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SLAG COMPOSITION FOR FLUID MOLD CASTING

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The present invention relates to a fluid mold casting process for producing ingot castings having improved surface quality and, more particularly, to a fluid mold casting process for producing nickel and nickel-base alloy ingots having improved surface and improved metallurgical quality and to a special casting slag composition for use in such a process.

Those skilled in the art know that ingot practice is a very important step in the production of wrought metal and alloy shapes. Ingots are usually produced by static casting in a permanent mold which may be of cast iron or other suitable metal. The ingot mold generally is placed in an upright position and the metal to be cast into ingots can be poured into the mold either from the top or from the bottom thereof. The ingot phase of operations involved in producing wrought shapes from nickel-containing heat-resistant, oxidation-resistant and/or corrosion-resistant alloys is even more critical than it is in the case of ordinary carbon steel. These alloys include alloys of nickel, iron and cobalt with each other and with chromium, copper, molybdenum, aluminum, titanium, columbium, tantalum, carbon, manganeses, silicon, vanadium, tungsten, etc., and may be such alloys as nickel-chromium alloys, nickel-chromium-iron alloys, nickel-copper alloys, stainless steels, etc. Alloys of this class are characterized by a refractory and very adherent oxide when heated to high temperatures. As a result, any folds, laps, scabs, metal splashes, or other mechanical defects on the surface of an ingot produced from such alloys must be mechanically removed from the ingot surface before the ingot can be subjected to further mill processing because oxides included beneath the ingot surface will remain as inclusions and will be elongated during further mill processing such as forging, rolling and the like and will be present in the final wrought shape with disastrous results upon the quality of the final material. It has been common practice to surface mill the entire ingot produced in such alloys or to use machine chipping and/or grinding to remove imperfections from the ingot which have occurred as a result of the ingot casting operations. These overhauling operations are very expensive in themselves and result in a further economic loss in that the metal removed from the ingot cannot be converted into acceptable mill products.

In an effort to overcome these difficulties, slag-casting processes or fluid-mold casting processes for producing ingots of steel and the like have been developed. Such processes provide steel ingots having improved surface quality and involve pouring a quantity of molten silicate slag into an ingot mold and then teeming molten metal into the thus-formed pool of molten slag. During teeming, the slag covers the rising metal surface in the mold and floats to the top of the ingot mold as a surface layer of some depth. The slag freezes continuously in contact with the ingot mold wall in advance of the rising molten metal surface and forms a thin shell between the ingot and the mold. In this way, the skin of the ingot does not touch the ingot mold and improvements in the surface quality of steel ingots are made possible.

The art has recommended silicate-type slags for use in the slag-casting process, e.g., slags containing about 25% to about 65% of silica, along with other ingredients such as alumina, magnesia, lime, etc., so as to have a basic ratio of about 0.3 to about 2. Sodium silicate (water glass) has also been suggested for this purpose. Although such slag reportedly provide satisfactory results in casting carbon steels, alloy steels and even some grades of stainless steels, it has been found that serious difficulties are encountered in attempting to utilize them in the slag-casting of nickel and nickel-base alloys containing, for example, 40% or more of nickel. Thus, it was found that the silicon content of metal in the circuit underwent an increase such that heats were rejected as falling outside the chemistry definition, although ingots of acceptable surface quality were obtained in some cases.

Attempts to utilize such silicate slags in fluid mold casting of nickel and nickel-base alloys containing about 1% or about 1.5% or more of age hardening elements such as aluminum, titanium, etc., resulted in very serious problems and produced defective ingots having a surface greatly inferior to that which was obtained in casting these metals directly into an ingot mold without using any slag at all. The observed defects included (1) a "notch" toward the toe of the ingot which comprised a peripheral indentation which resulted in overhaul costs and losses of metal before further processing of the ingot could be undertaken and (2) a "shotted" surface condition on the ingot which became more severe from the toe to the head of the ingot and which comprised irregular indentations and/or folds in the ingot surface and which also required very substantial overhauling before any further processing of the ingot could be undertaken if it could be undertaken at all. Furthermore, analysis of the resulting slag-cast metal showed an impermissible increase in silicon content indicative of a slag-metal interaction. Experience thus demonstrated that the recommended silicate slags could not be employed for slag casting age-hardenable nickel and nickel alloys.

Although other attempts were made to overcome the foregoing difficulties and other difficulties, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that a special casting slag composition provides improved results in the fluid mold casting of nickel and nickel alloys containing 1% or 1.5% or more of age hardening elements, enables the production of sound, clean ingots of such alloys and results in an ingot surface of such quality that the ingots can be forged, rolled or otherwise processed in the mill without overhauling.

It is an object of the present invention to provide an improved fluid-mold casting process for producing nickel-containing alloy ingots having improved metallurgical quality.

Another object of the invention is to provide a casting slag composition particularly adapted for the production of fluid-mold cast ingots of nickel-containing alloys.

The invention also contemplates providing a special casting slag composition useful for the production of ingots having improved surface quality in nickel-containing alloys which also contain about 1% or more of age hardening elements.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention contemplates a process for fluid mold casting nickel-containing alloy ingots comprising placing in the bottom of an upright

ingot mold a quantity of a molten casting slag containing about 10% to 60% calcium oxide (CaO), about 10% to 60% alumina (Al_2O_3), about 2% to 20% titanium oxide (TiO_2), up to about 10% magnesium oxide (MgO), up to about 10% sodium oxide (Na_2O), up to about 25% cryolite (Na_3AlF_6), up to about 25% sodium fluoride (NaF), and up to about 25% fluorspar (CaF_2), with the total amount of cryolite, sodium fluoride, and fluorspar being at least about 5% or about 10% but not exceeding about 50% of the slag composition and teeming into said ingot mold a quantity of molten nickel-containing alloy to substantially fill the mold.

The invention also contemplates the said casting slag compositions and these compositions are characterized by substantially maintaining their compositions while they are in contact, in the molten state, with molten nickel-containing alloys containing at least about 7% of nickel and at least about 1% or 1.5% of elements such as aluminum, titanium, magnesium, zirconium, etc., which form oxides having high free energies of formation and which can be employed to contribute age-hardening to the alloy. The casting slag is used in the amount of approximately forty pounds per ton of metal being cast, although greater or lesser amounts can be used.

Advantageously, the casting slag composition contains about 20% to 50% calcium oxide, about 20% to 50% alumina, about 2% to 10% titanium oxide, up to about 10% magnesia, up to about 10% sodium oxide, and about 5% to about 20% of a material from the group consisting of cryolite, sodium fluoride, and fluorspar. Preferably, the slag contains about 40% to 45% CaO, 40% to 45% Al_2O_3, 5% to 10% TiO_2, and 5% to 15% cryolite. A casting slag composition containing about 40% lime (CaO), about 40% alumina (Al_2O_3), about 5% titania (TiO_2), and about 15% cryolite gives very satisfactory results. These compositions are further characterized in that, upon freezing against the mold during the casting process, they provide a more substantial slag shell between the ingot and the mold, which shell has improved resistance to penetration by the molten metal. The thickness of this slag shell advantageously is on the order of approximately one-sixteenth of an inch in thickness. It will be appreciated that the thickness of the slag shell may vary due to irregularities in the ingot mold wall and due to many other factors, including slag temperature, metal temperature, mold temperature, etc., and the thickness can be up to about one-eighth of an inch. The casting slag should have a melting point in the neighborhood of 2300° to 2350° F., i.e., the slag composition should not have any thermal arrests on cooling from a temperature above this range, e.g., about 3000° F., to the range of 2300° to 2350° F.

In preparing the casting slag composition, lime and alumina more advantageously constitute the major proportion, i.e., at least 50% or more, of the ingredients used and these ingredients preferably are used in substantially equal amounts. The total content of lime and alumina (and magnesia if any be present) preferably is about 75% or more of the composition while the balance of the composition, including the titania, cryolite, sodium fluoride, fluorspar, and sodium oxide preferably does not exceed about 25% of the composition. The slag most advantageously is devoid of silica, although as much as 3% or even 5% silica may be present in some instances. Magnesia generally has the effect of unduly raising the melting point and, hence, should not be present in amounts exceeding about 10%. Titania has a markedly beneficial effect on the melting point of the slag and even 2% titania has a very real effect on this slag property. Generally, titania should not exceed 20% and, advantageously, this ingredient should not exceed about 10% of the composition because greater amounts unduly promote reactivity of the slag. Sodium oxide in amounts up to about 10% also helps promote fluidity of the slag but greater amounts are not used principally because of fuming. Cryolite, sodium fluoride, and fluorspar act as fluidizers in the slag and are present in amounts of 5% up to 50% therein. Cryolite and sodium fluoride are more effective than fluorspar and are preferred for this reason. The slag should be devoid of impurities such as arsenic, lead, tin, zinc, sulfur, etc., and should not contain more than about 1% each of metal oxides such as manganese oxide, iron oxide, chromium oxide, nickel oxide, copper oxide, etc. Boron oxides and borates should not be present in the slag.

A number of satisfactory slag compositions are set forth in the following Table I:

Table I

Slag No.	Percent Al_2O_3	Percent CaO	Percent TiO_2	Percent Na_3AlF_6	Percent CaF_2	Percent MgO	Percent Na_2O	Percent NaF
1	40	40	5	15				
2	25	25	10	10	10	10	10	
3	38	45	2	10	5			
4	45	40	2	9			4	
5	25	15	5	25	10	3	5	12
6	50	10	5	25	5		5	
7	10	50	4	20	10			6

In making up the slag composition, calcium oxide may be added in the usual commercial forms such as burned lime and limestone, titanium dioxide may be added as rutile, magnesia may be added as such or as dolomite and sodium oxide may be added as soda ash. The slag may be melted in any furnace capable of attaining temperatures on the order of about 3000° F. A convenient furnace for this purpose is a submerged electrode furnace having a water-cooled steel shell. The molten slag compositions are electrically conductive.

The special casting slag composition set forth herein provides special advantages in the fluid mold casting of nickel-containing alloys which include about 1% or about 1.5% or about 2% up to a total of about 8.5% or 10% of metals such as aluminum, titanium, magnesium, zirconium, and the like, which form oxides having high free energies of formation exceeding the free energy of formation of silica (SiO_2) and which are employed in such alloys for various purposes including deoxidation, age hardening, etc. These alloys may also contain up to about 30% chromium, up to about 75% iron, e.g., up to about 35% or 45% of iron, up to about 70% copper, up to about 10% columbium, up to about 30% cobalt, up to about 10% molybdenum, up to about 6% tungsten, up to about 5% manganese, up to about 4% silicon, up to about 0.3% carbon, up to about 2% vanadium, up to about 7.5% aluminum, up to about 7.5% titanium, up to about 0.2% zirconium, up to about 0.5% magnesium, and the balance essentially nickel, with the nickel content being at least about 7% and up to about 95% of the alloy.

Compositions of nickel-containing alloys which may satisfactorily be fluid-mold cast in accordance with the invention are set forth in the following Table II:

Table II

Alloy No.	Percent Ni	Percent C	Percent Fe	Percent Mn	Percent Si	Percent Other	Percent Cr	Percent Mo	Percent Al	Percent Ti
1	Bal	0.15	0.15	0.25	0.55				4.5	0.5
2	Bal	0.15	1	0.6	0.15	29.5 Cu			2.8	0.5
3	Bal	0.04	6.75	0.7	0.3	0.85 Cb	15		0.8	2.5
4	Bal	0.04	18	0.2	0.2	5.2 Cb	19	3	0.6	0.8
5	Bal	0.04	7.2	2.25	0.12		16			3
6	Bal	0.04	6.5	0.55	0.2		15		0.6	2.4
7	Bal	0.12	0.7	0.1	0.3	28.5 Co	15	3.75	3	2.2
8	Bal	0.04	0.35	0.05	0.2		15.6		3.4	0.7
9	Bal	0.05	34	0.45	0.4		13.5	6.2	0.25	2.5
10	Bal	0.02	48.5	0.4	0.5		5.4		0.65	2.4
11	Bal	0.04	44.5	0.75	0.35		20.5			1

Alloys such as those shown in Table II do not undergo any substantial change in composition when fluid-mold cast in the special casting slag provided in accordance with the invention. This is a very important feature of the invention as it permits employing the process of the invention in the regular mill circuit while maintaining chemical specification limits in the alloys produced. It will be appreciated that Alloys Nos. 1 to 10 in Table II are age-hardening alloys, and that the invention is particularly applicable to the fluid-mold casting of age-hardening alloys containing, for example, about 35% or 40% or more of nickel and containing about 2% or more of age-hardening elements.

In order to give those skilled in the art a better understanding of the invention, the following illustrative example is given:

A 9400-pound melt of an alloy containing about 6.75% iron, about 0.7% manganese, about 15% chromium, about 2.5% titanium, about 0.8% aluminum, about 0.85% columbium, about 0.04% carbon, and the balance essentially nickel was prepared for casting in an induction furnace. A casting slag melt made from a charge of dry ingredients including about 40% CaO, about 40% Al_2O_3, about 5% TiO_2, and about 15% cryolite was prepared in a submerged electrode furnace and was heated to about 3000° F. Two 18" x 18" square ingot molds were set up on copper stools having a cavity in the shape of an inverted pyramid. Each of the ingot molds was provided with an exothermic hot top material placed in a recess at the top of the mold. A quantity of the molten casitng slag was transferred to a ladle and about 100 pounds of the molten slag was poured into the bottom of the first ingot mold. This was sufficient to fill the cavity in the stool and to extend about two inches up the ingot mold wall. Metal from the induction furnace heat was then teemed from a bottom-pour ladle at a temperature of about 2900° F. into the ingot mold at a steady rate through the slag pool to completely fill the ingot mold with metal and to flush the excess casting slag over the top of the mold. The process was then repeated with the second ingot mold. In this way, two 18" x 18" ingots weighing about 4300 pounds apiece were prepared. The ingots were cooled to a red heat in the mold and were then stripped. Upon inspection, it was found that the ingots had an excellent surface which permitted the ingots to be forged without overhaul.

It is to be appreciated that the special casting slags provided in accordance with the invention enable the successful fluid-mold casting of alloys containing metals forming oxides having a higher free energy of formation than silica without encountering the severe difficulties and limitations met heretofore in fluid-mold casting of these alloys in silicate casting slags containing about 25% or more, e.g., up to about 65%, of silica. Thus, in carrying out the process contemplated in accordance with the invention, fluid-mold cast ingots of such alloys are obtained which have an improved cast surface and improved metallurgical quality as compared to the results attained when it is attempted to fluid-mold cast ingots of such alloys in silicate casting slags. It is found that, in carrying out the process of the invention, the ingots produced can be maintained within the close specification chemical limits which must be maintained in connection with these alloys. It is further found that ingots produced in accordance with the present invention are free from the "shotted surface" defect found when silicate slags are used and that the "slag-notch" defect is mitigated or eliminated entirely.

Those skilled in the art will appreciate that other fluorides of the alkali metal and alkaline earth metal group, e.g., lithium fluoride, potassium fluoride, barium fluoride, magnesium fluoride, strontium fluoride, etc., may be employed in the place of cryolite, fluorspar, and sodium fluoride in formulating the casting slag compositions contemplated in accordance with the invention. In addition, other alkaline earth metal oxides, such as barium oxide, strontium oxide, etc., may be employed in the place of calcium oxide, aluminum oxide and/or magnesium oxide in formulating the special casting slag.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A casting slag particularly useful in the molten condition in the fluid-mold ingot casting of molten metal to produce ingots having good surface quality, said moten metal consisting essentially of up to about 30% chromium, up to about 75% iron, up to about 70% copper, up to about 10% columbium, up to about 30% cobalt, up to about 10% molybdenum, up to about 6% tungsten, up to about 5% manganese, up to about 4% silicon, up to about 0.3% carbon, up to about 2% vanadium, up to about 7.5% aluminum, up to about 7.5% titanium, up to about 0.2% zirconium, up to about 0.5% magnesium, the balance essentially nickel with the nickel content being at least about 7% and up to about 95% of the alloy and the said molten metal being reactive with casting slags of the silicate type and producing with silicate type slags fluid-mold ingot castings having poor surface quality, said casting slag consisting essentially of about 40% to about 45% alumina, about 40% to about 45% lime, about 5% to about 10% titania, not more than about 1% manganese oxide, and about 5% to about 15% cryolite.

2. A casting slag particularly useful in the molten condition in the fluid-mold ingot casting of molten metal to produce ingots having good surface quality, said moten metal consisting essentially of up to about 30% chromium, up to about 75% iron, up to about 70% copper, up to about 10% columbium, up to about 30% cobalt, up to about 10% molybdenum, up to about 6% tungsten, up to about 5% manganese, up to about 4% silicon, up to about 0.3% carbon, up to about 2% vanadium, up to about

7.5% aluminum, up to about 7.5% titanium, up to about 0.2% zirconium, up to about 0.5% magnesium, the balance essentially nickel with the nickel content being at least about 7% and up to about 95% of the alloy and the said molten metal being reactive with casting slags of the silicate type and producing with silicate type slags fluid-mold ingot castings having poor surface quality, said casting slag consisting essentially of about 20% to about 50% alumina, about 2% to 10% titania, not more than about 1% manganese oxide, up to about 10% magnesia, up to about 10% sodium oxide, about 5% to about 20% of at least one fluoride from the group consisting of alkali and alkaline earth metal fluorides, and the balance essentially lime, with the lime content being about 20% to about 50% of the composition.

3. A casting slag particularly useful in the molten condition in the fluid-mold ingot casting of molten metal to produce ingots having good surface quality, said molten metal consisting essentially of up to about 30% chromium, up to about 75% iron, up to about 70% copper, up to about 10% columbium, up to about 30% cobalt, up to about 10% molybdenum, up to about 6% tungsten, up to about 5% manganese, up to about 4% silicon, up to about 0.3% carbon, up to about 2% vanadium, up to about 7.5% aluminum, up to about 7.5% titanium, up to about 0.2% zirconium, up to about 0.5% magnesium, the balance essential nickel and with the nickel content being at least about 7% of the alloy and the said molten metal being reactive with casting slags of the silicate type and producing with silicate type slags fluid-mold ingot castings having poor surface quality, said casting slag consisting essentially of a major proportion of ingredients from the group consisting of lime and alumina with these ingredients being present in substantially equal amounts, about 2% to about 10% titania, not more than about 1% manganese oxide, and a minor proportion of at least one fluoride from the group consisting of alkali and alkaline earth metal fluorides.

4. A casting slag particularly useful in the molten condition in the fluid-mold ingot casting of molten metal to produce ingots having good surface quality, said moten metal consisting essentially of up to about 30% chromium, up to about 75% iron, up to about 70% copper, up to about 10% columbium, up to about 30% cobalt, up to about 10% molybdenum, up to about 6% tungsten, up to about 5% manganese, up to about 4% silicon, up to about 0.3% carbon, up to about 2% vanadium, up to about 7.5% aluminum, up to about 7.5% titanium, up to about 0.2% zirconium, up to about 0.5% magnesium, the balance essentially nickel with the nickel content being at least about 7% and up to about 95% of the alloy and the said molten metal being reactive with casting slags of the silicate type and producing with silicate type slags fluid-mold ingot castings having poor surface quality, said casting slags consisting essentially of about 10% to about 60% alumina, about 2% to about 10% titania, not more than about 1% manganese oxide, up to about 10% magnesia, up to about 10% sodium oxide, up to about 25% cryolite, up to about 25% sodium fluoride, up to about 25% fluorspar, with the total amount of cryolite, sodium fluoride and fluorspar being at least about 5% but not exceeding about 50% of the slag composition, up to about 5% silica, and the balance essentially lime, with the lime content being about 10% to about 60% of the composition.

5. A casting slag particularly useful in the molten condition in the fluid-mold ingot casting of molten metal to produce ingots having good surface quality, said moten metal consisting essentially of up to about 30% chromium, up to about 75% iron, up to about 70% copper, up to about 10% columbium, up to about 30% cobalt, up to about 10% molybdenum, up to about 6% tungsten, up to about 5% manganese, up to about 4% silicon, up to about 0.3% carbon, up to about 2% vanadium, up to about 7.5% aluminum, up to about 7.5% titanium, up to about 0.2% zirconium, up to about 0.5% magnesium, the balance essentially nickel with the nickel content being at least about 7% and up to about 95% of the alloy and the said molten metal being reactive with casting slags of the silicate type and producing with silicate type slags fluid-mold ingot castings having poor surface quality, said casting slag consisting essentially of about 10% to about 60% alumina, about 2% to 20% titania, not more than about 1% manganese oxide, up to about 10% magnesia, up to about 10% sodium oxide, about 5% to about 50% of at least one fluoride from the group consisting of alkali and alkaline earth metal fluorides, up to about 5% silica, and the balance essentially lime, with the lime content being about 10% to about 60% of the composition.

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