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[54] **DESULFURIZATION OF VACUUM-INDUCTION-FURNACE-MELTED ALLOYS**

[75] Inventors: **Rene Schlatter,** Derry Township; **James P. Stroup,** Ligonier Township, both of Westmoreland County, Pa.

[73] Assignee: **Latrobe Steel Company,** Latrobe, Pa.

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[52] **U.S. Cl.** **75/53,** 75/57, 75/58, 75/82, 75/94

[51] **Int. Cl.** **C21c 7/02,** C22b 9/10

[58] **Field of Search** 75/53, 57, 58, 82, 94, 75/130.5, 49, 10–12

[56] **References Cited**

UNITED STATES PATENTS

3,099,552	7/1963	Landig	75/54
3,194,649	7/1965	Okazaki	75/130.5
3,198,624	8/1965	Bell	75/130.5
3,218,156	11/1965	Vander Sluis	75/49
3,396,100	8/1968	Gould	75/53
3,547,622	12/1970	Hutchinson	75/49
3,695,946	10/1972	Demeaux	75/49

Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—Peter D. Rosenburg
Attorney, Agent, or Firm—Buell, Blenko & Ziesenheim

[57] **ABSTRACT**

Nickel-base, cobalt-base and iron-base alloys melted in vacuum-induction furnaces are desulfurized to very low sulfur levels by reacting them with slag-forming mixtures comprising high purity lime and a fluxing agent, under reducing conditions, so as to form a slag no hotter than the melt. The alloys so produced display unexpected improvements in physical properties and in hot workability.

10 Claims, 3 Drawing Figures

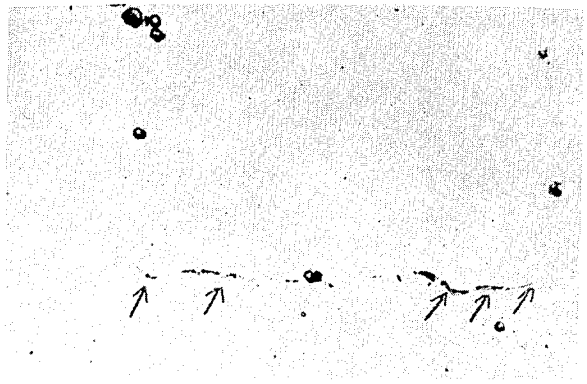


FIG. 1

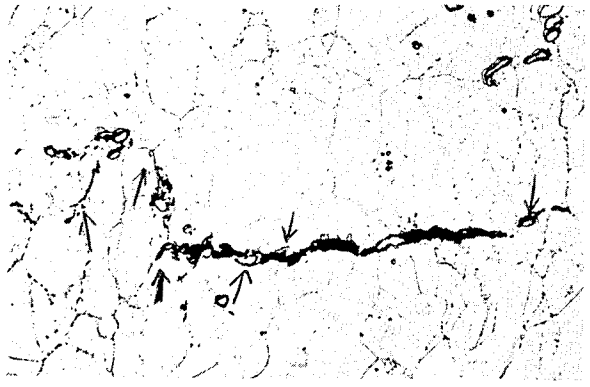


FIG. 2

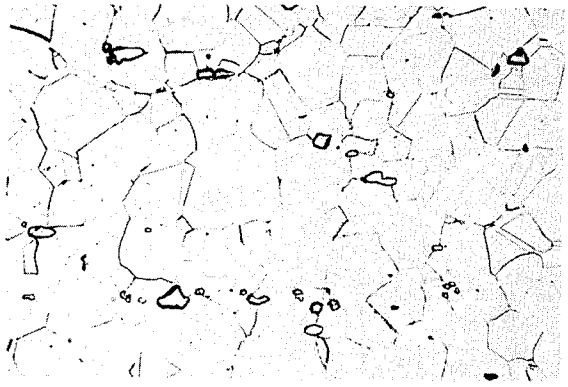


FIG. 3

DESULFURIZATION OF VACUUM-INDUCTION-FURNACE-MELTED ALLOYS

This invention relates to the desulfurization of nickel-base, cobalt-base and iron-base alloys melted in vacuum-induction furnaces. It is more particularly concerned with processes for treating melts of such alloys so as to reduce their sulfur contents to very low levels.

The properties of a considerable number of alloys are known to be sensitive to their sulfur contents. This is particularly true of some of the high-performance iron-base, nickel-base and cobalt-base alloys, sometimes called super alloys, and most of them have maximum sulfur content specifications of 0.01 percent.

Many alloys can be air-melted in the arc furnace, in which desulfurization of the charge is accomplished by the use of a basic slag. In the arc furnace, after melt down, the heat generated by the arc is transmitted to the slag which floats on the melt and then from the slag to the melt. The hearth is relatively shallow and the roof is domed, and reflects heat onto the slag below. The slag is, therefore, always hotter than the melt, by perhaps 200° to 300°F. The metal from an arc furnace is normally tapped into a ladle, which is then moved over a pit in which are located the ingot molds, and the metal is teemed from the ladle into the molds, one after another. The pouring pit may be at some distance from the furnace. There is an appreciable loss in temperature of the metal from the time it leaves the furnace to the time it goes into the last mold, and this is allowed for in adjusting the tapping temperature of the alloy. The furnace slag therefore, is necessarily hot. It is well-known that desulfurization is facilitated by high slag temperatures.

The compositions of many of the high performance alloys, however, are such that it is not feasible to melt them in air. They are melted in vacuum-induction furnaces. Refining of the metal under a slag for desulfurization can be carried out in addition to the usual vacuum refining done in these furnaces at usual production rates. The conditions in these furnaces as concern slag-metal reactions are in most respects, however, quite different from those in arc furnaces. The bath is relatively deep. The metallic charge is heated by currents induced in it, but the slag, being a poor conductor, is not so heated. It receives heat from the metal underneath it, and can never be hotter than the metal.

Furthermore, the tapping and teeming practice is different from arc furnace practice because of the nature of the vacuum-induction furnace layout. The furnace is operated inside an evacuated tank or shell and the ingots must be poured within the shell. A ladle is not used, but the metal is tapped from the furnace into a tundish which is constructed so that its tap hole can be aligned with respect to the ingot molds which are positioned within the tank. As heat can continue to be supplied to the melt while it is being tapped, the heat loss is substantially less than in air-melting practice and the tapping temperature of the furnace is lower than it would have to be for the alloy if it were melted and cast by conventional arc furnace practice. The slag on a vacuum-induction-furnace-melted heat is several hundred degrees colder than the slag on a heat air-melted in an arc furnace, and its desulfurizing action is much less vigorous. Desulfurizing practices which are effective in arc-furnace melting are generally not effective in vacuum-induction-furnaces.

It is an object of our invention to provide a process for reducing the sulfur content of vacuum-induction-furnace alloy melts to low levels. It is another object to provide such a process which comprehends reacting alloy melts with a slag of specified composition which has a temperature no greater than the metal temperature. Other objects of our invention will appear in the course of the description thereof which follows.

We have found that a melt of cobalt-base, nickel-base or iron-base alloy can be desulfurized in a vacuum-induction-furnace to a low sulfur content by causing it to react in a basic-lined crucible under reducing conditions with a slagforming mixture comprising high purity lime and a fluxing agent, in the manner hereinafter set out.

We have discovered that our process reduces the sulfur content of the alloy to a value which we believe to be below the solid solubility limit of the alloy and we have found that alloys made by our process exhibit unexpected improvements both in physical properties and in hot workability.

We preferably carry out our process in a vacuum-induction-furnace lined with magnesia-spinel refractory bricks. The charge is introduced into the furnace either in solid or in liquid form. Our desulfurizing mixture to be described may be added to the cold charge, or it may be added after the charge has melted and refining is in progress. Our mixture may be added in granulated or powder form, packed in bags, or it may be briquetted or otherwise compacted and added in that form.

The principal constituent of our slag-forming mixture is high-purity metallurgical lime comprising more than 98 percent calcium oxide. The burnt lime used in conventional alloy melting practice has a considerably lower calcium oxide content, on the order of 85 to 90 percent. The high purity lime we use should not contain more than 0.5 percent by weight of silica, not more than 0.3 percent iron oxide and not more than 0.3 percent manganese oxide for maximum effectiveness in desulfurization. It should also contain not more than 0.05 percent lead oxide, or oxides of other undesirable constituents, as in our process oxides tend to be reduced from the slag into the melt. We prefer to screen the lime through an 8 mesh screen and over a 32 mesh screen. Our mixture includes one or more neutral fluxing compounds such as calcium fluoride, barium fluoride, magnesium fluoride, sodium-aluminum fluoride (cryolite) or the rare earth fluorides. We may supplement these fluorides with alumina, barium oxide, nickel oxide, or molybdenum oxide. A fluxing agent is essential in our process to render the slag fluid and reactive at the relatively low slag temperatures in a vacuum-induction-furnace. The neutral fluxing compounds should be incorporated in amounts between about 5 percent and about 25 percent by weight of the mix.

Our process, to be fully effective, requires reducing conditions for the reaction between the slag-forming compound and the sulfur in the charge. If the charge contains strong reducing agents, such as aluminum or titanium in amounts of a few percent, or carbon in excess of about 0.3 percent, no reducing agents may be necessary in our slag forming mix. If the composition of the charge is deficient in reducing substances our mix also includes one or more reducing agents. Suitable

substances are carbon, calcium carbide, silicon, silicon carbide, calcium, calcium silicide, magnesium, aluminum rare earth metals, rare earth silicides or alloys of the above. The weight of the reducing agents should be between about 1 percent and about 15 percent of the mixture. The constituents of the mixture are well blended in any convenient mixing apparatus before the mixture is added to the alloy. In induction furnace melting of the alloys here concerned, the induced currents in the melt cause a circulation which effectively exposes the molten charge to the slag and so causes them to react on each other.

It has been found that the total amount of slag mixture required for effective desulfurization of iron, nickel, and cobalt-base alloys in large vacuum induction melting furnaces of 1 to 30 ton capacity is between 0.1 and 2 percent of the metal weight in the crucible. The desulfurizing flux mixture can be added in one portion to the charge materials or in one or several small portions to the liquid metal under inductive stirring. If the addition is made to the charge, care must be taken in cleaning the metallic raw material to avoid the presence of excessive amounts of heavy metal oxides. No principal changes in the usual melting practice or pressure level is necessary to accomplish desulfurization through the use of above described treatment mixture.

The nominal compositions of several alloys for which our process is suitable are set out in the accompanying Table I.

TABLE I

	ALLOY COMPOSITION													
	Cr	Co	Ni	W	Mo	Al	Ti	Cb+Ta	C	Mn	Si	S	V	Fe
Inconel 718	18.5	1.0+	53	—	3	.5	1	5	.04	.1	.1	.01+	—	Bal.
Rene 95	14	8	Bal.	3.5	3.5	3.5	2.5	3.5	.15	.1	.1	.01+	—	—
Marvac 315	—	15	18	—	3	.1	.2	—	<.01	.1+	.1+	.005+	.5	Bal.
M-50	4	—	—	—	4	—	—	—	.8	.3	.2	.01+	1	Bal.
D-979	15	—	43	4	4	1	3	—	.04	.1	.1	.01+	—	Bal.
Waspalloy	20	14	Bal.	—	4	1.4	3	—	.06	.1	.1	.01+	—	2+
MP 35N	20	35	34	—	10	—	.7	—	.01	.1	.1	.005+	—	1+

+ Maximum

We have discovered that these alloys are sensitive to even lower sulfur contents than were previously attainable. Specimens of D979 alloy, for example, containing 0.009 percent sulfur have room-temperature elongations of about 5 percent and reductions of area of about 8.6 percent, while similar specimens of the alloy made with sulfur contents of 0.005 percent exhibit room-temperature elongations of about 11 percent and reductions of area of about 15.6 percent. The sensitivity to sulfur content of Waspalloy specimens reduced to the same size from two different sizes of starting billet is shown by the listing of their significant physical properties in Table II. Ultimate tensile strength and yield strength are expressed in thousands of pounds per square inch.

TABLE II

Starting Billet Stock	Property	SULFUR CONTENT OF SPECIMENS .012%S	.006%S	.007%S
8" square	Ultimate tensile	167	194	193
	.2% Yield	134	142	135
	Elongation %	8	18	25
	Reduction in area %	11	21	30
5" square	Ultimate tensile	171	193	—
	.2% Yield	131	130	—
	Elongation %	11	20	—
	Reduction in area %	13	20	—

The hot-workability of alloys of the types above mentioned is also sensitive to their sulfur contents. This dependency is perhaps of even more importance to the producers of the alloys than to their users. The alloy is usually cast into an ingot of considerably greater cross-section than the bar or other shape supplied the customer. The ingot is then hot-worked, usually by forging, to a billet of a size which can be conveniently rolled to final dimensions. As the ranges of forging temperatures of the alloys here concerned are rather narrow, the forging must be interrupted from time to time to allow the partially reduced billet to be reheated. The successive reduction and reheating stages are detrimental to the surface of the billet and therefore it is common practice at some point in processing to condition the billet surface, by grinding or the like, to remove defects. The number of these steps is directly proportional to the sulfur content of the alloy. A 16 inch diameter ingot of the D979 alloy previously mentioned containing 0.01 percent sulfur may require 9 or 10 reheatings and 2 or 3 reconditioning treatments to bring it down to a 4¾ inch square billet. If its sulfur content is halved, it may require only 5 to 6 reheatings and one reconditioning treatment, while if its sulfur content is reduced to 0.002 percent it can be hot-worked to billet size with only 2 to 3 reheatings and no reconditioning. The reduction in manufacturing cost of alloys with sulfur contents of this order is thus very substantial.

The detrimental effect of sulfur on the properties of the alloys in question, even when the sulfur content is low by ordinary standards, appears to be occasioned by the presence of attenuated sulfide films which form along the grain boundaries of the alloy during its solidification. These films facilitate micro-cracking of the alloy, which leads to subsequent failure. There is evidence, however, that these films do not form when the sulfur content of the alloy is less than some low value, which is postulated to be the limit of solid solubility of sulfur in the alloy in question. This limit no doubt varies from one alloy to another and, as far as we know, has not been determined precisely for any of the alloys here concerned. Our experiments indicate that it must be less than about 0.006–0.007 percent and in some alloys as low as perhaps 0.002 percent. Thus, the limit of solid solubility of sulfur, for each alloy, marks the point at which a physical change in the alloy structure occurs,

and this change is accompanied by a very substantial change both in the response of the alloy to hot working and in the physical properties of the worked alloy.

The attached figures are photomicrographs of specimens from heats of D979 alloy having different sulfur contents, the lower sulfur contents being obtained by the process of our invention.

FIG. 1 is an unetched photomicrograph at a magnification of 500× of metal from a heat having a sulfur content of 0.009 percent. The elongated gray areas indicated by arrows are sulfide films. The isolated grains with black borders are remnants of carbide stringers. The photomicrograph shows that microcracking has commenced along the sulfide-matrix interface.

FIG. 2 is another photomicrograph of the same heat at the same magnification but etched with modified Fry's reagent. It shows another microcrack formed along a sulfide-matrix interface. Arrows point to the remnants of sulfide films.

FIG. 3 is a photomicrograph of another heat of the same alloy in which, by the process of our invention, the sulfur content has been reduced to 0.002 percent. It was taken at the same magnification as FIGS. 1 and 2 and the specimen was etched with the same modified Fry's reagent. No sulfide films or evidences of microcracking are observable. Some remnants of carbide stringers are visible as isolated grains surrounded by heavy black borders. It is in these areas that sulfides would have appeared first, if any had been present.

The following are examples of our process:

I

High Temperature Alloy Inconel -718

A 30,000 pound charge of this alloy having a calculated sulfur content of 0.005 percent was melted in a magnesia-spinel lined vacuum-induction-furnace together with a slag-forming mixture consisting of 100 pounds of high purity lime and 20 pounds of calcium fluoride. The melt was tapped at a temperature of 2,750°F. The sulfur content of the alloy at tap was 0.002 percent.

II

High Temperature Alloy Rene 95

A 15,000 pound charge of this alloy having a calculated sulfur content of 0.006 percent was melted in a magnesia-spinel lined vacuum-induction-furnace together with a slag-forming mixture consisting of 60 pounds of high purity lime, 10 pounds of calcium fluoride and 1 pound of aluminum. The melt was tapped at a temperature of 2,700°F. The sulfur content of the alloy at tap was 0.003 percent.

III

High Strength Steel Marvac -315

A 15,000 pound charge of this steel having a calculated sulfur content of 0.004 percent was melted in a magnesia-spinel lined vacuum-induction-furnace with a slag-forming mixture consisting of 50 pounds of high purity lime, 5 pounds of calcium fluoride and 20 pounds of nickel oxide. The tapping temperature was 2,830°F. The sulfur content of the steel at tap was 0.002 percent.

IV

Bearing Steel M 50

A 15,000 pound charge of M 50 steel having a calculated sulfur content of 0.007 percent was melted in a magnesia-spinel lined vacuum-induction-furnace with a slag-forming mixture consisting of 58 pounds of high purity lime, 12 pounds of calcium fluoride and 2 pounds of calcium carbide. The tapping temperature was 2,850°F. The sulfur content of the alloy at tap was 0.004 percent.

V

Cobalt-Nickel Alloy MP35N

A 30,000 pound charge of this alloy having a calculated sulfur content of 0.005 percent was melted in a magnesia-spinel lined vacuum-induction-furnace together with a slag-forming mixture consisting of 90 pounds of high purity lime, 10 pounds of calcium fluoride and 80 pounds of metallic calcium. The melt was tapped at a temperature of 2,750°F. The sulfur content of the alloy at tap was 0.002 percent.

VI

High Temperature Alloy D979

A 16,000 pound virgin charge of this alloy having a calculated sulfur content of 0.0041 percent was melted in a magnesia-spinel lined vacuum-induction-furnace together with a slag-forming mixture consisting of 60 pounds of high purity lime, 3 pounds of cryolite, and 1 pound of calcium carbide. The melt was tapped at a temperature of 2,700°F. The sulfur content of the alloy at tap was 0.002 percent.

In all the examples the heats were melted from a cold charge. Thus, the sulfur content of the charge had to be calculated from the known sulfur contents of the scrap and other charge constituents.

In the foregoing specification we have described a presently preferred embodiment of this invention, however, it will be understood that this invention can be otherwise embodied within the scope of the following claims.

We claim:

1. The method of desulfurizing an alloy of the group consisting of nickel-base, cobalt-base and iron-base alloys in a basic-lined vacuum vessel under reduced pressure comprising bringing the molten alloy into contact under reducing conditions with a basic slag having a temperature no higher than that of the alloy, the slag being formed by adding to the alloy a slag-forming mixture comprising lime having a calcium oxide content greater than about 98 percent and a neutral fluxing agent capable of rendering slag fluid and reactive at relatively low slag temperatures, in amount between about 5 percent and about 25 percent of the mixture by weight.

2. The method of claim 1 in which the lime contains not more than about 0.5 percent silica, not more than 0.3 percent iron oxide and not more than about 0.3 percent manganese oxide.

3. The method of claim 2 in which the lime contains not more than 0.05 percent lead oxide.

4. The method of claim 1 in which the neutral fluxing agent is one or more members selected from the group consisting of calcium fluoride, barium fluoride, magnesium fluoride, sodium-aluminum fluoride and the rare earth fluorides.

5. The method of claim 4 in which the neutral fluxing agent also includes one or more members selected from

the group consisting of alumina, barium oxide, nickel oxide and molybdenum oxide.

6. The method of claim **1** in which the reducing conditions are obtained by including in the slag-forming mixture a reducing agent in amounts between about 1 percent and about 15 percent of the mixture by weight.

7. The method of claim **6** in which the reducing agent is one or more of the constituents carbon, calcium carbide, silicon, silicon carbide, calcium, calcium silicide, aluminum, magnesium, the rare earth metals, the rare earth silicides, and alloys thereof.

8. The method of claim **1** in which the weight of the slag-forming mixture is between about 0.1 percent and about 2 percent of the weight of the melt.

9. The method of claim **1** in which the vessel is a vacuum-induction-furnace.

10. The method of claim **9** in which the basic lining of the vacuum-induction-furnace is a magnesia spinel refractory.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,853,540 Dated December 10, 1974

Inventor(s) Rene Schlatter and James P. Stroup

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the References, Patent No. 3,396,100, should read --3,396,010--.

Signed and sealed this 4th day of March 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

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