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54 Preparation of phosphorus-containing metallic glass-forming alloy melts.

57 Phosphorus rich transition metal alloys are protected by a layer of boron oxide during the melting process. The presence of the boron oxide layer prevents the evaporation of phosphorus values. Melting of phosphorus-containing iron/nickel/cobalt based glass-forming alloys under a refining metal oxide/boron trioxide flux reduces undesirable metal oxide impurities, such as titanium dioxide impurities, prevents oxidation of the melt, and reduces loss of phosphorus values from the melt.

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DESCRIPTIONPREPARATION OF PHOSPHORUS-CONTAINING METALLIC
GLASS-FORMING ALLOY MELTSBACKGROUND OF THE INVENTION

Recent advances in the metallurgical arts include development of alloys which, when rapidly quenched from the melt at rates in excess of about 10^4 to 10^6 °C per second, form glassy (amorphous) solids. Such glass-forming alloys commonly are based on transition metals, usually iron, nickel and/or cobalt, in conjunction with one or more metalloids of phosphorus, boron and carbon. Glass-forming alloys are, for example, described in U.S. Pat. 3,856,513 issued December 24, 1974 to Chen et al.

Preparation of phosphide based melts of glass-forming alloys under ambient atmosphere leads to oxide inclusions in the glassy metal product. The conventional method of excluding the ambient atmosphere by vacuum melting leads to possible losses of phosphorus values from the melt due to evaporation. Iron phosphide is a basic ingredient in many glass-forming metallic alloy compositions, and in the high purity form required for such purpose, it is quite costly. Inexpensive forms of iron phosphide available are impure and contain phosphorus in form which can evaporate upon heating, and which tends to form volatile phosphorus pentoxide, and which poses a safety hazard and results in changes of the alloy composition. Glassy solid structures are obtained from such alloys by processes such as the melt spin process wherein a fine jet of the molten alloy is impinged upon a rapidly moving chill surface for solidification. Orifice diameters in this process are exceedingly small, and orifice

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pluggage on account of solid impurities contained in the melt can represent serious problems. Iron, cobalt or nickel based phosphorus-containing glass-forming alloys which additionally contain boron as a metalloid are particularly prone to contamination with solid particles. In such alloy, these particles were found to be predominantly small particles of TiO_2 and/or $TiBO_3$, both of which have high melt points, and both of which are relatively insoluble in the melt. It was found that titanium is an impurity commonly contained in ferrophosphorus, which is used as a source of phosphorus in making these alloys, although titanium may also be present as contaminant in other raw materials employed in making these alloys.

The present invention provides refining flux for reducing oxidation of and loss of phosphorus values from phosphorus-containing alloys, especially phosphorus-containing iron, nickel and/or cobalt-based alloys.

SUMMARY OF THE INVENTION

Phosphorus-containing metallic glass-forming alloy melts are covered with a layer of molten boron trioxide flux. Such layer protects the melt from oxidation, dissolves oxide particulates and impurities from the molten metal alloy and prevents the evaporation of phosphorus values. The flux floating on the alloy melt will not interfere with subsequent casting or spinning operations, and the alloy melt can be replenished directly through the flux layer. Alloys prepared according to the process of the present invention leave minimum residues in the jetting crucible in subsequent melt spin operations.

Phosphorus-containing iron, nickel and/or cobalt-based alloys are desirably melted under a boron trioxide flux additionally comprising oxides of iron, nickel and/or cobalt. The flux layer protects the molten alloy from oxidation, reduces or eliminates contamination of the melt with particulate matter, especially metal oxides, and prevents loss of phosphorus values by vaporization.

DETAILED DESCRIPTION OF THE INVENTION

5 Metallic glass-forming alloys which benefit from protection by boron trioxide flux contain phosphorus as a metalloid component, alone or together with other metalloids, such as boron, carbon and silicon. The phosphorus component of such alloys is usually contributed by ingredients having the formulas FeP_x , NiP_x , CoP_x , MnP_x , wherein x is between about 0.3 and 1.1 and preferably between about 0.5 and 1. Preferred alloy compositions include alloys utilizing as source of phosphorus FeP_x wherein x is between about 0.5 and 1. Preferred alloy compositions include transition metal alloys containing between about 3 and 25 weight percent phosphorus. These alloys have a phosphorus partial pressure of less than 20 micron, and melting points of between about 900°C and 1200°C.

15 Phosphorus-containing alloys based on one or more of iron, nickel and/or cobalt which benefit from melting under the refining boron trioxide flux which additionally contains oxides of iron, nickel and/or cobalt have the general formula $M_a P_b Y_c$ wherein M is a metal selected from one or more of the group consisting of iron, cobalt and nickel; P represents phosphorus; Y represents a metalloid selected from one or both of the group consisting of boron and carbon; and a, b and c are in atomic percent, wherein a is about 70 to 90, b is 0-20, but desirably at least 1, the sum of b + c is about 10 to 30, the sum of a + b + c being 100. In the above formula, up to about 80 percent of M may be replaced by one or more of any transition metal other than iron, cobalt and nickel. Suitable replacements include silicon, chromium, vanadium, aluminum, tin, antimony, germanium, indium, beryllium, molybdenum, titanium, manganese, tungsten, zirconium, hafnium and copper, for example. The phosphorus content of the alloy will ordinarily be derived from ferrophosphorus, which may be of any suitable phosphorus content, such as commercially available grades containing about 18 and 25 percent by weight phosphorus.

35 The boron trioxide flux comprises compositions

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of the formula B_2O_3 of about 95 weight percent purity, preferably better than about 98 weight percent purity, the balance being represented by incidental impurities or intentional additives which are substantially inert, that is to say, that they do not materially interfere with the intended function of the boron trioxide flux.

Suitable boron trioxide fluxes have a melting point between about 400°C and 600°C, preferably between about 400° and 500°C, and have a vapor pressure of below about 20 micron.

In the fluxes of the present invention which additionally contain an oxide of iron, cobalt and/or nickel, the oxide is suitably chosen to correspond to the major metal component of the alloy. For example, if iron is the only or major metal component of the alloy, the oxide component in the flux desirably, but not necessarily, is an oxide of iron. Nickel-containing melts desirably are refined under a flux-containing nickel oxide. The flux desirably contains from about 20 to 80 percent by weight boron trioxide.

In the melting operation the metal oxide (e.g. iron, cobalt or nickel oxide) coacts with the boron trioxide to obtain the desired result. It is believed that oxygen from the metal oxide combines with titanium metal contained in the melt as an impurity, perhaps forming TiO_2 , which is then bound in the molten flux. The boron trioxide seems to act as a coagulant for the titanium dioxide as well as for other particulate matter which may be contained in the melt. Moreover, the boron trioxide, because of its acidic character, seemingly tends to prevent oxidation of phosphorus, if present, to the five valent oxide state, as might occur due to presence of small amounts of oxygen in the melt. In the five valent state, phosphorus is volatile under refining conditions encountered in making the alloys here under consideration.

Of the oxides of iron, namely FeO , Fe_2O_3 and Fe_3O_4 , all are suitable, FeO being preferred. Likewise,

any of the oxides of cobalt, CoO , Co_2O_3 , as well as Co_3O_4 , may be employed. However, for reasons of high cost, use of oxides of cobalt is not ordinarily preferred. Nickel oxide, for reasons of availability as well as effectiveness, is the preferred metal oxide. Metal oxides of commercial degree of purity are suitable for use.

The boron trioxide (B_2O_3) similarly may be of any degree commercial purity.

In the metal oxide containing fluxes, the boron trioxide is desirably employed in amount of 20 to 80 percent by weight, preferably 30 to 70 percent by weight, most preferably 40 to 60 percent by weight of the flux, the balance being represented by the metal oxide. Of course, if desired, other components which do not materially interfere with the protective and refining functions of the flux may be included in the flux composition for any desired purpose, e.g. melting point reduction, although addition of other components is not ordinarily preferred.

The flux compositions are employed in amount sufficient to provide a flux layer of between about 1 and 50 millimeter thickness, preferably between about 2 and 10 millimeter thickness on top of the molten metal alloy. It is an advantage of these flux compositions that their solubility in the alloys is generally low, so that gross contamination of the alloy with the flux is avoided. Furthermore, minor contamination of the alloy with boron values from the flux is generally not deleterious, that is to say that such contamination would not adversely affect the glass-forming capabilities of the alloy, nor its properties in the solid state.

The temperature of the alloy melt can be between about 1000°C and 1500°C , and preferably between about 1100°C and 1400°C . The temperature of the boron trioxide flux can be between about 900°C and 1400°C .

To prevent oxidation and loss of phosphorus value from the alloy, the boron trioxide flux should be present at temperatures leading normally to oxidation

and/or evaporation of phosphorus values, and in particular the boron trioxide should be present when the alloy is in the molten state. The boron trioxide, to obtain the full benefit of its function, is desirably added to the cold charge. If it is added after the alloy is melted, considerable amounts of phosphorus can be lost.

To fulfill its refining function, the flux should remain in contact with the surface of the melt at melting temperature for a time period for at least about one minute, desirably of at least about 5 minutes. Contact times of, say, between about 5 minutes and 5 hours, desirably of between about 30 minutes and about 3 hours are eminently suitable. If desired, the melt may be agitated. Suitable melting furnaces include those lined with high temperature ceramic materials. Preferred furnace linings are made from magnesia, zirconia and alumina. If desired, suitable inert atmospheres may be provided above the flux, including such as those provided by helium or argon. Alternatively, the melting operation may be conducted under vacuum. However, provision of inert atmospheres is not essential. If an inert atmosphere is supplied, argon is preferred.

EXAMPLES 1-5

Iron, nickel, phosphorus, and boron containing glass-forming alloy compositions were prepared by melting together under vacuum raw materials of the following purity: iron, 99.9 weight percent pure; nickel, 99.9 weight percent pure; nickel boride, 99 weight percent pure having boron content of between about 17 and 19 weight percent; ferrophosphorus (Type I) containing 61.43 weight percent iron and 20.39 weight percent boron; ferrophosphorus (Type II) containing 79 weight percent iron and 21 weight percent phosphorus. To each charge there was added an amount of $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ (atomic percent) metal alloy to provide an initial susceptor for induction heating of the charge. No $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ was added in case of sample 5 since the ferrophosphorus employed coupled sufficiently with the radiation. The charge was contained

in a magnesia crucible covered with boron trioxide and heated by means of induction heating coils. The melt of Examples 1, 2, 4, 5 was maintained under vacuum under a layer of B_2O_3 flux at a temperature of $1200^\circ C$ for one hour, before casting it into ingots. The melt of Example 3 was soaked at $1300^\circ C$ for 1 hour. The amounts of materials charged are summarized in Table 1 below:

Table 1
Charge (grams)

Example	Ferro-phosphorus	$Fe_{40}Ni_{40}P_{14}B_6$ alloy	Fe	Ni	NiB	B_2O_3
1	915 (I)	400	263	895	193	136
2	1200 (I)					1030
3	823 (I)	707	358	895	199	154
4	4937 (I)	2265	2151	5370	1160	300
5	3818 (II)		898	3654	773	

The cast ingots were subjected to analysis for insolubles, oxygen, silicon, calcium, iron, nickel, phosphorus, and boron. The ingot obtained in Example 3 was further subjected to a second melt cycle at $1200^\circ C$ for 1 hour in vacuum under a flux of B_2O_3 . The remelted alloy was again cast into an ingot and subjected to analysis. The results of the analysis are shown in Table II below.

Iron, nickel, boron and phosphorus were determined by wet chemistry; oxygen was determined by placing pieces of raw alloy in a graphite boat in a Leco oxygen analyzer. This method determines only dissolved oxygen, but not chemically bonded oxygen. The procedure for determining insolubles involved dissolving a 2 gram sample of the solid ingot in 100 milliliter of a reagent solution composed of 50 milliliter nitric acid (70% HNO_3); 10 milliliter of sulfuric acid (100% H_2SO_4) and 40 milliliter of water. The alloy was refluxed in the reagent solution until dissolved. The resultant solution was filtered through an analytical filter to determine insoluble content as ash residue. Silicon and calcium were determined by taking an aliquot part of the solution, evaporating the solution, mixing the residue with spec-

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refining and holding time at the 1,180° to 1,200°C is about 45 to 60 minutes. The refined alloy is then cast at about 1,000°C.

Using identical raw materials, alloy of the
5 above composition prepared using the NiO/B₂O₃ flux as above described had a titanium content of only 0.04 percent by weight, whereas an alloy obtained under otherwise identical conditions from the same raw materials, but without use of the flux, had a titanium content about
10 0.16 percent by weight. Furthermore, alloy prepared under conditions of the present invention had significantly lower contamination with other oxidizable elements which tend to form insoluble solid oxides. As a consequence, metal refined in accordance with the present invention,
15 as above described, caused substantially less restriction of a casting nozzle in a subsequent spin casting operation.

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We claim:

1. A process of melting phosphorus-containing glass-forming transition metal alloys characterised in that the exposed surface of said metal alloy is covered with a layer of a molten flux composition comprising boron trioxide.
2. The process of claim 1 wherein said alloy has a phosphorus content of between about 3 weight percent and about 25 weight percent.
3. The process of claim 1 wherein said flux in contact with the melt is at a temperature within the range of about 900°C to 1400°C.
4. The process of claim 1 wherein the flux composition is employed in amount sufficient to provide a flux layer of between about 2 and 50mm thickness.
5. The process of claim 1 where in the alloy has the formula $M_a P_b Y_c$ wherein.
M is a metal selected from the group consisting of iron, cobalt, nickel, and mixtures thereof in any proportion;
P represents phosphorus;
Y is a metalloid selected from the group consisting of boron, carbon, and mixtures thereof in any proportion; a, b and c are in atomic percent; and
a is about 70 to 90,
b is 0 to 20
the sum of b + c is about 10 to 30,
the sum of a + b + c being 100,
and wherein the flux comprises oxides of iron, nickel, and/or copper together with boron trioxide.
6. The process of claim 5 wherein the flux comprises between about 20 and 80 percent by weight of B_2O_3 , and between about 80 and 20 percent by weight of one or more oxides of iron, cobalt and nickel.
7. The process of claim 5 wherein the alloy is an alloy of iron and nickel.
8. The process of claim 7 wherein the alloy contains both phosphorus and boron, in combination.

9. The process of claim 8 wherein the flux comprises between about 20 and 80 weight percent of B_2O_3 , and correspondingly between about 80 and 20 weight percent of NiO.

5 10. The process of claim 5 wherein the alloy comprises about 46 ± 1 percent by weight of Fe; about 45 ± 1 percent by weight of Ni; about 8 ± 0.5 percent by weight of P; about 1 ± 0.5 percent by weight of B, where-
10 in the phosphorus is derived from ferrophosphorus, where-
in the flux comprises about equal amounts of NiO and B_2O_3 , and the molten alloy is held in contact with the flux for a period of between about 5 minutes and 5 hours.

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D, A	DE - C - 245 197 (AEG) * page 1, line 28 * --	1	C 22 C 1/06 C 22 C 33/04 C 22 B 9/10 C 21 C 7/076
	DE - C - 639 131 (SOCIETE D'ELECTRO- CHIMIE, D'ELECTROMETALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE) * page 2, line 34 * --	1	C 21 C 7/076
	DE - C - 649 284 (SOCIETE D'ELECTRO- CHIMIE, D'ELECTROMETALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE) * page 1, line 55 * --	1	TECHNICAL FIELDS SEARCHED (Int. Cl.) C 21 C 7/076 C 22 B 9/10 C 22 C 1/06 C 22 C 33/04
	DE - C - 678 763 (HERAEUS-VACUUMSCHMEL- ZE) * page 1, line 30 * --	1	C 21 C 7/076 C 22 B 9/10 C 22 C 1/06 C 22 C 33/04
	DE - B - 2 246 723 (VEREINIGTE DEUT- SCHE METALLWERKE) * column 1 * --	1	CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
	DE - B - G 10845 VI/18b (BOCHUMER VEREIN) * pages 1 and 2 * --	1	&: member of the same patent family, corresponding document
	US - A - 3 856 513 (ALLIED CHEMICAL) ----		
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
Berlin	29-10-1979	SUTOR	