Patented Jan. 30, 1934 1,945,260

UNITED STATES PATENT OFFICE

1,945,260

COMPOSITION OF MATTER AND PROCESS OF TREATING MOLTEN METALS

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No Drawing. Application March 7, 1932
Serial No. 597,415

21 Claims. (Cl. 75—48)

The present invention relates to a new composition of matter for and a method of treating metals when in molten condition. As pointed out in application Serial No. 275,265, of which this application is in part a continuation, and in application Serial No. 253,781, of which this application is also in part a continuation, one object thereof has been to provide a composition or combination of substances which when used in connection with or introduced into a mass of molten metal in predetermined quantities and under proper conditions according to his method will produce an ultimate product of definitely superior character and quality. For example, when his improved composition is used in producing iron and steel, the resulting metal possesses a novel and highly beneficial even distribution of all its elements and the amalgamation thereof in a substantially homogeneous mass. A very active beneficial effect accompanies the use of his improved composition which operates in part as a scavenging agent to eliminate or reduce the undesirable impurities and imperfections commonly encountered in commercial metals.

What he has referred to as the beneficial effect is in his opinion produced by the combined action of potassium chlorate and manganese dioxide, while the scavenging effect is produced by borax or boracic acid and/or sodium fluoride and/or soda ash. For the treatment of ordinary ferrous metals in which the characteristics vary chiefly with variation of the carbon content, he uses a mixture of the above ingredients in the following proportions:

	Pounds
Potassium chlorate	3 to 5
Manganese dioxide	¼ to 1
Borax and/or boracic acid	½ to 4
Soda ash and/or sodium fluoride	½ to 2

In preparing his composition of matter for commercial use, he prefers to reduce the ingredients while in a dry state substantially to a powder of the fineness of 120 mesh. It is not essential that so fine a reduction be effected, but the action of the composition is more rapid and more widely distributed where the particles thereof are reduced to a relatively minute size. The charge can be administered in powdered form or in any other desired or convenient form, such as briquettes, packages or otherwise. However, he prefers to package predetermined amounts of the mixture in suitable containers such as metallic capsules, cans or cartridges, or in bags or cartons of paper or cloth to which a coating of paraffin or other moisture-resisting material is applied on the outer surface thereof. This tends to retain the powdered materials in practically dry condition and protects them from accidental wetting such as might easily take place in and about a large manufacturing plant or in transportation.

His composition may be introduced into the molten mass in various ways with favorable results. He prefers, however, in large iron and steel operations to confine appropriate quantities of composition in metallic containers or capsules which may be of gray iron or other suitable material. With gray iron a wall thickness of approximately ¼ inch is desirable. To treat a mass of molten iron or steel in the ladle, he presses a charge-carrying capsule down through the mass to an underlying or bottom portion thereof and holds it there until the capsule disintegrates or is about to disintegrate. Thereupon the active charge is released into the metal. Important results are observed even where the composition is introduced by different methods as by dumping or depositing in loose form into the molten mass, throwing it into the ladle of metal in packages or briquettes, or securing a confined quantity in the ladle prior to pouring.

From the foregoing description, it will be apparent that no unusual technical difficulties are involved in the use of his improved composition. Iron and steel produced by methods which utilize this composition present a number of distinguishing and advantageous properties and characteristics over products of normal contemporary manufacturing practice. With the use of his invention these products are substantially free from occluded gases, free oxides and/or manganese sulphide, slags, segregations, piping and blow holes, and display a homogeneous, small close grain texture. Furthermore, by varying the ratio of elements in the composition and/or the amount of composition utilized, he is able to control the sulphur and phosphorus content as well as the carbon content of a ferrous product. Other valuable and important advantages result directly or indirectly from the use of his composition either by reason of the characteristics of the improved metals produced, the simplification of the operations involved in their production, or both.

In the practical application of his invention, he is able to improve and to advantageously and effectively control or maintain the character of the product at or through any stage in the process of manufacture where the metal attains a molten or mushy plastic condition. In producing the most widely used types of ferrous products, the metal usually is melted in one or more of the following:

1. Blast furnace
2. Cupola
3. Air furnace
4. Bessemer converter
5. Open hearth
6. Crucible
7. Electric furnace.

In blast furnace practice a widely varying range of improved results is is secured by the use of his method depending in part on the nature of the raw material, the conditions under which it is melted, the composition and/or quantity of his controlling charge, the temperature at which the charge is introduced or at which successive charges are introduced where they are used at intervals in the same heat, and other factors involving most of the variables encountered in this complex art. For example, he secures more rapid melting of the ore and an improved product where he introduces with each increment of ore as it is fed into the stack a composition of matter which may for convenience be referred to as a "controlling charge" and which for this particular operation comprises relatively concentrated agents as potassium chlorate and manganese dioxide and scavenging agents as borax and/or boracic acid and sodium fluoride and/or soda ash in the following proportions:

	Pounds
Potassium chlorate	3
Borax and/or boracic acid	2
Sodium fluoride and/or soda ash	2
Manganese dioxide	1
Total	8

Potassium chlorate and manganese dioxide are referred to herein as "concentrated deoxidizing agents" because of what seems to be deoxidizing effect produced by them and he uses the term with the understanding and explanation that further research may suggest its inaccuracy or insufficiency. A similar explanation is offered with respect to his use of the term "scavenging agent". Beneficial results are observed where this charge, hereinafter identified as #1, is introduced in a varying ratio of 1 to 3 pounds to a ton of metal in the form of hematite ore between each increment of metal and an increment of flux. The ratio variation depends in part on the character of the ore, the ultimate product desired, and the amount of ore treated at the same time. In general, the amount of charge per ton diminishes as the tonnage treated increases. In a typical furnace approximately 90 feet in height and operated under normal conditions, a given increment of metal will reach the hearth in molten condition about 15 hours after it is dumped into the top of the stack. Where his controlling charge is used and other conditions remain the same, this time may be cut down by 1 to 3 hours, thus increasing the effective capacity of the furnace. Furthermore, his method produces a uniformly superior pig iron or, more strictly a new type of cast iron having properties never before controllably attained in ferrous metal in commercial amounts at the pig iron stage.

The quality of the ferrous product of the blast furnace is also materially improved by the use of his controlling charge in the hearth either after its previous introduction as above described or where such a charge has not been used. When applied to the molten mass in the hearth, he employs the same composition as before, namely charge #1 and in the same quantitative ratio to the amount of metal in the hearth. The observed operating results are a temporary violent reaction and a substantial rise in the temperature thereof persisting for a considerable time after the agitation has ceased. The amount of controlling charge to be introduced at any one time is limited somewhat because of the violence of the reaction and should therefore be sufficiently small to maintain safe working conditions. In hearth and other treatments, it is possible to introduce repeated charges from time to time depending on the metal content, container size and the quality of product desired. Each application of the charge has the effect of creating and maintaining over substantial periods an increase in the temperature and in the fluidity of the metal so that tapping is greatly facilitated. The range of temperature increase has not been determined but increases up to 500° Fahrenheit have been observed. The product may be run off into ladles or mixers for further treatment or directly into pigs, ingots or castings, as desired. By further additions of the charge to the molten metal whether in ladle or mixer, its carbon content can be controllably reduced through the whole gamut from cast iron down to low carbon steel and without the further application of heat from external sources or the intervention of physio-chemical or mechanical operations now commonly utilized in iron and steel production.

One novel product which he derives directly from the original melting of ore in the blast furnace by his process is a ferrous metal of the nature of iron and characterized in part by castings thereof in any size having the property of malleability without heat treatment, even where the carbon content exceeds 2.20%. The term malleability is used here to identify that property by which so-called "malleable iron" is distinguished from "hard iron". This figure is given on the authority of Stoughton, in "The Metallurgy of Iron and Steel", Third Edition, page 5, and he uses it for the purposes of this specification to indicate the approximate dividing line between iron and steel or the approximate proportion of carbon in known ferrous metals beyond which malleability as a property of carbon steel ceases.

To avoid the repetition involved in pointing out all the distinguishing features of each of the variously identified ferrous products resulting from the practice of his method as compared with corresponding known products, it is here noted that in general they all have the following in common; substantially

No occluded gases,
No free oxides and/or manganese sulphide,
Controlled sulphur and/or phosphorous and/or manganese content, and
Controlled carbon content.

His theory is that the potassium chlorate and the manganese dioxide produce what appears to be an intense deoxidizing effect and apparently other chemical reactions in the molten or mushy plastic mass, while borax and sodium fluoride, and/or soda ash as scavenging agents combine with or otherwise liberate impurities and bring the oxides, surplus cementites and pearlites, manganese sulphide, sulphur, phosphorus, graphitic carbon and other undesired substances or gases to the top where they are taken up in the slag or pass off in fumes. Whatever may be the chemical or physio-chemical reactions in the molten mass, castings taken therefrom exhibit among others the following physical properties when subjected to microphotographic inspection with well known apparatus: substantially

Homogeneous small grain texture,
No piping, blow holes, or gas pockets, and
No segregations.
Freedom from hard and soft spots.

Other methods of testing indicate greater

Specific gravity,
Tensile strength,
Elongation,
Ductility, and toughness,

than ferrous products derived from the same material but not treated according to his method. It is possible that more exhaustive investigation of his improved product will disclose distinctive features therein in respect to crystalline structure and/or relationship or novel molecular or other phenomena which will explain in whole or in part the presence in his product of the highly desirable properties or characteristics hereinabove set forth, as well as others which have been or may be noted under wider and more varied conditions of use.

Gray iron foundry practice

He will now consider the application of his method to gray iron foundry practice which centers around the treatment of ferrous metal in the cupola and air furnace. Here again, where charge #1 is introduced into the cupola or furnace with the pig iron and/or other metal, he uses 1 to 3 pounds thereof with each ton of metal. The melting time is measurably shorter than when no controlling charge is used and the iron comes down very hot and fluid so that initial tappings come off hot and a uniform product is produced throughout the run. Another beneficial result observed in connection with the use of his method is that the cupola or furnace lining is preserved as the melt progresses instead of being rapidly destroyed as is the case where present methods only are employed. This same result is effected in any furnace, ladle, or the like where the charge is used.

Further and more accurate control of the product is attained by introducing charge #1 in the ladle whether the charge has been used in the cupola or not. A collateral but almost equally important result thereof is that the metal in the ladle can be maintained over extended periods of time in a free pouring fluid condition without applying external heat by repeating charge #1 at proper intervals. Here again, the amount of a given charge and the interval between successive applications thereof will depend upon a number of factors such as those referred to in connection with the control of metal in the ladles or mixers appurtenant to the blast furnace. In cupola practice ladle treatment alone is sufficient and preferred where the amount of metal is 500 pounds or less. He uses a charge of 2 to 3 pounds of #1 for 1 ton of metal and decreases the quantity of additional charges, if used, as the quantity of metal in the ladle is diminished by pouring or otherwise.

The product according to his invention is superior to gray iron made by any other method with which he was familiar. Metal which if poured from the ladle untreated would show a tensile strength of 3000 pounds is raised to a tensile strength of 10000 pounds by the use of his controlling charge in the ladle. It also possesses the other desirable qualities hereinabove set forth, machines to a finish not unlike that of nickel steel, and presents very marked rust-resisting properties. His improved metal is of uniform hardness throughout, is very resistant to shock, and is in condition for machining without annealing, an example being that screw threads are turned on the unannealed casting stock without chipping or crumbling.

It is contemplated that in some cases it will be desirable to secure effective application of his composition to the metal by having the essential ingredients thereof incorporated in a coating applied to the lining of the ladle, hearth, or other container, or applied to or coated on the exposed surface of said lining in position to be in contact with the molten metal therein.

One of the broad effects of the application of his method to iron and steel manufacture is that the products of different operations more closely resemble each other than the products of corresponding operations according to known methods. This is true of cast iron and so-called malleable iron. His product of high carbon content, namely over 2.2% inherently has the malleability characteristic of malleable iron without annealing so that special melting and annealings are not essential to the making of malleable iron. However, in plants where malleable iron has been manufactured from metal melted in air furnaces or otherwise or where for other reasons air furnace melting is preferred, his method is effective in producing a superior product. For example, the #1 charge may be put into the air furnace with the pig iron and/or other metal in the ratio of from 1 to 3 pounds to a ton of metal, or the #1 charge may be introduced into the ladle if desired. Where the charge is applied in the furnace, there are important and advantageous operating results such as material reduction in the time of melting, free flowing metal and substantially uniform quality of product. Either way, however, he produces sharp castings of homogeneous metal substantially free from slag oxides and occluded gases. The tensile strength, bending strength, and other factors of this malleable iron are superior to known grades of malleable iron without annealing or other heat treatment.

Steel castings—Foundry practice

His invention produces particularly important and valuable results in its application to the making of steel castings, those of so-called low grade carbon steel being now considered. The #1 charge hereinabove described is introduced into the molten metal at any desired stage, in the open hearth furnace, converter or ladle, or in any one or all of them. When used in the furnace in the ratio of 1 to 3 pounds of charge to 1 ton of metal, violent agitation and material rise in temperature are observed. Furthermore, the time of heating is reduced, for example, in a heat of 90 tons, by 1 to 2 hours. The metal as tapped runs to the ladle in a free flowing stream of uniform color. Inasmuch as each charge has an effect on the carbon, sulphur, manganese, and phosphorus, the proportion of these ingredients in the product may be accurately controlled by the number and/or amount of the controlling charges administered. It is his theory that carbon, sulphur, manganese and phosphorus whether free or in solution or combination in the molten metal are released and removed either in liquid or gaseous combination in such a way that excess amounts of these ingredients are not permitted to remain in non-combined or other detrimental form on crystallization of the mass. He does not commit himself to the foregoing theory inasmuch as further research may disclose a more accurate or plausible explanation of the reactions which take place and which seem to bear a casual relation to some or all of the observed superior properties of his metal product.

When metal treated as above indicated, is poured into molds it flows freely and quietly. In simple castings, risers may be eliminated because the metal solidifies in the mold as a homogeneous mass substantially without piping, occlusions, blow holes, segregations or other imperfections which occur almost universally in the casting of steel. His improved cast metal shows no hard and soft spots on fracture and machines evenly and easily to a fine finish. The metal of these castings shows its superiority over known steel of approximately the same derivation and chemical analysis in its superior tensile strength, ductility and toughness. For example, castings containing .14 to .18 carbon and made according to his invention showed a tensile strength of 65000 pounds as against 52000 pounds for castings from the same heat but not subjected to the action of charge #1. Furthermore, castings of his improved steel, regardless of carbon content have malleability and ductility with a very fine grain structure comparable to that of steel after hot or cold working. There is here an apparent contradiction between the hardness of the metal and its workability at high temperatures. Another feature of his improved steel is that it may be raised to and maintained at white heat without "burning". This permits working under advantageous conditions because the piece being worked remains plastic for a longer time, besides having a very high initial plasticity.

The exact crystalline or other structural features of his improved steel which might explain the properties referred to above are not definitely identified, but, so far as resistance to burning is concerned, his theory is that the metal is substantially free from the occluded gases which in ordinary steel of corresponding grade become superheated at white heat and break down and through the surrounding metal structure. In general, small grain size is usually associated with rapid cooling, but with his improved steel of small grain size the casting remains red much longer than a casting of the same size made of the same material without his process. This phenomenon indicates possibly a continued heat evolving molecular action down through the critical temperatures and the absence of piping and segregations suggests a complete amalgamation of all ingredients with practically no free or uncombined inclusions and no substantial interruption of the close-knit crystalline structure. This metal machines evenly and at least as readily as annealed steel of equivalent carbon content.

Steel mill practice

As previously stated, #1 charge is introduced at any desired stage of the melting operation and its beneficial results are far reaching in steel mill practice where the metal, initially in the form of ingots, is rolled or otherwise reduced to plates, bars, rods, wire or the like. In addition to the advantages previously pointed out, his method eliminates losses in time and material which are now a serious burden on mill operation. The treated metal flows freely at a high temperature, cools slowly and contracts uniformly in the ingot mold. The resulting ingots are substantially free from pipes, occlusions and segregations and require no special machinery to separate them from the molds. Probably the most important factor is the homogeneous quality of the metal throughout the ingot which insures a low percentage of waste or scrap. In rolling operations, these ingots may be heated much higher than the ordinary ingot due, according to his previously suggested theory, to their freedom from occluded gases and/or other uncombined ingredients which at high temperatures appear to promote burning of the metal.

From the foregoing, it is apparent that his method is capable of widely extended application to the making of iron and steel, and references to particular operations or apparatus are not intended to suggest a limitation in that respect. For example, he has not described the operation of his method in connection with puddling, electric furnace practice, die casting, centrifugal casting and many other branches or phases of the iron or steel industry. Wherever used in this field, a unique product will be produced. For example, charge #1 was introduced in the ladle after melting in an electric furnace. His metal showed over 56% greater tensile strength, 3.7% greater elongation in 2 inches, and over 450% greater area reduction in 2 inches with an increase of .02% carbon and manganese and .002% lower sulphur and phosphorus. The metal is a seeming anomaly in that ductility increases with carbon content and tensile strength. So far as he knew, there is no carbon steel in regular practice which shows this phenomenon and he considers it a novel and highly useful product. To illustrate, he gives the following comparative analysis, column A being of a steel according to regular practice and column B being of a specimen of his improved steel taken from the same heat:

	A	B
Carbon	.36	.38
Manganese	.46	.48
Silicon	.36	.36
Sulphur	.036	.034
Phosphorus	.039	.037
Tensile strength	27,000 lbs.	42,280 lbs.
Elongation in 2 inches	0	3.7
Reduction in area 2 inches	.8	4.47

Other tests show that a similar unusual relationship exists between the properties of tensile strength and ductility in different varieties of his improved metal and it may therefore readily be identified by its great ductility where ordinary carbon metal under the same conditions would be relatively brittle.

In practice, wherever the charge is introduced in the ladle, he preferred to divide it and introduce substantially equal parts at different stages while the ladle is being filled, for example, in a 40-ton heat ⅓ of the charge into the first 10 tons, ⅓ after the pouring of the next 10 tons and the remaining third after the pouring of the third 10 tons.

In the practice of his method as described thus far, he was able to maintain in predetermined relative proportions the ingredients forming the molten mass in a given heat within practical limits. By varying the charge in some respects, he was able also to controllably vary the proportions of the ingredients in the molten mass. For example, assuming that a test from the heat indicates a sulphur content of .04% and it is desired to reduce the sulphur to .03 without diminishing the carbon content, he adds to the #1 charge 1% by weight of potassium chlorate and manganese dioxide, the amounts of these additional ingredients, of course, depending upon the amount of metal to be treated. When a charge including this additional percentage of potassium chlorate and manganese dioxide is introduced into the molten metal, the usual violent reaction is observed and the sulphur and phosphorus contents are substantially reduced without reduction of the carbon content.

He has previously referred to the physical characteristics of his improved metal which suggest a complete amalgamation of all the ingredients thereof. He uses this term to distinguish his metal from the ordinary ferrous metal in both molten and solidified conditions. There is reason to believe that his method of treatment brings about the intimate combination of all of the ingredients of the metal with these ingredients evenly distributed throughout. This phenomenon is indicated by the fact that the molten metal presents a uniform color during pouring, whereas ordinary ferrous metal exhibits a variety of colors during this operation. Furthermore, whatever may be the degree or character of the combining of the ingredients of ordinary ferrous metal in the molten state, it presents substantially inhomogeneity after solidification. The homogeneous character and uniformly small grain size of my metal in castings together with the other phenomena observed in connection therewith, leads him to conclude that an initial amalgamation of the elements of the metal takes place during his method of treatment and persists down to and through the solidifying stage. In this sense, he considers it a part of his invention to combine the elements of the molten metal in such a way that they remain in a permanent amalgamation.

What is claimed is:

1. A composition of matter for use in metallurgical operations comprising alkali metal chlorate, a boron compound, sodium carbonate and manganese dioxide.

2. A composition of matter for use in the treatment of molten metals comprising alkali metal chlorate, manganese dioxide and a scavenging agent including sodium carbonate.

3. A composition of matter for use in metallurgical operations comprising potassium chlorate, boracic acid, soda ash and manganese dioxide.

4. A composition of matter for use in metallurgical operations comprising 12 to 20 parts of potassium chlorate, 2 to 8 parts of boracic acid, 2 to 8 parts of soda ash, and 1 to 4 parts of manganese dioxide.

5. The process of treating molten metals including subjecting the molten metal to the action of a mixture of an alkali metal chlorate, manganese dioxide, and a scavenging agent including sodium carbonate.

6. The process of treating molten metals including subjecting the molten metal to the action of a mixture of alkali metal chlorate, borax, alkali metal carbonate and manganese dioxide.

7. The process of treating molten metals including subjecting the molten metal to the action of a mixture of potassium chlorate, manganese dioxide, sodium carbonate and borax.

8. The process as in claim 5 wherein the molten metal is a ferrous metal.

9. The process as in claim 6 wherein the molten metal is a ferrous metal.

10. The process as in claim 7 wherein the molten metal is a ferrous metal.

11. A composition of matter for use in the treatment of molten metals comprising alkali metal chlorate, manganese dioxide and a scavenging agent including soda ash and sodium fluoride.

12. A composition of matter for use in the treatment of molten metals comprising alkali metal chlorate, manganese dioxide, borax, soda ash, and sodium fluoride.

13. The process of treating molten metals including subjecting the molten metal to the action of a mixture of an alkali metal chlorate, manganese dioxide and a scavenging agent including soda ash and sodium fluoride.

14. The process of treating molten metals including subjecting the molten metal to the action of a mixture of an alkali metal chlorate, manganese dioxide, borax, an alkali metal carbonate and alkali metal fluoride.

15. The process of treating molten metals including subjecting the molten metal to the action of a mixture of an oxygen liberating agent, borax, sodium fluoride and soda ash.

16. The process as in claim 13 wherein the molten metal is a ferrous metal.

17. The process as in claim 14 wherein the molten metal is a ferrous metal.

18. The process as in claim 15 wherein the molten metal is a ferrous metal.

19. The process of treating molten metals including subjecting the molten metal to the action of a mixture of an alkali metal chlorate, manganese dioxide, and at least two from the group comprising the following, borax or boracic acid and sodium fluoride or sodium carbonate.

20. The process of treating molten metals including subjecting the molten metal to the action of a mixture of an alkali metal chlorate, manganese dioxide and boracic acid and sodium fluoride.

21. The process of treating molten metals including subjecting the molten metal to the action of a mixture of an alkali metal chlorate, manganese dioxide, boracic acid and sodium carbonate.

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