the metal to form a continuous coating of oxide will be seen to be below those sintering temperatures. Any metal oxide formed in the prior application before or after sintering was found not to be continuous nor possessed of the high insulating properties herein mentioned as an indication of continuity in the oxide coating of the finished product. Said prior patent disclosed continuity in the metal phase to exist when the
metal content of the metal ceramic was between about 50% to 75% by volume and the ceramic content of the metal ceramic between about 50% to 25% by volume.

I claim:

1. In a sintered metal ceramic consisting substantially of chromium and alumina and having a combined chromium and alumina content constituting at least 62.8 percent by weight of said metal ceramic, the improvement which increases the resistance of said metal ceramic to penetration by molten metals, comprising a continuous metal oxide coating on a surface of said metal ceramic of alumina and oxide of interdispersed continuous phase which is in at least a substantial part of chromium oxide, said metal coating having an electrical resistance of at least about 100 megohms.

2. A metal ceramic object according to claim 1 which is a tube having a closed end and having said metal oxide on at least an outer surface.

3. A protective tube according to claim 2 having said metal oxide also on an inner surface.

4. A method of forming an oxide coated metal ceramic object consisting essentially of chromium and alumina and having a combined chromium and alumina content constituting at least 62.8 percent by weight of said metal ceramic and also having a continuous metal oxide surface coating of alumina and oxide of interdispersed continuous phase metal which comprises sintering said metal ceramic in an atmosphere inert to said metal ceramic, and then, after sintering, heating said metal ceramic in an oxidizing atmosphere at a temperature below that at which said metal ceramic was sintered but above 1000° C. thereby forming said continuous metal oxide surface coating on said object which comprises in at least a substantial part chromium oxide, and continuing said heating until said coating has an electrical resistance of at least about 100 megohms.

5. A method according to claim 4 in which the heating in an oxidizing atmosphere was between about 1000° C. and 1400° C.

6. A method of treating a metal ceramic tube according to claim 4 in which the surface of a metal ceramic tube is mechanically cleaned before the same is subjected to said oxidizing atmosphere.

7. In a sintered metal ceramic object consisting essentially of chromium and alumina and containing between about 50% to 75% by volume of chromium metal and between about 50% to 25% by volume of aluminum oxide ceramic with the metal being in continuous phase, the combination therewith of the improvement for enhancing the resistance of said metal ceramic to penetration by molten metals, said improvement comprising a metal oxide coating which is continuous, comprises alumina and an oxide of interdispersed continuous phase metal, has an electrical insulation resistance of at least about 100 megohms, and is at least in substantial part chromium oxide on a surface of said metal ceramic.

8. In a sintered metal ceramic object consisting essentially of chromium and alumina and having between about 50% to 75% by volume of chromium metal, between about 50% to 25% by volume of aluminum oxide ceramic with the metal being in continuous phase, the improvement for enhancing the resistance of said metal ceramic to penetration by molten brass, which comprises a metal oxide coating of alumina and oxide of interdispersed continuous phase metal which is continuous, has an electrical insulation resistance of at least about 100 megohms, and is at least in substantial part chromium oxide on a surface of said metal ceramic.

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