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REFRACTORY SULFIDE CASTING CORES

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This invention relates to the casting of molded articles and, more particularly, to refractory sulfide containing cores for use in providing openings in cast metal articles.

One method for obtaining openings such as holes, pores and channels in cast molded articles is through the use of one of a group of materials sometimes called "removable cores" or "casting cores." The cores, generally shaped according to the opening desired, can be arranged in a mold and material of the article cast around the cores. After the material of the article has set, the article can then be removed from the mold. Upon removal of the core either by chemical means such as by dissolution or "leaching out" or by mechanical means such as drilling, the desired opening is provided in the article. Generally cores are removed from complex shaped articles only by chemical means because of such difficulties as drill guidance and inexcessibility of drills to the cores.

Cores used in casting high temperature metals or alloys into complex articles having openings for the passage of a cooling medium during high temperature operation must have certain properties in order to be useful. Included are such properties as thermal shock resistance, strength at the casting temperature, low wettability, nonreactivity with the material being cast, low volatility to prevent porosity through introduction of vapor or gas in the casting. In addition, the ease of removal of a core by a method or material which will not harm the cast article is very important. In some applications it may be desirable to use a relatively "ductile" core that can be mechanically worked such as in forging and swaging along with the material of the article.

Most of the presently available core materials are silicious in nature and may include volatile oxides or impurities which result in porosity or "gassing" in the cast article. Such cores tend to be lacking either in thermal shock resistance or bending strength characteristics at elevated pouring temperatures. Thus core integrity and positioning cannot be maintained in mold shapes. Most significant of all, they either are very difficult to remove from the casting without harm to the material of the article, or they require long periods of chemical processing. In addition, they usually must include an access hole along their axis to afford passage of the chemical solution to facilitate removal. The problem of removal becomes even more troublesome in articles provided with holes having a high length to diameter ratio.

It is an object of this invention to provide a new high strength casting core useful up to temperatures higher than those at which silicious type cores can be used.

A further object is to provide a core readily removed by dissolution in relatively mild chemical solutions without requiring a chemical solution access hole.

Another object is to provide a casting core of workability and strength sufficient to allow it to be nondestructively shaped along with the cast article prior to core removal.

These and other objects and advantages will become more apparent when viewed in connection with the detailed description and succeeding examples which are illustrative of rather than limitations on this invention.

The present invention provides a removable core, the removable portion of which comprises a refractory sulfide. In one form, the invention includes a casting core having a metallic inner element and an outer coating of refractory sulfide or mixture of refractory sulfides. In another form, the core is comprised throughout of a refractory sulfide or mixture of refractory sulfides.

This invention recognizes the remarkable properties of refractory sulfides or mixtures of sulfides such as those of cerium and thorium which make them attractice for use in cores in the casting of articles. These sulfides, and especially those of cerium (Ce_2S_3, Ce_3S_4 and particularly CeS), are known for their high temperature stability and unusual refractory properties.

For example, the normal cerium sulfide CeS, up to about 1900° C. has no known chemical reaction with metals except platinum, has complete spalling resistance to 2300–2500° C., will resist thermal shock even when heated or cooled as fast as 1,000 C° per minute and can be mechanically worked even at room temperature. It has sufficient high temperature strength to be used at casting temperature up to about 2000° C. and has a vapor pressure of only 10^{-3} mm. at 1900° C., thus to avoid production of gas, one cause of porosity in casting. It has low wettability in the presence of liquid or solidified metals and has thermal conductivity which allows it to more closely approximate the expansion characteristics of metals than can other silicious type core materials. Extremely important in the ease of removal of CeS and the other cerium sulfides from castings by substantially non-corrosive reagents including a number of mineral acids.

Controlled additions of small amounts of oxygen, as described later, will strengthen cores made from cerium sulfide. However, CeS in general reacts with oxygen at temperatures above about 300° C. Therefore it should be protected above that temperature during casting and mold preparation such as through use in a vacuum, in inert or reducing atmospheres or by coating the core with an oxidation resistant coating.

Refractory sulfides, which are usually prepared by powder metallurgical techniques, resist wetting by molten metals. For use as cores, they can be applied as coatings over metal wires and rods of various materials and shapes depending on the intended shape of the opening. It has been noted that the wires and rods based on such elements as tungsten and molybdenum have been particularly useful in the casting of articles of refractory alloys. This combination takes advantage of the additional high temperature strength of the metals used in the cores and yet prohibits such metals from contaminating the alloy being cast. Thus a casting core combining a refractory metal center and an outer layer of a refractory sulfide or mixture of sulfides results in high temperature strength and workability advantages in a core in addition to those advantages already enumerated.

Wires and rods of various sizes have been coated by first dipping them into a slurry including CeS and a binder such as naphthalene dissolved in ether and then air drying. This process is continued until the desired diameter of core or thickness of coating is obtained. To obtain extremely close tolerances in core diameter or coating thickness, the coated wire can be passed through a circular die by extrusion methods. This "green" core is then fired at about 1700° C. to sinter the CeS.

It is contemplated that a variety of wire and rod coating methods can be used to coat the wires and rods for use in cores. The thickness of coating, its tolerance and the size of core depends on its application. It has been noted that thin wires such as of 0.02" diameter coated with relatively thin coatings of CeS, for example to a thickness of about 0.02", can be shaped or contoured with no apparent damage to the CeS coating.

Another form of casting core of this invention is one which does not include a metallic inner portion but has been made substantially from refractory sulfides or mix-

tures thereof by such methods as extrusion and subsequent sintering of the refractory sulfide material. In some cases, it has been found necessary to add small amounts of strengthening or stiffening materials for room temperature handling. One example of such a stiffener is cerium oxysulfide, Ce_2O_2S, which with CeS forms a eutectic harder and stronger than CeS alone. However, for high temperature applications, it is preferred that the addition of Ce_2O_2S be limited to about 5% because of the eutectic's lower melting point than that of CeS alone. Because of the addition of Ce_2O_2S to CeS, stronger cores as small as about 0.02" can be made. This is possible for the additional reason that no chemical solution access hole is required for ease of removal.

One of the most inviting properties of the refractory sulfides is the ease with which they react and dissolve in a variety of dilute acids. Thus corrosion or erosion of the surrounding refractory metal of an article is eliminated. During acid reaction or dissolution the gases H_2S and H_2 are liberated. By the addition of a wetting agent the gas bubbles can be made to escape in a finely divided state. It is not necessary, therefore, to consider recycling or pumping systems to effect core removal since the gas evolution provides the necessary agitation.

A metal casting including refractory sulfide cores of both types with and without metal inner portions was submerged in an aqueous solution of HCl (1:1) containing about 0.5% by volume of a wetting agent of the sulfonated alkyl acid type. A temperature of about 150° F. was maintained. Time of removal was in the order of 1 hour per inch of core. In the case of those cores including an inner wire or rod, after the CeS was dissolved, the wires or rods were loose within the holes and were easily pulled out.

Although gas evolution causes agitation within the hole sufficient to result in rapid core removal, nevertheless ultrasonic and electrolytic type supplementary removal aids can further increase the speed of core removal. The electrical conductivity property of cerium sulfide makes possible electrolytic removal processes.

To test the cores of this invention under actual metal casting conditions, a series of molds were prepared by first coating with a mold slurry a wax pattern including properly positioned CeS cores of both the plain and inner wire type. The coated patterns were then heated to about 870–980° C. to melt and remove most of the wax. This wax removal step can be conducted in air but, since the CeS is air (oxygen) sensitive, this heating should be limited to about 30 seconds. After this first wax melting removal step, it is preferred that additional wax be eliminated by inverting the mold and heating at about 120° C. to protect the CeS from catastrophic oxidation which occurs above about 300° C. After cooling the mold, all traces of any remaining wax can be removed by degreasing in a solution such as trichloroethylene devoid of free acid.

The mold is then sintered in an inert or reducing atmosphere or in vacuum at about 870–980° C. for about 15–25 minutes prior to pouring of the metal to be cast. The metal cast into molds prepared as described above was a nickel base high temperature alloy comprising in percent by weight 16 Cr, 3.5 Ti, 5 Al, 4 Mo, 5 Fe, 0.1 B with the balance essentially nickel. The cores were removed by an aqueous HCl (1:1) solution according to the previously described method.

Prior to this invention, the problem of core removal was a major issue in the casting of good articles including long narrow holes or openings. Danger to the surrounding metal by vigorous alkali or acid reagents required to remove silicious type cores was the basis for the problem. However, through the use of this invention, the variables of time of core removal and danger to surrounding metal have been minimized so dramatically as to be insignificant among other variables present in the manufacture of cast articles.

In another form of this invention, refractory sulfides are encased in a metal tube which is positioned in the casting mold as would be a core. After casting, the tube becomes part of the casting and the refractory sulfide is removed as has been described. This type of metal encased core is particularly useful in connection with the casting of articles from such metal or alloys based on titanium and zirconium. It has been found that refractory sulfide filled tubes can be reduced in size or shaped such as in forging, swaging and rolling without harm to the refractory sulfide.

To demonstrate the feasibility of CeS for this purpose, it was encased by a metal tube the composition of which comprised in percent by weight C 0.04, Cr 16, Fe 7 with the balance essentially nickel. This tube, which had an outside diameter of about 0.183" and an inside diameter of 0.12", was heated for five minutes at 2300° F. in hydrogen. It was then removed and immediately swaged to 0.125" outside diameter in one pass. The CeS was reduced proportionately.

Since the refractory sulfide cores can be made by powder metallurgy techniques, one can obtain any desirable surface roughness by a judicious choice of particle size and binder as well as sintering temperature. The end product is a core capable of withstanding at least 4000° F. while maintaining strength, and neither reacting with the molten metals in contact with it nor giving off any contaminants because of its negligible vapor pressure. Curved cores or other shapes can be made to fit advanced designs.

Although this invention has been described in connection with specific examples, one skilled in the art will readily understand the variations and modifications of which the invention is capable.

What I claim is:

1. For use in casting articles including an opening produced by the removal of cores, a core having a removable portion consisting essentially of up to about 5% by weight Ce_2O_2S with the balance essentially cerium sulfide.

2. For use in casting articles including an opening produced by the removal of cores, a core having a removable portion consisting of CeS.

3. A casting core characterized by its low surface volatility and ease of removal from a casting comprising an inner portion and an outer surface, said outer surface consisting essentially of a sulfide selected from the group consisting of cerium sulfides, thorium sulfides and their mixtures.

4. For use in casting articles including an opening produced by the removal of a core, a core having a removable portion consisting essentially of a sulfide selected from the group consisting of cerium sulfides, thorium sulfides and their mixtures.

5. For use in casting articles including an opening produced by the removal of a core, a core having a removable portion consisting essentially of a sulfide of cerium.

6. A casting core characterized by its low surface volatility and ease of removal from a casting having a metallic inner portion and an outer surface consisting essentially of a sulfide selected from the group consisting of cerium sulfides, thorium sulfides and their mixtures.

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