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METHODS AND APPARATUS FOR DESULPHURIZATION OF FERROUS METALS

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This invention relates to the desulphurization of ferrous metals and particularly to the desulphurization of iron and steel in furnaces. This application is a continuation in part of my application Serial No. 380,365, filed September 15, 1953, now abandoned. The problem of desulphurizing ferrous metals has become of increasing importance to the iron and steel industry by reason of the increased use of lower grade ores and lower grade fuel supplies. As a result the production of iron and steel has shown a gradual increase in sulphur content over that of the past practices.

Sulphur in any substantial amount is recognized as an undesirable impurity producing hot shortness and other undesirable qualities. It is accordingly necessary to remove the sulphur below certain recognized acceptable levels in order to produce iron and steel satisfactorily for most purposes. This is particularly true in alloy steels and special steels such as the stainless steels.

Many methods of desulphurization have been heretofore proposed. For example, it has been heretofore proposed to desulphurize steel by pouring the steel through several different slags containing desulphurizing agents such as caustic soda. These practices have been expensive, time consuming and in many cases not entirely satisfactory.

I have found that ferrous metals can be more effectively desulphurized by introducing into the molten bath of ferrous metal a stream of molten caustic soda together with an adjuvant agent. In addition to desulphurizing the molten ferrous metal I have found that my practice imparts improved physical properties and particularly greatly improved tensile strengths. In a preferred practice of my invention I employ the steps of forming a bath of molten mixture of caustic soda and adjuvant, delivering a stream of the molten mixture into the body of the molten ferrous bath beneath the surface thereof preferably at or adjacent to the bottom, permitting the mixture of caustic soda and adjuvant to diffuse into the bath upwardly through the molten metal to react with the sulphur to form sulphur products which go into the slag. Preferably the adjuvant agents which I employ are calcium carbide, manganese dioxide, magnesium oxide, calcium boride, rare earth oxides, calcium cyanamide and fluorspar. The adjuvant agent should appear in an effective amount up to about 20% with the balance of the mixture being caustic soda.

Caustic soda and adjuvant are fused in a gas fired boiler on the operating floor of the production shop to form a liquid mixture which is pumped from the boiler by a caustic pump through a high temperature alloy lance into the bottom of molten bath. Preferably the mixture is held at a temperature between about 850° F. to 1500° F. depending upon the nature of the adjuvant being used. Preferably the amounts of adjuvant agent are between about 0.05% to 12%. The caustic soda fraction of the mixture may be substantially pure or it may contain the usual impurities found in commercial caustic soda. For example, small amounts of sodium chloride and sodium nitrate may be present in the caustic soda and may be even advantageously added in small amounts in order to reduce the melting point of the mixture.

I have found that the method of this invention has the advantage that the molten caustic passing through the metal lance acts as a coolant for the lance. As a

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result the lance may be used for a considerable period of time without destruction in the bath.

The method of this invention will be more clearly understood by reference to the following examples:

Eight heats of cupola iron were made in a 500-pound reduction furnace. These heats were treated, some with molten caustic soda and some with a mixture of 90% caustic soda and 10% calcium carbide. The results of these tests are tabulated in Table I hereinbelow:

Table I

Heat No.	Additive	Percent Sulphur		Percent S. Removed	# NaOH per # S. Removed
		At Start	At Finish		
7	NaOH	.154	.007	93.5	10.3
10	NaOH	.184	.014	87.0	7.2
11	NaOH	.178	.005	97.2	9.0
12	NaOH	.188	.009	95.0	10.2
14	NaOH	.097	.006	93.1	5.56
24	NaOH+CaC ₂	.152	.006	94.9	7.7
25	NaOH+CaC ₂	.136	.005	96.0	7.75
26	NaOH+CaC ₂	.187	.008	95.4	8.1

It will be apparent from the foregoing table that the presence of the calcium carbide adjuvant greatly increased the efficiency of sulphur removal with a reduced amount of caustic soda.

Similar results have been achieved by mixtures of adjuvant agents. For example basic cupola iron was treated as in the foregoing example with a mixture of 90% caustic soda, 7% manganese dioxide and 3% calcium carbide. The mixture was lanced into the molten metal at 950°. The sulfur reductions were similar to those achieved in Table I above. A very significant increase in tensile strength has been achieved by this practice. For example the iron treated with the foregoing mixture of caustic soda, manganese dioxide and calcium carbide gave the following results:

Table II

Heat No.	Tensile before Treatment	After Treatment, 90% NaOH, 3% CaC, 7% MnO ₂	After Treatment, NaOH
31	14,375	49,150	
32	12,700	54,100	14,650
33	12,850	53,350	14,750
34		49,700	
35		51,700	
36		54,450	

Comparison of these tensile strengths shows an increase of several hundred percent when the mixture of this invention was used over the tensile strength without treatment or when caustic soda was used alone.

Similar results were obtained by using 10% manganese dioxide and 90% caustic soda and lancing the fused mixture at temperatures between 850° F. to 1100° F. into cupola iron. Like results were also obtained with caustic soda admixed with magnesium oxide, calcium boride, rare earth oxide, calcium cyanamide, fluorspar and with mixtures thereof. In every case the amount of caustic soda necessary to give a particular sulphur removal was greatly reduced and the tensile strength of the resulting iron materially increased. Along with the increase in tensile strength there was a general physical improvement overall in the final iron.

These desirable results have been obtained in plain steels, alloy steels including stainless steel, silicon steel, zirconium steel and boron stainless steels used for hydrogen fused equipment and atomic fission. Comparison

tive tests of such materials show that a low grade high sulphur steel may be upgraded by this treatment to the equivalent in quality of an electric furnace steel of low sulphur content.

I preferably add the mixture of fused caustic soda and adjuvant by the device illustrated in the accompanying figure.

In the accompanying drawing, I have illustrated a salt melting and storage pit 10 in which the mixture of caustic soda and adjuvant are fused and held. The pit 10 is made up of an inner steel shell 11 and an outer unit insulator 12 between which are placed strip heaters 13 used to heat and hold the fused caustic at the desired temperature. The fused mixture is delivered from the pit 10 through an outlet valve 14 and nozzle 15 into a delivery capsule 16 made up of an inner steel shell 17 surrounded by strip heaters 18, all enclosed by unit insulation 19. The molten caustic is delivered from the nozzle 15 of the pit through an inlet tube 20 and valve 21 on the capsule 16. The capsule 16 is suspended on a ring 22 fixed to the shell 17. Preferably the ring 22 is suspended on a hook 23 from a weighing device 24. An air pressure inlet line 25 communicates through a valve 26 to the interior of the capsule 16. A pressure gauge is provided in the line 25 to indicate the pressure within the capsule 16. A relief valve 28 is provided to vent the capsule in the event that excess pressures are built up. A pyrometer well 29 extends vertically from the shell 17 into the interior of the capsule 16. An outlet line 30 is provided in the bottom of the capsule 16 communicating with the interior of the shell 17. This outlet line 30 is provided with a high speed clip valve 31 and a quick opening flange 32. A steel lance 33 provided with a mating quick opening flange 34 is attached to flange 32. Preferably, an outer protective shell 35 of carbon or other refractory material covers the lance 33. The lance is adapted to extend into a ladle 36 or furnace in which the ferrous metal to be treated is held.

In operation, the capsule 16 is loaded from the pit 10 to inlet line 20 and valve 21. Air is applied to the interior of the capsule through the line 25 until a desired pressure is achieved. The capsule is then transferred to the area of the molten bath to be treated. The lance 33 is inserted in the molten bath, valve 31 is opened and the air pressure forces the fused mixture of caustic and adjuvant into the bath until a desired amount as indicated by the scale 24 has been delivered to the bath at which point valve 31 is closed and lance 33 removed from the molten bath.

While I have illustrated and described a present preferred embodiment of my invention it will be understood that the invention may be otherwise practiced and embodied within the scope of the following claims.

I claim:

1. A method of desulphurizing a molten ferrous bath comprising the steps of delivering a stream of a molten mixture of caustic soda and an adjuvant agent selected from the group consisting of calcium carbide, manganese dioxide, magnesium oxide, calcium boride, rare earth oxides, calcium cyanamide and fluorspar into the body of the molten bath beneath the surface thereof maintaining the bath molten while the caustic mixture diffuses through the body of the molten steel bath to react with the sulfur and separating the remaining molten metal from the slag formed by the caustic mixture-sulfur reaction.

2. A method of desulphurizing a molten ferrous bath comprising the steps of forming a bath of molten caustic soda, pumping a stream of a molten mixture of caustic

soda and an adjuvant agent selected from the group consisting of calcium carbide, manganese dioxide, magnesium oxide, calcium boride, rare earth oxides, calcium cyanamide and fluorspar into the body of the molten ferrous bath through a hollow steel lance beneath the surface thereof, maintaining the bath molten while the caustic mixture diffuses through the body of the molten bath to react with the sulfur, permitting the resulting caustic mixture-sulfur reaction product to enter into a slag layer on the molten bath and separating the remaining molten metal from the resulting slag.

3. A method of desulphurizing a molten steel bath in an open-hearth furnace comprising the steps of delivering a stream of a molten mixture of caustic soda and up to about 20% of an adjuvant agent selected from the group consisting of calcium carbide, manganese dioxide, magnesium oxide, calcium boride, rare earth oxides, calcium cyanamide and fluorspar equal in amount to about 4 to 9½ pounds per ton of molten steel into the body of the molten bath adjacent the bottom beneath the surface thereof, maintaining the bath molten while the caustic mixture diffuses through the body of the molten steel bath to react with sulfur and separating the remaining molten metal from the slag formed by the caustic mixture-sulfur reaction.

4. A method of desulphurizing a molten steel bath in an open-hearth furnace comprising the steps of delivering a stream of a molten mixture of caustic soda and up to about 20% of an adjuvant agent selected from the group consisting of calcium carbide, manganese dioxide, magnesium oxide, calcium boride, rare earth oxides, calcium cyanamide and fluorspar equal in amount to about 5 pounds per ton of molten steel into the body of the molten bath adjacent the bottom beneath the surface thereof, maintaining the bath molten while the caustic mixture diffuses through the body of the molten steel bath to react with the sulfur and separating the remaining molten metal from the slag formed by the caustic mixture-sulfur reaction.

5. A method of desulphurizing a molten steel bath, comprising the steps of forming a bath of molten caustic soda, pumping a stream of molten mixture of caustic soda and up to about 20% of an adjuvant agent selected from the group consisting of calcium carbide, manganese dioxide, magnesium oxide, calcium boride, rare earth oxides, calcium cyanamide and fluorspar into the body of the molten steel bath through a hollow steel lance until about 4 to 9½ pounds of caustic soda per ton of molten metal has been introduced into the bath beneath the surface thereof, maintaining the bath molten while the caustic mixture diffuses through the body of the molten bath to react with the sulfur, permitting the resulting caustic mixture-sulfur reaction product to enter into a slag layer on the molten bath and separating the remaining molten metal from the resulting slag.

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