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(54) **Coated cores and metal casting therewith**

(57) Beryllium alloys, particularly beryllium-aluminum alloys during melt casting, have been found to react with and corrode materials used to form cores and some molds. Selected coatings have been found which protect the core (and mold when necessary) material during casting of the molten alloys. Of particular interest are

alloys of beryllium and aluminum having from about 20 to about 80% by weight beryllium. Cores are formed from metals or ceramics, particularly stainless steels or silica-based ceramics. Coatings found to be stable and to protect such cores (and molds) against the molten alloy during casting include selected oxides, borides, nitrides and cermets.

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Description

FIELD OF THE INVENTION

In the preparation of castings of beryllium alloys, particularly beryllium-aluminum alloys, many of the alloys have been found to be corrosive to the core (and in some cases the mold) materials leading to degradation of the core (and mold) and poor quality castings. It has been found possible to protect the core (and if necessary, the mold) with selected coatings which do not react sufficiently during the casting process to allow the core (and mold) to be detrimentally affected.

BACKGROUND AND THE PRIOR ART

Aluminum and magnesium castings have desirable properties for many applications where light weight, good corrosion resistance and reasonable strength are important. Various alloys of these metals have been developed to improve the strength and high temperature properties.

Certain beryllium alloys, particularly beryllium-aluminum alloys, have high stiffness, low density and high melting points giving a desirable combination of properties. In applying the casting techniques to these alloys, it was found that the higher casting temperatures and corrosiveness of these alloys caused substantial and unacceptable degradation of the core as well as poor metallurgical integrity of the casting. Reaction products formed from cast alloy and core become detrimental defects in the casting.

Beryllium-aluminum alloys are difficult to cast due to mutual insolubility and wide solidification temperature range leading to undue microporosity and coarse microstructure causing reduced strength and ductility. To reduce these effects various ternary, quaternary and higher order alloys have been developed including additives such as silicon, silver, copper, nickel or cobalt. Alternatively or additionally powder metallurgy techniques have been applied to these alloys in efforts to reduce these difficulties. However, the problem of reaction with core (and some mold) materials during melt casting still is present with the various higher order alloys. Typical ternary and higher order alloys are described in U.S. Patents 5,417,778, May 23, 1995 and 5,421,916, June 6, 1995, both issued to Nachtrab et al. In PCT Application Publication No. WO 95/27088, October 12, 1995, Grensing et al., certain aluminum alloys containing beryllium, and formation and investment casting of these alloys, are disclosed.

It would be desirable to form cores able to withstand the effect of these molten alloys during casting, giving high quality castings and allowing removal, and in some cases, reuse of the cores.

SUMMARY OF THE INVENTION

It has been found that core materials (and susceptible mold materials) can be protected during melt casting of beryllium alloys by providing on the core (and optionally the mold) a coating selected to be substantially inert or non-reactive during the casting process. By substantially inert or non-reactive is meant not reacting during the casting process sufficiently to detrimentally affect either core or casting.

One object of the present invention includes the provision, in a process of casting beryllium alloys in which mold or core materials are reactive to a significant extent with the molten alloys, characterized in that the process comprises: utilizing at least one of a mold and a core coated with a protective coating which is selected to be substantially non-reactive during the casting process.

The invention further includes a shaped mold or core or combination for beryllium alloy casting, the mold and/or core having a protective coating selected to be substantially non-reactive with the beryllium alloy being cast throughout the casting process.

The invention includes, more particularly, a process of casting beryllium-aluminum alloys having from about 20 to about 80% by weight beryllium, comprising: providing a casting mold and at least one core yielding the desired shape; coating the core, and optionally the mold, with at least one of the group consisting of oxides, borides, nitrides and cermets selected to be inert to the molten alloy; casting the alloy while molten, into the mold and about the core; cooling, removing the mold, and recovering the cast part.

In some cases, the mold may be used to form further castings. In cases Where the core is removed intact from the casting, the core can be re-used also. Some of the core coatings may serve as parting agents which facilitate core removal.

Another object of the present invention is to provide a process for casting beryllium alloys wherein mold surfaces which contact and which react with the molten metal are coated similarly to the core surfaces. The benefits of this are reduced reactivity with molten metal and improved quality of the casting. A preferred embodiment is where the coating serves as a parting agent as well as a protective barrier, thus facilitating removal of both mold and core.

Those coatings found to have parting agent properties (on casting beryllium alloys) are MgO, ZrO₂, TiN and Al₂O₃. Particularly preferred as combined protective chemical barrier coating plus parting agent is ZrO₂ or Al₂O₃.

Preferably, the beryllium alloys are beryllium-aluminum alloys containing from about 20 to about 80% by weight beryllium and having additives to improve the microstructure, strength and ductility. More preferably, the alloys will have from about 50 to about 70% beryllium.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The casting alloys may contain up to about 80% by weight beryllium. The beryllium alloys, which are amenable to casting, include those containing from about 20 to about 80% by weight beryllium; from about 20 to about 75% aluminum, and the balance additives selected from silicon, silver, magnesium, copper, nickel, cobalt and impurities. All of these alloys melt at temperatures above about 1150°C (beryllium melts at 1277°C).

Any casting technique involving molten beryllium alloys and the use of reaction-susceptible molds or cores, including investment casting, shape casting, sand casting, permanent mold and die casting, can be improved by the invention. Normally, a vacuum or an inert gas atmosphere (e.g. argon, helium) is maintained during casting.

Mold materials commonly used in such casting techniques include sand-plus-binder, ceramics such as alumina (with binder), silica, alumina-silicate mixtures, zircon, sodium and potassium silicates, zirconia (with binder), gypsum, graphite, and magnesium/iron silicates. Any of the known processes for shaping the mold may be used. Many of these mold materials will react with molten beryllium alloys and can be coated similarly to the cores to protect against reaction.

The cores may be formed of a) suitable metals (or alloys) which melt above the casting temperatures, b) suitable ceramics, for example alumina/binder or silica-base ceramics, and c) mixtures thereof. Such mixtures may comprise e.g. stainless steels + silica-base ceramics; titanium + Al_2O_3 + binder and mixed ceramics. Frequently, alumina is used with some form of binder and the binder has been found to be reactive with the molten alloy. Examples of metals useful in forming cores are various stainless steels, e.g. 304, 316 and 321; titanium and Ti-base alloys such as Ti6Al4V; nickel and Ni-base alloys such as IN-100. Such cores have been found to react with the beryllium alloys during casting.

The core base may be shaped by any known metallurgical technique (in the case of metals) or ceramic molding technique (in the case of ceramics and mixtures). The cores may be hollow, e.g. as metal tube or slip-cast fired ceramic; or substantially solid, e.g. as metal rod or sintered ceramic powder. If the cores are to be removed from the finished part, the core material should be susceptible to chemical dissolution or mechanical disruptions. These mechanical removal processes might include vibration, drilling, abrasion, and/or grinding. Depending on the process, residual core coating material might remain in the casting without detriment. If the protective coating also acts as a parting agent, it may be possible to remove the core as a unit or in several pieces.

Selected coatings have been found which are substantially non-reactive during casting and able to protect the mold and/or core from molten beryllium alloys. The

coatings are selected from oxides, e.g. alumina, magnesia, beryllia, thoria, titania and zirconia; and borides, e.g. beryllium boride, aluminum boride, titanium boride; as well as nitrides, e.g. beryllium nitride, boron nitride, aluminum nitride and titanium nitride. Cermets may also be used e.g. Be + beryllia; Be + alumina; Be + zirconia; Mo + alumina; Ta + alumina and Ta + zirconia. Intermetallic oxides or borides or nitrides or cermets may be used e.g. Be-Ti boride; B-Al nitride; beryllia-zirconia; alumina-thoria.

The coating is formed on the core by any suitable technique, e.g. plasma spraying, vapour deposition, dipping, electro-deposition, injection around core body, brushing, spraying, impregnation, painting, and flow or gravity or cascade coating. Vaporization, melt or sintering temperatures will be reached in forming the coating, as required.

The thickness of the coating should be selected to constitute an effective diffusion barrier during the entire casting process. Usually the thickness will be within the range of about 20 to 1000 microns, preferably about 50 to 200 microns. Multi-layer coatings may be used: examples include Al_2O_3 under ZrO_2 and Al_2O_3 under TiO_2 .

A preferred coating is plasma-sprayed or physical vapour deposited alumina having a thickness of about 50-100 microns. Another preferred coating is ZrO_2 .

The cast products have been found to be improved (when these coated molds and/or cores were used) in aspects such as smooth and defect free detailed passages, pockets and cavities.

Coated molds and cores, when able to be removed intact, can be re-used. If necessary a coating layer can be re-applied.

The following examples are typical and illustrative and are not intended to be limiting or exhaustive.

EXAMPLES

Example 1

A core constructed from a stainless steel tube (321) was plasma coated with 100 microns thickness of Al_2O_3 . Using technology known to the art of investment casting, the core was located inside the internal cavity of a ceramic shell mold. The ceramic shell was preheated in the range of 900°C-1250°C (preferably 1200-1250°C) and then molten aluminum-beryllium 40:60 alloy in the range of 1200°C-1470°C (preferably 1400-1450°C) was poured into the shell, filling the internal cavity and surrounding the Al_2O_3 -coated tube. During casting and cooling, an argon gas atmosphere was maintained. Once the casting was cool, it was cleaned and prepared in a manner similar to the usual procedure for aluminum and magnesium castings. The Al_2O_3 -coated tube was found to be resistant to the molten alloy and to result in high quality castings.

Example 2

All processing was the same as Example 1 except the core was coated by dipping in a ceramic slurry (a water-base slurry of beryllium oxide) followed by sintering. The beryllia-coated tube was found to be resistant to the molten alloy and to result in high quality castings.

Example 3

All processing was similar to Example 1 except the core was formed from a tube of titanium base metal and coated with aluminum boride by plasma spraying. The boride-coated tube was resistant to the molten alloy and resulted in high quality castings.

Example 4

All processing was similar to Example 1 except the coating was plasma-sprayed thoria. Good quality castings resulted.

Example 5

All processing was similar to Example 1 except the coating was vapour-deposited alumina-zirconia. The alumina-zirconia coated core was resistant to the molten alloy and resulted in high quality castings.

Example 6

The procedures in Example 1 were repeated except the ceramic shell mold also was coated with 100 microns of plasma-sprayed alumina on all surfaces exposed to the molten alloy. Very high quality castings resulted when mold and core were removed.

Example 7

A SiO₂-based ceramic core was coated with Al₂O₃ to a thickness of 50 microns. Plasma spraying which produced a sound and chemically inert barrier, was used to provide the layer. The coated ceramic core was located inside the internal cavity of an investment casting ceramic shell so that part of the core would be exposed in the casting. The ceramic shell was preheated in the range of 900°C-1250°C and then molten aluminum-beryllium alloy of 65% beryllium at a temperature in the range of 1200°C-1450°C was poured into the shell, filling the internal cavity and surrounding the Al₂O₃-coated tube. Once the casting was cool, the casting was cleaned and prepared in a manner similar to known aluminum and magnesium casting procedures. The exposed ceramic core was then removed by leaching in a solution of hydrofluoric acid. A high quality casting resulted.

Example 8

All processing was similar to that in Example 7 except the coating was plasma-sprayed magnesia. The magnesia-coated core was resistant to the molten alloy and yielded a high quality casting.

Example 9

The procedures were similar to those in Example 7 except the core coatings were formed from the following ceramics: ThO₂, ZrO₂, MgO, TO₂, AlN, BeN, BN, TiN. In each case, the coated cores were resistant to the molten alloy and yielded high quality castings.

Example 10

The procedures were similar to those in Example 7 except the coating was derived from at least two layers of the different ceramic materials alumina and zirconia. Superior quality castings resulted.

Example 11

The procedures were similar to those in Example 7 except the coating was derived from the cermet Be + alumina. Superior quality castings resulted.

Although embodiments of the invention have been described above, it is not limited thereto and it will be apparent to those skilled in the art that numerous modifications form part of the present invention insofar as they do not depart from the spirit, nature and scope of the claimed and described invention.

Claims

1. In a process of casting beryllium alloys, in which mold or core materials are reactive to a significant extent with the molten alloys, the improvement characterized in that the process comprises:
utilizing at least one of a mold and a core coated with a protective coating which is selected to be substantially non-reactive during the casting process.
2. The process of claim 1, characterized in that the alloy contains up to about 80% by weight beryllium and sufficient to cause reaction with the core and mold materials.
3. The process of claim 1, characterized in that the core is formed of a material selected from the group consisting of metals, ceramic, and mixtures thereof, which are reactive with the molten alloy and solid at casting temperatures.
4. The process of claim 1, characterized in that the

coating is formed of a material selected from the group comprising: oxides; borides; nitrides; and cermets which are solid at the molten alloy temperature.

5. The process of claim 1, characterized in that the core material comprises a stainless steel or a silica-based ceramic, and the coating material comprises alumina, beryllium oxide, thorium oxide, magnesium oxide, titanium oxide, zirconium oxide or a mixture of at least two of said oxides. 5 10
6. A shaped mold or core for beryllium alloy casting processes, the mold or core being reactive with the alloy and having a protective coating which is selected to be substantially non-reactive at the casting temperatures with the alloy being cast. 15
7. The core of claim 6, characterized in that the core material comprises a metal selected from stainless steels, titanium, Ti-base alloys, nickel and Ni-base alloys. 20
8. The core of claim 6, characterized in that the core material comprises a ceramic selected from silica-based ceramics. 25
9. The mold or core of claim 6, characterized in that the coating comprises an oxide, boride, nitride or cermet which is solid at the molten beryllium alloy temperature. 30
10. The mold or core of claim 9, characterized in that the coating comprises at least one of alumina, beryllium oxide, thorium oxide, zirconium oxide, titanium oxide and magnesium oxide. 35
11. The mold or core of claim 9, characterized in that the coating comprises an intermetallic boride or nitride. 40
12. The mold or core of claim 6, in combination as a mold and core unit.
13. The combination of claim 12, characterized in that both mold and core surfaces to be exposed to the alloy are coated with said protective coating. 45
14. A process of casting beryllium-aluminum alloys having from about 20 to about 80% by weight beryllium, characterized in that it comprises: 50

providing a casting mold and at least one core yielding the desired shape;
coating the core, and optionally the mold, with at least one of the group consisting of oxides, borides, nitrides and cermets selected to be inert to the molten alloy;

casting the alloy while molten, into the mold and about the core;
cooling, removing the mold and optionally the core, and recovering the cast part.

15. The process of claim 14, characterized in that the mold and core are recovered, optionally recoated, and returned to the casting step and used to form further castings.
16. The process of claim 14, characterized in that the mold surfaces to be exposed to the molten alloy are reactive with the molten alloy and are coated similarly to the core, before casting.
17. The process of claim 14, characterized in that the coating is selected to have a parting agent effect also.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 10 8688

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 8450 Derwent Publications Ltd., London, GB; Class L02, AN 84-311590 XP002039778 & SU 1 090 483 A (CHELYABINSK POLY) , 7 May 1984 * abstract *	1,2,6	B22C3/00 B22D21/00
A	US 4 947 927 A (HORTON ROBERT A) 14 August 1990 * whole document *	1-17	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B22C B22D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 4 September 1997	Examiner Riba Vilanova, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document	

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