system. The vacuum system will remove the air within the vessel until the system achieves a pressure preferably lower than 1 mbar.

After achieving the reduced pressure condition, preferably lower than 1 mbar to assure removal of the nitrogen-containing atmosphere, the pressure within the system can be raised using a non-nitrogenous gas such as an inert gas, e.g., argon, or oxygen and the like, to a pressure up to about 200 mbar to facilitate removal of by-products formed during the thermite reaction. Once the thermite mixture is ignited, the pressure rises with the evolution of gases formed during the reaction, and, as the reaction products solidify and cool, the volume of the gases formed as a result of the reaction contracts and the pressure decreases but is always below 1 mbar. In this manner, the reduction process is completed under reduced pressure over a period of time commensurate with the load weight, typically a few minutes. The process results in the formation of metallic chromium or a chromium-containing master alloy containing below 10 ppm nitrogen. This is most important since there is ample evidence of the remarkable difficulty to remove nitrogen once it is present in chromium metal or chromium-containing alloys, even by resorting to techniques such as the much more expensive electron beam melting process.

The resulting melt obtained by the two-step process described above is permitted to solidify and cool down to a temperature low enough to permit safe handling under the same reduced pressure atmosphere so as to avoid nitrogen absorption in these final stages. It is considered critical in achieving the low nitrogen content metals and alloys of embodiments of present invention that the entire process from pre-ignition, ignition, solidification and cooling be conducted under reduced pressure as described herein.

Preferably, the metals or master alloys produced will contain less than about 5 ppm nitrogen by weight. Most preferably, the metals or master alloys produced will contain less than about 2 ppm nitrogen by weight, and most preferably, 0 ppm nitrogen.

Once the master alloy charge is effected, temperature and pressure are adjusted to the desired tapping value, any minor, easily vaporizable elements, e.g., magnesium, and the like, then can be added, if necessary or desired, and the resulting molten liquid alloy in the crucible can then be tapped into a tundish or launder and conveyed to a metallic mold or can be tapped directly into the metallic mold depending on the furnace configuration.

Alternatively, the molten liquid can be tapped at the end of the carbon boil and allowed to solidify and cool down in a metallic mold, after which it will be loaded again in the same type of furnace, melted and re-heated to about the same temperature it was when previously tapped. Once re-heated to the molten liquid stage, the process can be conducted in the manner described above, charging the remaining raw materials, i.e., the low nitrogen chromium and/or chromium-niobium master alloy, to the molten liquid, adjusting the temperature and pressure to the desired tapping values, adding any minor elements generally the easily vaporizable elements as may be desired, and tapping into a metallic mold, either directly or via a tundish or launder. In either case, once in the mold, the metallic liquid is allowed to solidify and cool down to a temperature low enough for safe handling, under reduced pressure, i.e., under 1 mbar.

Examples

The following examples were conducted to establish the effectiveness of embodiments of the present invention in obtaining low nitrogen, essentially, nitride-free chromium and chromium plus niobium-containing nickel-based alloys.

Example 1

An original charge consisting of low nitrogen solubility elements: 38.70 kg nickel, 13.5 kg iron, and 2.30 kg molybdenum was loaded into an aluminum oxide/magnesium oxide crucible situated within a vacuum induction melting furnace. The pressure within the system was evacuated to below 0.1 mbar and the power was turned on. After the charge was

above, to form a thermite mixture. The thermite mixture was ignited, solidified and cooled under reduced pressure to obtain a chromium niobium alloy having less than 10 ppm nitrogen.

40.3kg of the original charge together with 0.40 kg nickel and 0.30 kg iron were loaded into an aluminum oxide/magnesium oxide crucible in a vacuum induction melting furnace. The system was evacuated to a pressure below 0.1 mbar and the power turned on. After complete melt down, 9.7 kg of the low nitrogen chromium and 4.5 kg of the low-nitrogen chromium niobium alloy produced as described above were added to the melt. After complete melting of the added low nitrogen materials, the temperature was raised to 1460°C and 0.57 kg titanium and 0.10 kg aluminum were added to the melt. Then, 0.40 kg of nickel magnesium (15% mg) was added to the melt and, after complete melting of all added materials, the temperature of the melt was adjusted to the tapping target of 1460°C and the molten mass was tapped to an ingot mold, allowed to solidify and cool until it was safe to handle. Thereafter, the ingot was re-melted in a vacuum arc re-melting furnace, allowed to homogenize in a re-heating furnace and then forged into a 3 x 3 inch bar. As in Example 1, samples were taken from the bar, polished and analyzed with the same scanning electron microscope equipped with an energy dispersive spectrometer as employed in Example 1. The sample was found to contain 0.8 ppm nitrogen (average of two samples). Since the solubility limit of titanium nitride in alloy 718 is 5ppm, it is concluded that the superalloy produced in this Example is essentially nitride free.

Numerous variations of the parameters of embodiments of the present invention will be apparent to those skilled in the art and can be employed while still obtaining the benefits thereof. It is thus emphasized that the present invention is not limited to the particular embodiments described therein.

CLAIMS

1. Process for producing low nitrogen, essentially nitride-free chromium - containing nickel-based alloys comprising:

a) charging elements or compounds of elements which do not dissolve appreciable amounts of nitrogen in the molten state to a refractory crucible within a vacuum induction furnace and melting said elements or compounds therein under reduced pressure lower than 0.1 mbar;

b) effecting heterogeneous carbon-based bubble nucleation of the resulting melt in a controlled manner, thereby effecting substantial removal of nitrogen and oxygen from the melt;

c) upon cessation of bubble formation, adding low nitrogen chromium - with a nitrogen content of below 5 ppm to the melt, said chromium having been prepared by:

i) vacuum-degassing a thermite mixture comprising chromium compounds and metallic reducing agents, contained within a vacuum vessel capable of withstanding a thermite reaction, to an initial pressure less than 1 mbar; and back filling the vessel with an inert gas to a pressure of about 100-200 mbar;

ii) igniting the thermite mixture to effect reduction of the chromium compounds within said vessel under reduced pressure;

iii) solidifying the reaction products under reduced pressure; and

iv) cooling the reaction products to about ambient temperature under reduced pressure,

wherein steps ii) through iii) are conducted under a pressure between about 100 to 200 mbar;

d) melting and distributing said added chromium throughout the melt under reduced pressure;

e) bringing the resulting combined melt to a temperature and surrounding pressure to permit tapping; and

f) tapping the resulting melt, directly or indirectly, to a metallic mold and allowing the melt to solidify and cool under reduced pressure, wherein the resulting alloy has a nitrogen content less than 5 ppm by weight.

2. Process according to claim 1, wherein the reducing agent employed in the process to which the chromium compounds were previously subjected is aluminum.

3. Process according to claim 1, wherein the thermite mixture employed in the process to which the chromium compounds were previously subjected additionally comprises at least one energy booster.

4. Low nitrogen, essentially nitride-free chromium and chromium plus niobium-containing nickel-based alloys according to claim 1 containing 5 ppm or less nitrogen.

5. Low nitrogen, essentially nitride-free chromium and chromium plus niobium-containing nickel-based alloys according to claim 1 containing essentially no detectable nitrogen.

6. Alloy 718 produced by the process of claim 1 containing below 5 ppm nitrogen.

7. Alloy 718 produced by the process of claim 1 containing essentially no detectable nitrogen.

8. A chromium-niobium containing alloy additionally containing one or more elements selected from the group consisting of nickel, iron, cobalt, boron, carbon, silicon, aluminum, titanium, zirconium, hafnium, vanadium, tantalum, molybdenum, tungsten, rhenium, copper, and mixtures thereof having a nitrogen content less than 5 ppm, prepared by the process of claim 1.

9. Process according to claim 1 where the heterogeneous carbon-based bubble nucleation of the resulting melts is effected by the controlled injection of graphite.

10. Process as defined in claim 1 wherein the resulting alloy is re-melted in a vacuum arc re-melting furnace, allowed to homogenize, and then forged into a desired shape.

11. Process for producing low nitrogen, essentially nitride-free chromium plus niobium-containing nickel-based alloys comprising:

a) charging elements or compounds of elements which do not dissolve appreciable amounts of nitrogen in the molten state to a refractory crucible within a vacuum induction furnace and melting said elements or compounds therein under reduced pressure lower than 0.1 mbar;

b) effecting heterogeneous carbon-based bubble nucleation of the resulting melt in a controlled manner, thereby effecting substantial removal of nitrogen and oxygen from the melt;

c) upon cessation of bubble formation, adding a low nitrogen chromium- niobium-containing master alloy with a nitrogen content below 5 ppm to the melt, said master alloy having been prepared by:

i) vacuum-degassing a thermite mixture comprising chromium and niobium compounds and metallic reducing agents, contained within a vacuum vessel capable of withstanding a thermite reaction, to an initial pressure less than 1 mbar; and back filling the vessel with an inert gas to a pressure between about 100 to 200 mbar;

ii) igniting the thermite mixture to effect reduction of said compounds within said vessel under reduced pressure;

iii) solidifying the reaction products under reduced pressure; and

iv) cooling the reaction products to about ambient temperature under reduced pressure, wherein steps ii) through iii) are conducted under a pressure between about 100 to 200 mbar;

d) melting and distributing said added chromium-niobium-containing master alloy throughout the melt under reduced pressure;

e) bringing the resulting combined melt to a temperature and surrounding pressure to permit tapping; and

f) tapping the resulting melt, directly or indirectly, to a metallic mold and allowing the melt to solidify and cool under reduced pressure, wherein the resulting alloy has a nitrogen content less than 5 ppm by weight.

12. Process according to claim 11, wherein the reducing agent employed in the process to which the chromium-niobium-containing alloys were previously added is aluminum.

13. Process according to claim 11, where the thermite mixture employed in the process to which the chromium-niobium-containing alloys were previously subjected additionally comprises at least one energy booster.

14. Process according to claim 11, wherein the heterogeneous carbon-based bubble nucleation of the resulting melt is effected by the controlled insertion of graphite.

15. Process as defined in claim 11 wherein the resulting alloy is re-melted in a vacuum arc re-melting furnace, allowed to homogenize, and then forged into a desired shape.

16. Process as defined in claim 11, wherein the carbon-based bubble nucleation is effected by controlled insertion of carbon in the form of a member selected from the group consisting of particulate carbon, carbon in the form of a bar, tube or cylinder, and combinations thereof.

17. Process as defined in claim 11, wherein the carbon-based bubble nucleation is effected by controlled insertion of carbon in the form of a member selected from the group consisting of particulate carbon, carbon in the form of a bar, tube or cylinder, and combinations thereof.