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(54) **Cooling of molten media processes.**

(57) An improvement to processes in which molten materials are handled at elevated temperatures is described. The improvement is the use of a polyorganosiloxane fluid as a cooling medium instead of water. This improvement eliminates the safety hazard of steam explosions which can occur when water is contacted with molten materials at elevated temperatures.

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COOLING OF MOLTEN MEDIA PROCESSES

This invention relates to the use of polyorganosiloxane fluids as cooling media for processes which include handling of molten salts, metals, metalloids, or alloys. More specifically, this invention relates to improved safety of these processes by eliminating the hazard of a steam explosion when water is used as a cooling medium.

Water is the most common liquid heat transfer medium because of its availability and low cost. However, water poses the significant safety hazard of a steam explosion if water is allowed to contact molten salt or molten metal, metalloids, or alloys thereof at elevated temperatures. Steam explosions are characterized by extremely rapid increase in pressure resulting in subsequent rupture of a containing vessel. The release of this explosive force could cause risk to life and property. While the mechanism of steam explosions is not completely understood, this occurrence is a phenomenon which is more than a pressure build-up due to rapid vaporization of liquid water.

Electric smelting furnaces to produce metals, metalloids, and alloys thereof are examples of processes which handle molten materials. Submerged electric arc furnaces are used extensively in the reduction of oxygen-containing compounds to produce metals, metalloids, and alloys thereof. More recently, plasma technology is being applied to the above-noted oxide reductions. Examples of such metals, metalloids, and alloys are iron, aluminum, silicon, steel, ferrosilicon, and other ferroalloys. The very high temperatures reached in these smelting operations, up to and above 2000°C., require that cooling be provided to protect the structural integrity of certain parts of the furnace. These parts may include the electrode holders, furnace hoods, furnace covers, tapping spouts, lance tubes, and others in conventional electric arc furnaces. In plasma furnaces, the main concern is cooling the plasma torch.

In the present state of the art, water is used as the cooling medium for smelting furnaces. Kuhlmann in U.S. 4,206,312, issued June 3, 1980, discloses a cooled jacket for electric arc furnaces. The only liquid coolant specifically disclosed by Kuhlmann is water.

A review of steel manufacturing, <u>The Making, Shaping, and Treating of Steel, Tenth Edition</u>, United States Steel (1985), pp. 346-347, pg. 350, pp. 533-535, pp. 608-609, pg. 625, pg. 635, pp. 647-652, and pg. 668 outlines the use of water as a cooling medium in both electric arc furnaces and furnaces which use a plasma as the energy source. No other liquid cooling medium than water is disclosed.

It is an objective of this invention to improve the safety of operation of processes which handle molten materials at elevated temperatures.

Nelson and Duda, "Steam Explosion Experiments with Single Drops of Iron Oxide Melted with a CO_2 Laser. Part II. Parametric Studies," Sandia National Laboratories, Albuquerque, New Mexico, NUREG/CR-2718, SAND82-1105, R3, printed April, 1985, discuss laboratory studies on the phenomenon of steam or vapor explosions using molten iron oxide and water. In Appendix C of this reference, Nelson and Duda disclose the testing of n-pentadecane with molten iron oxide. Nelson and Duda were not able to create a vapor explosion with n-pentadecane as had been created with water.

Polydiorganosiloxanes provide a safer alternative to water as a liquid heat transfer fluid. The significantly higher boiling point and subsequent lower vapor pressure of polydiorganosiloxanes lessens the hazard caused by a coolant leak into the furnace due to the rate of pressure rise and level of ultimate pressure, particularly in the case of a closed furnace. More significantly, it has been unexpectedly found that polydimethylsiloxanes do not exhibit an explosive reaction, similar to a steam explosion, when exposed to a molten medium at elevated temperatures. For the purposes of this invention, the term "elevated temperatures" means temperatures greater than 500°C. This unexpected finding is discussed in an example, infra. This unexpected finding is a marked improvement in the operation of processes handling molten materials at elevated temperatures, since it greatly reduces the hazard to life and property.

Additionally, polydimethylsiloxane fluids afford an improved heat transfer fluid as compared to conventional organic heat transfer fluids such as mineral oils, higher boiling aliphatic materials such as n-pentadecane, and high phenyl-containing materials such as the Dowtherm® J. Dow Corning Corporation technical bulletins, "Information about Syltherm® 800 Heat Transfer Liquid," Form No. 22-761G-86, and "A Guide to Specifying Syltherm® 800 Heat Transfer Liquid," Form No. 24-183A-86, outline the advantages of polydimethylsiloxanes fluids as compared to conventional organic heat transfer fluids. Among these advantages are lower incidence of fluid degradation and fouling, with subsequent prolonged fluid life and heat transfer capabilities; reduced hazard due to fire because of the self-extinguishing characteristics of the polydimethylsiloxane fluids; and minimal toxicological effects as compared to many organic fluids. The self-extinguishing characteristics of polydimethylsiloxane fluids is inherent in the formation of solid silicon dioxide upon combustion of the polydimethylsiloxane material. Nowhere do the above-cited Dow Corning references disclose the unexpected finding of the instant invention that polydimethylsiloxane fluids do not create a vapor explosion on contact with a high-temperature, molten medium.

Halm in U.S. 4,122,109, issued October 24, 1978, discloses a method for preparing a thermally stable methylpolysiloxane fluid and compositions therefrom. Halm in U.S. 4,193,885, issued March 18, 1980, discloses a heat-transfer system comprising a heat source, a heat exchanger, a methylpolysiloxane heat transfer fluid, and a means for conveying the fluid. Nowhere does Halm disclose the unexpected finding of the instant invention that polydimethylsiloxane fluids do not create an explosive situation similar to a steam explosion, when brought into contact with the extremely high temperatures of processes in which molten materials are handled.

In accordance with the instant invention, there is provided an improvement to processes in which molten materials are handled at elevated temperatures under conditions that will be delineated herein. What is described, therefore, is an improvement in a process, said process comprising (a) providing a molten medium, the molten medium being at a temperature greater than about 500°C.; (b) providing means for containing the molten medium; (c) using a heat transfer fluid for cooling the means for containing the molten medium; (d) providing means for removing heat from the heat transfer fluid; and (e) providing means for conveying the heat transfer fluid between the means for containing the molten medium and the means for removing heat from the heat transfer fluid, the improvement comprising using a polyorganosiloxane fluid as the heat transfer fluid.

The molten medium may be a molten salt; a molten metalloid; a molten metal; a mixture of a molten metalloid and a molten metal; a mixture of molten metals; a molten metalloid oxide; a molten metal oxide; a mixture of a molten metalloid oxide and a molten metal oxide; a mixture of metal oxides; a mixture of a molten metalloid oxide and a corresponding molten metalloid; a mixture of a molten metal oxide and a corresponding molten metal; a mixture of a molten metalloid oxide, a molten metal oxide, and a corresponding molten alloy; and a mixture of molten metal oxides and a corresponding molten alloy. Many of these combinations of molten materials describe conditions that exist within metallurgical furnaces.

A steam explosion or a vapor explosion is characterized by extremely rapid increase in pressure which occurs when liquid water contacts a molten material. While the mechanism of steam explosions is not completely understood, this occurrence is a phenomenon which is more than a pressure build-up due to rapid vaporization of liquid water. A steam explosion usually results in the rupture of the vessel containing the molten material with the associated hazards to life and property. A temperature of a molten medium of greater than about 500°C. is believed by the inventors to be a lower temperature limit at which a steam or vapor explosion becomes a significant safety hazard. As an example, smelting furnaces to produce materials such as silicon and steel operate at temperatures in excess of 1500°C.

The metalloid produced may be silicon and the like. The metals produced may be iron, aluminum, and the like. The alloys produced may be steel, ferrosilicon, and the like.

"Means for containing the molten medium" for the purposes of the instant invention can be structures such as bath bodies for containing molten salts for heat transfer purposes. These structures may also be furnaces used in smelting metalloid oxides, metal oxides, or mixtures thereof to produce metalloids, metals, or alloys thereof.

The furnaces for smelting processes may be of any design known in the art. Smelting furnaces may be of open or closed design. A closed furnace design would pose the greatest hazard in pressure build-up and vessel rupture in event of a steam or vapor explosion. Examples of such furnace design are submerged electric arc furnaces and furnaces in which the electrical energy is supplied by a transferred arc plasma or a non-transferred arc plasma.

The heat transfer fluid used for cooling the means for containing the heat source is a polyorganosiloxane fluid. The polyorganosiloxane fluid should be low enough in viscosity to facilitate ease of circulation through the zones of a furnace requiring cooling. The viscosity can be in the range of 1 to 50 centistokes. The polyorganosiloxane fluid may be a polydiorganosiloxane fluid. The polydiorganosiloxane fluid may be a polydimethylsiloxane fluid. Further, the polydimethylsiloxane fluid may be a trimethylsiloxy-endblocked fluid containing heat-stabilizing additives. An example of a commercially available polydimethylsiloxane fluid containing heat-stablizing additives is Dow Corning Syltherm® 800 Heat Transfer Liquid. Typical properties of Dow Corning Syltherm® 800 Heat Transfer Liquid (as supplied) are:

Viscosity @ 25°C...........9.1 centipoise
Flash point, closed cup....320°F.
Vapor pressure at 400°C....200 psia.

Further details on Syltherm® 800 are contained in the two Dow Corning Corporation technical bulletins cited, supra.

"Means for removing heat from the heat transfer fluid" for the purposes of the instant invention can be any conventional means of transferring heat from a hot liquid. These means can include use of the hot fluid to vaporize water to generate steam and to recover heating value, cooling by conventional heat exchange with cooling water or ambient air, and the like.

"Means for conveying the heat transfer fluid between the means for conveying the molten medium and the means for removing heat from the heat transfer fluid" for the purposes of the instant invention can be any conventional means of moving a liquid. These means can include a recirculating pump with associated piping and tankage; and the like.

A preferred molten medium temperature for using the polyorganosiloxane fluid is a temperature greater than about 500°C. A more preferred molten medium temperature for using the polyorganosiloxane fluid is a temperature greater than about 750°C. The most preferred molten medium temperature for using the polyorganosiloxane fluid is a temperature greater than about 1000°C.

A preferred polyorganosiloxane fluid is a polydimethylsiloxane fluid. A more preferred polyorganosiloxane fluid is a trimethylsiloxy-endblocked polydimethylsiloxane fluid. The most preferred polyorganosiloxane fluid is a trimethylsiloxy-endblocked polydimethylsiloxane fluid containing heat-stabilizing agents. The composition and method for preparing the trimethylsiloxy-endblocked polydimethylsiloxane fluid containing heat-stabilizing agents are disclosed by Halm in U.S. 4,122,109, issued October 24, 1978; and in U.S. 4,193,885, issued May 18, 1980.

The preferred viscosity of the polydimethylsiloxane fluid is in the range of about 5 to 20 centipoise.

So that those skilled in the art can better understand and appreciate the instant invention, the following example is presented. The example is illustrative of the instant invention and is not to be construed as limiting the instant invention delineated herein.

Example 1

A study was made on the impact of contacting a polydimethylsiloxane fluid with a molten metal. The molten metal used was tin. The cooling fluids studied were water, n-pentadecane, Dowtherm® J, and Syltherm® 800.

The general procedure used for these studies were:

1. 1800 milliliters (ml.) of the cooling fluid to be tested were placed into a 2-liter beaker. The beaker and contents were weighed and then placed in a laboratory hood equipped with a plexiglass door.

2. 12 grams (gm.) of tin were weighed and placed into a porcelain crucible and melted in a muffle furnace at a temperature of 650°C.

3. The crucible and molten metal were handled with tongs. Using the Plexiglass® door as a shield, the crucible was positioned no higher than 3 inches above the beaker and the molten tin was poured into the liquid.

4. Observations were made and recorded. The observations included:

   a. Fluid behavior in the vicinity of the molten tin drop
   b. Vapor release of the fluid
   c. Audible evidence of an explosion
   d. Loss of fluid from the beaker.

Three trials were made with each fluid to be evaluated.

Water reacted very vigorously when the molten tin was poured into the beaker. A violent boiling action with vapor release and an audible "pop" were noted as soon as the molten tin contacted the water. The metal also splattered as it contacted the water. In one of the three trials, molten tin was actually thrown from the beaker onto the bottom of the laboratory hood. The solidified tin from the bottom of the beaker was a very spongy mass, moss-like in appearance.

Three trials, each, were made with Syltherm® 800, Dowtherm® J, and n-pentadecane. Similar behavior was noted for all three fluids. Very little boiling action and vapor release were noted when the molten tin contacted the liquid being evaluated. There was a squealing sound noted as molten tin was poured into Dowtherm® J and n-pentadecane. Very little vapor release was noted.

Minor differences were noted in the behavior of the tin as it dropped through the beaker filled with Syltherm® 800, Dowtherm® J, and n-pentadecane. The tin in passing through Syltherm® 800 formed bead-like droplets which flowed together in the bottom of the beaker. Bubbles of vapor were noted coming off the beads of metal as they dropped through the Syltherm® 800. As the molten tin passed through the Dowtherm® J, there was less tendency to form beads, as noted with the Syltherm® 800. As molten tin passed through n-pentadecane, the tin appeared to stay in one drop which splattered upon contacting the bottom of the beaker.

These above results demonstrate the phenomenon of a vapor explosion when a molten material is contacted with water. The results further demonstrate that Syltherm® 800, a trimethylsiloxy-endblocked polydimethylsiloxane fluid does not create a vapor explosion when contacted with a molten material.

Claims

1. A process comprising (a) providing a molten medium, the molten medium being at a temperature greater than about 500°C.; (b) providing means for containing the molten medium; (c) using a heat transfer fluid for cooling the means for containing the molten medium; (d) providing means for removing heat from the heat transfer fluid; and (e) providing means for conveying the heat transfer fluid between the means for containing the molten medium and the means for removing heat from the heat transfer fluid, characterised in that the heat transfer fluid, is a polyorganosiloxane fluid.

2. The process according to claim 1 wherein the molten medium is at a temperature greater than about 750°C.

3. The process according to claim 1 wherein the molten medium is at a temperature greater than about 1000°C.

4. The process according to any of claims 1 to 3, wherein the molten medium is a molten salt, a molten metalloid or a molten metal.

5. The process according to any of claims 1 to 3, wherein the molten medium is an alloy formed from a mixture of a molten metalloid and a molten metal or a mixture of molten metals.

6. The process according to any of claims 1 to 3, wherein the molten medium is a mixture selected from

(i) a mixture of a molten metalloid oxide and a corresponding molten metalloid;

(ii) a mixture of a molten metal oxide and a corresponding molten metal;

(iii) a mixture of molten metalloid oxides, molten metal oxides, and a corresponding molten alloy; and

(iv) a mixture of molten metal oxides and a corresponding molten alloy.

7. The process according to any of claims 1 to 6, wherein the polyorganosiloxane fluid is a polydiorganosiloxane fluid.

8. The process according to claim 7, wherein the polydiorganosiloxane fluid is a polydimethylsiloxane fluid.

9. The process according to claim 8, wherein the polydimethylsiloxane fluid is a trimethylsiloxy-endblocked polydimethylsiloxane fluid.

10. The process according to claim 9, wherein the polydimethylsiloxane fluid is a trimethylsiloxy-endblocked polydimethylsiloxane fluid containing heat-stablizing agents.

11. The process according to any of claims 1 to 10, wherein the viscosity of the polyorganosiloxane fluid is less than about 50 centistokes.

12. The process according to claim 11 wherein the viscosity of the polyorganosiloxane fluid is in the range of about 5 to 20 centistokes.

13. The process according to any of claims 6 to 12, wherein the metalloid, metal or alloy produced is selected from silicon, iron, aluminium, ferrosilicon and steel.