Our invention relates to the casting of ingots, particularly of ferrous metals, where the ingots are intended for rolling into sheet or plate metal. It is well known that various inclusions which are likely to be in the molten metal teemed into the ingot molds, and which tend to float on the metal as it rises in the mold, are likely to be trapped near the skin of the ingot. These skin inclusions cause skin lamination and other defects in the rolled product.

The inclusions are of various kinds. Oxides formed in the metal during its purification, or formed in the metal as a result of deoxidation or alloying treatments practiced upon the metal prior to teeming, are important as a source of trouble. Thus steel killed with aluminum is likely to retain considerable aluminum oxide. Steel containing residual aluminum may pick up more oxide during ladling or teeming. Other foreign materials such as brick, hot top slurry, and other refractories are also frequently present. We shall refer to all of the various inclusions of foreign material as "ingot scum."

It has hitherto been suggested that the difficulty with inclusions of foreign material in the ingot surfaces might be lessened or avoided by adding to the molten metal a material which would flux them, forming a slag having a lower melting point than the metal being cast. Ingot mold scums have a density not far from iron and barely float because they tend to form a sort of slurry with the iron and are either in solid form at the temperature of the molten metal or tend to solidify with the iron and hence are easily trapped. It was thought that a flux would prevent the formation of a slurry and would provide a fluid slag having a substantially lower specific gravity than iron. Hence it would float freely and would not be trapped in the iron as the iron solidified against the mold surface.

It was known, for example, that cryolite was an excellent solvent for most refractory oxides including aluminum oxide, and was capable of forming with them slags of fairly low melting point. It has been suggested that a quantity of cryolite be added to the ingot molds prior to the introduction of the molten metal. The results however, have been disappointing and unpredictable, sometimes apparently producing beneficial effects and sometimes clearly increasing the quantity of skin inclusions as well as inclusions elsewhere in the ingot.

The conditions in an ingot mold during teeming are delicate; and may easily become unbalanced. The metal chills and solidifies very rapidly against the ingot mold walls and the outer skin does not become liquid again. The rapidity of the freezing depends very largely on the heat in the metal being teemed, and the addition of any foreign substances such as cryolite tends to abstract heat from the metal. In many instances, we believe, the cryolite does not fully melt; and even so, such a short time for the solution of alumina or other refractory materials is available after any melting which occurs that they are not adequately dissolved. The addition of a material such as cryolite, capable itself of forming inclusions if not melted and floated to the surface of the metal, simply increases the total quantity of inclusions likely to be trapped in the solidified skin and the center of the ingot.

It is an object of this invention to avoid these difficulties, and to provide a method of casting ingots in which the quantity of skin inclusions is very greatly cut down. It is an object of this invention to provide a method of casting ingots in which center laminations and the total quantity of inclusions are not increased in spite of a noticeable reduction in the number of skin inclusions in the rolled product. Hence an object of our invention may be broadly stated to be the casting of more perfect ingots.

These and other objects of our invention which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications, we accomplish by that procedure of which we shall now describe an exemplary embodiment.

In the practice of our invention, we employ a flux capable of forming with refractory impurities a slag which has a lower specific gravity and a lower melting point than iron; but we employ it in such fashion that its melting is assured together with sufficient time for the solution by it of the refractory materials; and we employ it in such a way that its tendency to cool the iron and hence to promote more rapid freezing is greatly minimized. To this end we add to our flux materials capable of generating heat spontaneously. In general, these materials comprise a fuel and an oxidizing agent. The addition of such materials along with the flux is not, however, sufficient in itself. As will hereinafter be set forth, it is necessary that the flux be proportioned to the heat forming materials in view of the casting practice and the temperature at which the metal is teemed. Also the quantity of flux should be proportioned to the impurities in the metal being teemed. By carefully controlling all of these factors we have succeeded in commercial operation in producing ingots having a notably reduced quantity of skin inclusions without an increase in those ingot defects resulting from center inclusions and center laminations in the rolled product, all as we shall now set forth in detail.

Various compositions may be employed as the oxidizing agent, the nitrates being cheap and available. Our preference among them is for sodium nitrate because, after reaction, it becomes...
sodium oxide, itself a powerful flux. Other nitrates may, however, be employed such as potassium nitrate, as well as other inorganic compounds capable of giving off oxygen at high temperatures, such, for example, as the chlorates, peroxides, perborates, perchlorates, and the like.

As fuels, we prefer to use carbonaceous substances where permissible, such as carbon itself or hydrocarbons such as tar and asphalt. These latter substances are advantageous since they are capable of acting as binders. For treating ferrous materials to which carbon may not be added, we employ non-carbonaceous fuels as hereinafter set forth.

For a given fuel, the ratio of fuel quantity to the quantity of oxidizing agent should be fairly constant, and is conveniently determined by ascertaining the ratio necessary to produce maximum heat. For example, a mixture of sodium nitrate and lampblack produced approximately the maximum temperature where 3 parts by weight of sodium nitrate were used with 1 part of lampblack, according to the chemical reaction:

$$5C + 2NaNO_3 = 5CO + Na_2O + N_2$$

Again, and in a similar fashion, where asphalt is the fuel, 13 parts of this substance to 37 parts of sodium nitrate is expressive of a ratio giving maximum heat of combustion, in accordance with a formula such as the above in which (C.H.) is substituted for C.

Various amounts of fluxing material can be added to such an optimum mix. But since the flux will exert a cooling effect on the mix, the actual temperature attained upon combustion can be controlled to a very large extent by varying the ratio of the flux to the heating mixture while keeping the ratio of oxidizing agent and fuel constant in the latter.

When the ingot scum is largely alumina or aluminum silicate, cryolite (AIF₃.NaF) is one of the most active solvents or fluxes which may be used. For aluminum treated steels, an excellent composition is 13% asphalt, 37% NaN₃ and 50% cryolite, the percentages being by weight. The amount of cryolite may be varied while the ratio of NaN₃ to asphalt is maintained constant. This will vary the heat producing properties of the mixture. Since the effective temperature attained by the mixture is also affected by external temperature conditions, e.g. the heat in the metal being teemed, the amount of flux which can be melted thoroughly and instantaneously by any given quantity of the fuel-oxidizing agent mixture will vary to some extent with such conditions. We have, for example, successfully used mixtures containing 77% asphalt, 22% NaN₃ and 5% cryolite, all by weight.

Other ingredients than cryolite, asphalt and sodium nitrate can be used. The employment of non-carbonaceous fuels is advisable when the mixture is to be employed in the formation of ingots of stainless steel. We are not limited as to the mixture, with the titania being many substances which can be employed for the purposes of this invention. The nature of the metal being cast into ingots should be considered in connection with the composition of our mixture. By way of an example, in stainless steel which has been stabilized with titania, the source of titania is aluminum oxide and titanium oxide or nitride. A flux which has a high dissolving power for such compounds, e.g. soda ash, is selected and a fuel of non-carbonaceous nature, such as powdered ferro manganese is used. Even metals in a reduced and finely divided state may be employed in our mixtures instead of carbon or hydrocarbons.

In forming our mixtures all of the ingredients are finely powdered and are thoroughly mixed. In our practice with the cryolite mixture given above, the asphalt and cryolite are powdered to the extent that all of these materials will pass through a screen of 100 meshes to the inch. The sodium nitrate may, however, be used in granulated form.

Our mixtures may be used as thoroughly mixed powders; but it is frequently more convenient to use them in various associated forms. When asphalt or tar is used as the fuel, benzol or other suitable solvent may be employed to distribute the asphalt through the mix, forming a paste. This paste is then dried in an oven and finally crushed or granulated so as to pass a 20 mesh screen. Our mixtures may also be compressed into briquettes of a size which may vary from one to another. The briquettes may be made by a number of methods. The mixture may be moistened with water, briquetted by any suitable pressure briquetting machines and then dried at a suitable temperature. Where tar or asphalt is present, a temperature may be used at which these hydrocarbons melt and distribute themselves throughout the mixture, forming, when cool, hard dense briquettes capable of being handled without crumbling.

Our mixtures may be added to the molten metal during teeming in various ways. We prefer to feed our mixtures by means of a funnel-shaped feeder to the stream of molten metal as it flows into the ingot mold and to continue the addition throughout the operation of teeming. It is possible to introduce the mixtures into the ingot mold prior to teeming but this is not preferred since it is likely to result in violent and non-homogeneous activity. However, with briquetted mixtures it is quite feasible to add all of the mixture to the ingot mold before or soon after the teeming is started, as distinguished from proportioning the addition of mixture to the stream throughout the teeming.

As soon as the mixture of oxidizing agent, fuel and flux strikes the stream of molten metal, the fuel and oxidizing agent combine with the evolution of considerable heat, melting or assisting in the melting of the flux. The increased time during which the flux is molten and active (prior to the freezing of the skin) allows the flux to dissolve more and larger particles of alumina, silica or other refractory oxides and remove them from the portion of the ingot being chilled to form a skin against the ingot mold. By the practice of our process in commercial operations we consistently attain a reduction in skin laminations in our ingots of 50% or more.

The addition of our mixtures to a metal being teemed is proportioned to the amount of ingot scum which are likely to be formed by the metal composition and teeming conditions so as to promote efficient fluxing. By way of a single example, in an aluminum killed medium carbon drawing steel containing .03 to .05% metallic aluminum we added to the metal being teemed in each lot of 12,000 lbs. of the first cryolite mixture given above, the ingots being of the order of 12,000 lbs. In weight and 23 by 37 inches in cross section at the top. Temperature has an important effect upon the
internal cleanliness of killed steel, and cold heats, i. e. heats in which the metal in the teeming ladle is at a relatively low temperature, tend to be dirty. This effect is exaggerated by the use of our mixtures principally because there is more material to be floated out of the ingot prior to the freezing of the metal. Thus experience has shown that, all other conditions remaining the same, the addition of our mixtures to killed steel during the casting or ingots decreases the number and extent of skin laminations in the rolled production, but on the other hand, tends to increase to a limited extent the number of center laminations. The latter effect may be avoided, however, by increasing the temperature at which the metal is teemed. We prefer, therefore, to accompany the use of our mixtures by an increase in the temperature of the heats with which it is employed.

It is not, however, necessary to adhere to specified temperatures. At temperatures at which killed steel is ordinarily teemed in good commercial practice, e. g. 2860° F. to 2875° F. as measured by an optical pyrometer corrected for molten steel emissivity, the use of our materials as herein taught will produce a marked and useful decrease in skin laminations without producing an important increase in center laminations. As the teeming temperature is progressively lowered the tendency toward center laminations increases, slowly at first, and then more sharply. At temperatures higher than about 2880° F. we have succeeded in general in effecting a great reduction in skin laminations without increasing center laminations at all. At still higher temperatures a consistent reduction in both skin and center laminations is attained. In our commercial work we endeavor to teem the metal at as high a temperature as is consistent with good commercial practice for the metal being teemed and for the available furnace and teeming equipment.

Modifications may be made in our invention without departing from the spirit of it. Having thus described our invention in certain exemplary embodiments, what we claim as new and desire to secure by Letters Patent is:

1. A method of casting ferrous ingots which comprises teeming molten metal into an ingot mold and adding to the ingot mold not later than during the early part of the teeming an exothermic substance comprising a fuel, an oxidizing agent and a flux for refractory impurities of the metal, said ingredients being in intimate admixture with each other, the quantity of fuel and the quantity of oxidizing agent being in substantially molar proportions to produce substantially maximum temperature upon combustion, and the quantity of flux being related to the total quantity of fuel and oxidizing agent to be very rapidly melted thereby when in contact with the molten metal being teemed.

2. The process of claim 1 wherein the flux is soda ash and the fuel is ferro-manganese.

3. The process of claim 1 wherein the flux is soda ash and the fuel is ferro-manganese, and wherein the metal being teemed is a stainless steel containing titanium.

4. A method of casting ferrous ingots which comprises teeming molten metal into an ingot mold and adding to the ingot mold not later than during the early part of the teeming an exothermic substance comprising a fuel, an oxidizing agent and a flux for refractory impurities of the metal, said ingredients being in intimate admixture with each other, the quantity of fuel and the quantity of oxidizing agent being in substantially molar proportions to produce substantially maximum temperature upon combustion, and the quantity of flux being related to the total quantity of fuel and oxidizing agent to be very rapidly melted thereby when in contact with the molten metal being teemed, and maintaining the temperature of the metal being teemed at a value inhibiting an increase in center laminations in the ingot.

5. A process of casting ingots of aluminum killed steel which comprises teeming the metal into ingot molds and adding to the metal not later than during the early stages of teeming a granular exothermic mixture comprising by weight substantially 13% bitumen, substantially 37% sodium nitrate, and substantially 50% cryolite.

6. A process of casting ingots of aluminum killed steel which comprises teeming the metal into ingot molds and adding to the metal in the mold during at least the early stages of teeming a mixture comprising by weight substantially 13% bitumen, substantially 37% sodium nitrate, and substantially 50% cryolite, and in which mixture the said ingredients are in finely divided form and intimate admixture, with the bitumen distributed substantially uniformly throughout the mass.

7. As a material for the purpose described an intimate admixture of substantially 13% asphalt, substantially 37% sodium nitrate, and substantially 50% cryolite, all percentages by weight.

8. An intimate admixture of substantially 13% asphalt, substantially 37% sodium nitrate, and substantially 50% cryolite, all percentages by weight, said material being in briquetted form.

9. As a material for the purpose described, an intimate admixture of asphalt in an amount substantially 7% to 13%, sodium nitrate in an amount substantially 22% to 37%, and cryolite in an amount substantially 50% to 70%, all percentages by weight.

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