

[54] GRAIN REFINING OF METALS AND ALLOYS

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[57] ABSTRACT

An innoculating additive comprised of a nickel carrier and tungsten oxide particles is useful in grain refining alloys such as nickel-base superalloys.

11 Claims, No Drawings

GRAIN REFINING OF METALS AND ALLOYS

The subject invention is addressed to the grain refinement of metals and alloys, particularly nickel-base superalloys, during the process of solidification from the molten state.

As the metallurgist is aware, reduction in the grain size of a metal or alloy can be effected if solid particles which act as nuclei are added to a molten bath of the metal to be cast. To that end, in our United Kingdom patent specification 1,239,066 we advanced the concept of incorporating in a molten metal matrix a grain refining nucleating additive consisting of particles of metal oxide dispersed in a carrier metal, the additive having been formed by internal oxidation of an alloy. Upon being introduced into the melt the metal carrier dissolves, the oxide particles being left as a fine dispersion in the melt matrix. We specifically proposed the use of inoculants consisting of internally oxidized copper-nickel, copper-cobalt, copper-nickel-cobalt, copper-iron and copper-iron-nickel alloys, the nickel, cobalt and iron oxidizing preferentially to the copper and acting as the grain refining nuclei.

We further deemed it most preferable that nucleating oxide particles be less than 1 micron (μm) in size, though particles up to two microns might be used. This followed from the fact that in general the smaller the oxide particle size the greater is the degree of grain refining in the melt. This, however, desirable though it be, gives rise to attendant difficulties for it is both difficult and expensive to prepare additives containing, for example, nickel oxide particles smaller than 1 μm . Too, the presence of copper in some alloys is undesirable, if not actually detrimental. Furthermore, subsequent investigation reflected that the grain refining effect of the copper-containing additives was not as pronounced in respect of thicker section castings.

In any case, it has now been found unexpectedly that if instead of nickel, cobalt or iron the preferentially oxidized metal is tungsten and that nickel as opposed to copper is the carrier metal, then the degree of grain refinement obtained by this special combination is not dependent to the same extent on oxide particle size. This obviates the need for oxide particles of very small size. And, of course, recourse to a copper carrier is eliminated. It might be mentioned that copper is seldom, if ever, an intentionally added constituent in nickel-base superalloys.

Furthermore, it was also found that when using tungsten oxide particles in very slowly cooled ingots, substantially better grain refinement was experienced than by the use of any other tested oxide particles. This lends markedly to producing thick section castings. Indeed, an integrally precision cast nickel-base superalloy turbine wheel, i.e., blade and hub, has been prepared using tungsten oxide as the inoculant on a nickel strip carrier and the grain size in the hub was actually as fine as that in the blade. Insofar as we are aware, this has never been accomplished heretofore, at least by the incorporation of a nucleating agent.

Accordingly, the present invention provides a process for grain refining a metal or alloy during solidification from the molten state by introducing to a melt of the metal or alloy at least a small but effective amount of a grain refining additive comprised of a nickel carrier and tungsten oxide particles preferably formed by internal oxidation, so that the nickel dissolves and solid tungsten oxide nuclei are introduced into the melt, the

oxide particles not being restricted to sizes of less than 1 μm as a practical matter. A particle size of up to at least 2 μm can be used quite satisfactorily.

To form the additive by internal oxidation a nickel-tungsten alloy must be used. While a wide range of nickel-tungsten alloys can be utilized, the size of the oxide particles formed is dependent on the alloy composition. Thus, as the tungsten content of the alloys increases, the rate of internal oxidation decreases and the size of the oxide particles formed tends to become larger. In this connection, it might be said that the larger a given size does mean a smaller ratio of oxide particles to nickel carrier strip and this could add to cost. For such reasons the tungsten content of the alloy should not exceed 17% and more advantageously should not exceed 6%. On the other hand, should the tungsten content be too low, the number of particles formed by oxidizing a given weight of the alloy decreases, so that an excessive amount of the carrier needs to be introduced. It is therefore preferred that the alloy contains at least 1% of tungsten and more preferably at least 3%.

The nickel-tungsten alloy should preferably be single-phased since in a two-phased alloy the second phase may enter the melt as undissolved particles which, while not necessarily harmful, could nonetheless interfere with the nucleation of grains. The efficiency of nucleation is found to fall off as the temperature of the melt rises, and in treating nickel-based alloys particularly the temperature of the melt preferably should not exceed about 1500°C. and more beneficially should not exceed about 1470°C.

The internal oxidation of the alloy to obtain the oxide nuclei is most conveniently effected by heating the alloy in air, although other atmospheres such as carbon dioxide can be used. It is preferable, in order to obtain as many oxide nuclei as possible, to carry out the oxidation process for a period sufficient such that the alloy is internally oxidized virtually right through the center. However, to avoid excessive scaling losses, the heating should be stopped once the desired oxidation has been achieved. We have found that scaling losses are reduced if the oxidation process in air is continued to the point that an external article coating is formed and the remainder of the oxidation process is conducted in a substantial vacuum. This particularly applies to nickel-tungsten alloys containing less than about 10% tungsten. The alloy may become oxidized externally as well as internally. It is of advantage that surplus oxide be removed as by brushing or pickling, before the additive is introduced into the melt. The additive may also advantageously be degreased before use.

To ensure that the nuclei become uniformly dispersed throughout the melt, it is important to prevent local chilling of the melt when the additive is introduced. For this reason, it is advantageous to use additives which have a small cross section, and it is particularly advantageous to use strip or foil from 0.05 to 0.4 mm. in thickness. Another reason for using such foil is that the depth of penetration of the internal oxidation is a function of time and temperature, so that an alloy of greater thickness requires a longer time at the oxidizing temperature if it is to be fully internally oxidized. With a fully internally oxidized alloy, as little as 0.1% additive by weight of the melt would introduce sufficient nuclei to be effective in refining the grains, but in general from about 0.2 or 0.3 to 0.5 or 0.8% of additive by weight of the melt is a suitable addition.

Additives containing tungsten oxide particles are particularly useful in the grain refining of a wide range of melts of alloys containing nickel, such as alloys having as their base nickel and copper or nickel and chromium or nickel, chromium and cobalt, in each case with or without iron up to 50%. Such alloys include those which have a base composed of from 20 to 80% nickel, 5 to 35% chromium, 0 to 40% cobalt and 0 to 50% iron, and which may also contain one or more of the elements such as aluminum or titanium up to 10% each, and molybdenum, niobium, tantalum, tungsten, vanadium, zirconium, boron and hafnium in the amounts commonly present in high temperature alloys, e.g., up to 15% molybdenum, up to 8% of niobium and/or tantalum, up to 25% tungsten, up to 3% vanadium, up to 2% zirconium, up to 0.5 or 1% boron (preferably less than 0.1% boron), and up to 5% hafnium.

The additive may also be useful for treating melts which are refined and cast at lower temperatures, for example, melts of copper-aluminum alloys, stainless steel and other alloy steels, and brasses, e.g., 70% copper-30% zinc brass.

The following data is given as generally illustrative of the invention.

Three nickel-tungsten alloys containing 2%, 4%, and 15% tungsten, respectively, in the form of strip 0.12 mm. thick were degreased and internally oxidized by heating in air. The Ni-2%W and Ni-4%W alloys were heated at 1140°C. and the Ni-15%W alloy at 1200°C. In each case the heating was continued for four hours, but with the 2% and the 4% tungsten alloys the air was removed after 20 minutes and the heating completed in vacuum and this minimized scaling losses. The vacuum technique was unsuitable for the Ni-15%W alloy since the internal oxidation proceeded extremely slowly. The predominant composition of the additives thus prepared was Ni-3% tungsten oxide for the additive made from the alloy containing 2% tungsten, Ni-5% tungsten oxide for the additive made from the alloy containing 4% tungsten and Ni-19% tungsten oxide for the additive made from the alloy containing 15% tungsten. The average size of the oxide particles was 0.2 μ m, 0.4 μ m and 1.5 μ m, respectively.

The oxidized strip was quenched into water, and surface oxide film removed by rubbing with emery paper, or by scratch brushing, preferably after cold-rolling slightly to fracture the scale, or by pickling, for example, in hydrochloric acid.

Melts of a nickel-base superalloy (No. 1) containing, by weight, 0.09% carbon, 0.46% silicon, 0.54% iron,

An additive in the form of the strip prepared as described above and attached to a silica stirrer was introduced into melts of this alloy. The melts were poured into sythetic mullite molds (2.8 inches in diameter, 7.5 inches high, 1 inch wall thickness) preheated to 800° to 1000°C. and a hot-topping compound was then added, the melts being allowed to solidify.

The extent of grain refinement was determined by comparing the as-cast structure of a transverse section of the inoculated ingots with that of a similar section taken from an untreated ingot otherwise prepared in the same fashion. The sections were taken from a position mid-way between the bottom of the shrinkage pipe and the bottom of the ingot avoiding columnar crystals grown from the bottom.

The results are set forth in Table I.

TABLE I

Ingot No.	Tungsten Oxide Amount in Additive (%)		Pouring Temp. (°C)	Ingot Structure	Proportion of each grain(%)
	Amount in Additive (%)	Amount Added (%)			
1	None	—	1470	C _{cc}	100
2	3	0.3	1470	C _c + E _m	35 - 65
3	5	0.3	1470	C _c + E _m	40 - 60
4	19	0.3	1470	C _c + E _m	40 - 60

The following was used to classify the ingot structures:

E_m — medium equiaxial grain; 2.5 to 4.5 mm. diameter

C_m — medium columnar grain; 2.5 to 4.5 mm. diameter

E_c — coarse equiaxial grain; 4.5 to 6.0 mm. diameter

C_c — coarse columnar grain; 4.5 to 6.0 mm. diameter

C_{cc} — very coarse columnar grain; >6.0 mm. diameter

It can be seen that grain refinement occurred in all instances in which the nickel-tungsten oxide additives of varying oxide particle size were employed. It would appear that the extent of grain refinement is substantially independent of oxide particle size since the particle size in ingot No. 4 was 1.5 μ m and the results were quite satisfactory.

To illustrate that grain refinement can be obtained with the aid of tungsten oxide-containing additives over a wide range of temperatures of the melt, further tests were carried out in which Ni-5% tungsten oxide additive was added to melts of alloys having the compositions shown in Table II.

TABLE II

COMPOSITION (Wt. %)														
Alloy No.	C	Si	Fe	Mn	Mg	Cr	Ti	Al	Ni	Co	Mo	Nb	B	Zr
2	0.07	<1.0	<1.0	<1.0	0.012	19.5	2.35	1.40	bal.	<2.0	<0.3	—	0.0025	0.06
3	0.13	<1.0	<1.0	<1.0	—	15.0	1.2	4.7	bal.	20.0	5.0	—	0.006	0.10
4	0.05	<0.35	bal.	<0.35	—	19.0	1.0	0.6	53	<1.0	3.0	5.3	0.0025	—
5	0.05	<0.25	<1.0	<0.1	—	20.0	2.3	0.4	bal.	14.0	4.5	5.0	0.0025	0.03

19.2% chromium, 2.46% titanium, 1.5% aluminum and 16.4% cobalt, the balance being essentially nickel, were prepared in a high frequency induction furnace.

The results are reported in Table III which show that significant grain refinement was achieved in each case:

TABLE III

Ingot No.	Alloy No.	Tungsten Oxide		Pouring Temp. (°C.)	Ingot Structure	Proportion of each grain (%)
		Amount in Additive (%)	Amount Added (- %)			
5	2	None	—	1445	C _m	100
6	2	5	0.3	1445	E _m	100
7	3	None	—	1425	C _r	100
8	3	5	0.3	1425	C _m + E _m	20-80
9	4	None	—	1450	C _m	100
10	4	5	0.3	1450	C _m + E _m	40-60
11	5	None	—	1395	C _{co}	100
12	5	5	0.3	1395	E _m	100

As indicated herein, a turbine wheel was integrally precision cast using the subject nickel-tungsten oxide nucleating additive. In this connection, the alloy used to produce the wheel was of the nickel-base superalloy type and was of the following approximate composition: 0.05%C, 11.75%Cr, 4.5%Mo, 6%Al, 0.7%Ti 2%Nb, 0.01%B, 0.1%Zr, balance nickel. The alloy was vacuum melted and cast in investment shell molds preheated to 800°C. with a metal temperature of 1460°C. The wheel was cut in half to show the grain size in the hub as well as the blade. The grain size was uniform throughout both sections, being less than about 1/16 inch in the hub. A similar wheel was cast without aid of the inoculant and the grain size in the hub was approximately ¼ to ½ inch, approximately 4 to 8 times larger. It has been considered that as a consequence of the fact that the blades and hubs operate under different loads and are exposed to different elevated temperatures, it would be of considerable benefit if the grain size in the hub region could be reduced, the thought being that a fine grain was more important in the hub than in the blade section.

In addition to the above information and data, the subject invention has been used to grain refine a 25%Cr-20%Ni stainless steel and an 18%Ni maraging steel. It is considered that copper base alloys can be grain refined. Superalloys containing 50% or more of nickel, from 6% to 30% chromium, up to 30% iron, aluminum in an amount of at least 0.4 or 0.5% to 8%, up to 6% titanium, e.g., 0.5 to 5% titanium, up to 8%, e.g., 1 to 6%, molybdenum, up to 20%, e.g., 1 to 5%, tungsten, up to 8%, e.g., 1 to 6%, niobium, up to 8%, e.g., 1 to 6%, tantalum, together with amounts of vanadium, boron, zirconium and hafnium given herein, are generally representative of other compositions deemed responsive to the invention.

As reflected by the above description, the process of the invention can be used both in the casting of ingots and in the production of castings, i.e., articles and parts made by casting. The castings may be made by investment casting in vacuum, air or an inert atmosphere, or by conventional sand casting methods.

While the oxide formed by internal oxidations of nickel-tungsten alloys is referred to in this specification as "tungsten oxide", it is suspected that in practice the oxidation of such alloys may lead to additives containing some amount of nickel oxide. In other words, a mixed oxide, for example, NiO WO₃, may be dispersed in the nickel carrier. Irrespective of this, the actual tungsten oxide content should preferably be from 1 or 2 to 8%.

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 process for grain refining a metal or alloy during solidification from the molten state which comprises introducing into a melt of the metal or alloy an inoculating additive comprised of a nickel carrier and tungsten oxide particles in at least a small but effective amount sufficient to induce grain refinement upon solidification, nickel dissolving in the melt and solid tungsten oxide nuclei being dispersed therein.

2. A process according to claim 1 in which the additive is in the form of strip from 0.05 to 0.4 mm. thick.

3. A process according to claim 1 in which the additive comprises an internally oxidized single-phase alloy.

4. A process according to claim 3 in which the additive comprises an internally oxidized nickel-tungsten alloy containing 1 to 17% tungsten.

5. A process according to claim 1 in which the alloy contains from 1% to 6% tungsten.

6. A process according to claim 1 in which the melt is an alloy with a base of nickel or nickel and copper or nickel and chromium or nickel, chromium and cobalt, in each case with or without iron up to 50%.

7. A process according to claim 1 in which the melt is an alloy having a composition falling within the following ranges: 20 to 80% nickel, 5 to 35% chromium, 0 to 40% cobalt and 0 to 50% iron, up to 10% aluminum, up to 10% titanium, up to 15% molybdenum, up to 8% niobium, up to 8% tantalum, up to 25% tungsten, up to 3% vanadium, up to 2% zirconium, up to 1% boron and up to 5% hafnium.

8. A process according to claim 1 in which the melt is an alloy having a composition falling within the following ranges: from 6% to 30% chromium, up to 30% iron, aluminum in an amount of at least 0.4 to 8%, up to 6% titanium, up to 8% molybdenum, up to 20% tungsten, up to 0.25% carbon, up to 6% niobium, up to 6% tantalum, up to 3% vanadium, up to 0.5% boron, up to 2% zirconium, up to 5% hafnium, and at least about 50% nickel.

9. A process according to claim 1 in which from 0.2 to 0.8% additive by weight of the melt is introduced.

10. A process according to claim 1 in which from 0.2 to 0.5% additive by weight of the melt is introduced.

11. A process in accordance with claim 1 in which the tungsten oxide was formed by heating in air to the point that an external coating was formed and the remainder of the oxidation process was conducted in a substantial vacuum whereby scaling losses are reduced.

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