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METALLURGICAL SCAVENGER AND METHOD OF MAKING SAME

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My invention relates to improved forms of compounds employed in metallurgical operations for cleansing and improving metals when added thereto while such metals are in a molten state, such compounds being adapted to combine chemically with the impurities of the molten metals to form compounds including slags that rise to the surface of the underlying molten metal. More particularly, the objects of my invention are, among other things, the production of mechanical mixtures of titanium carbide or zirconium carbide or both with iron in briquetted forms that are especially adapted for introduction into the molten metal bath to cleanse such molten metal of its impurities.

In the treatment of metals, such as molten iron or steel, with minor quantities of other metals or alloys or compounds thereof to effect either an alloying of the major with the minor metal or a cleansing of the major metal by virtue of the scavenging effect of the minor metal upon impurities in the major metal, it has formerly been the practice to use so-called alloys prepared principally in the electric arc furnace, such as alloys of titanium with iron, or alloys of zirconium with iron.

In the preparation of titanium alloys, such as ferro-carbon-titanium made according to United States Patents to Rossi and Meredith No. 1,039,672 of September 12, 1912 and No. 1,094,022 of April 21, 1914, it has been found difficult or impossible to have the carbon content as low as desired due mainly to the fact that the fused charge tends to take up and become supersaturated with carbon; the result is that commercial ferro-carbon-titanium as prepared according to these patents contains about twice as much carbon as would be combined with titanium as the carbide (TiC). The following is a typical analysis of the ferro-carbon-titanium of commerce:— Titanium about 16%, carbon about 8% and the balance about 76% comprising chiefly iron and other substances.

Although this ferro-carbon-titanium is entirely suitable for many purposes, it has long been recognized that if an alloy containing about 16% of titanium, 4% or less of carbon with the balance iron could be produced, it would find extended application in the treatment of certain grades of iron where it is required that the carbon be kept as low as possible, and in which the normal content of carbon in ferro-carbon-titanium is objectionable.

So far attempts to produce by fusion or melting in the electric arc furnace, a ferro-carbon-titanium alloy containing, say 16% of titanium and less than 6% carbon, have not been successful, and at present it is not indicated that an alloy containing the desired low percent of carbon may be obtained by this Rossi and Meredith process which specifies, among other things, that sufficient carbon should be present to ensure such uncombined carbon content as may be desirable.

In working on this problem I conceived the idea of preparing a mechanical mixture of titanium carbide, TiC, with iron, in form of briquettes in such a manner as to produce suitably sized briquettes containing for example, the following constituents:

	Per cent
Titanium	16
Carbon	4
Iron (and others)	80
	100

My conception of the metallurgical phases involved is as follows:—

The common ferro-carbon-titanium contains two forms of carbon, namely, carbon as combined with titanium, and carbon in the graphitic form. I believe that the carbon combined with the titanium may not leave any residual carbon in the metal with which it is treated, while the free carbon probably remains with the treated metal and serves to increase the carbon content thereof. My belief is predicated on the fact that in dissolving the usual form of ferro-carbon-titanium in acids, about one-half the carbon remains as a black residue, while approximately one-half the carbon content passes off directly as a gas. Titanium carbide (TiC) as well as zirconium carbide (ZrC), dissolve to a perfectly clear solution in acids, but if dissolved or free carbon be present, such carbon remains as a black residue.

Therefore I understand that in scavenging or in alloying operations, the carbon combined with the titanium, etc. probably is yielded readily and passes off as a gas, while the free carbon may undesirably remain in the metal treated. Either titanium or zirconium carbide has too high a melting point and dissolves too slowly in the metal bath to serve effectively as scavengers or as alloying substances, and, if used as a powder, the loss would be excessive.

According to my invention I have discovered that by preparing a briquette of the titanium carbide and iron, a metallurgical scavenging product is produced which remains in the molten bath, and, as the iron melts, the carbide particles act upon the impurities, and a scavenging effect is produced without the incidental introduction of excess carbon which accompanies the use of ferro-carbon-titanium prepared by the Rossi and Meredith methods.

In preparing my new product, I crush the carbide of titanium or zirconium to suitable fineness and then mix it in suitable proportion with iron metal powder, using a small amount of a suitable bond such as a sodium silicate solution,

natural gums, glue, dextrine and synthetic plastic or resinous materials, forming a mix of suitable consistency for pressing, and then compact same by pressing to form a sufficiently hard, coherent mass consisting of a mechanical mixture of, for instance, titanium carbide, iron and a binder substance. Zirconium carbide may be substituted for the titanium carbide with similar results.

The following example will serve to illustrate how a titanium carbide iron briquette is made:—

Example A.—Titanium carbide is crushed to obtain a product passing through forty mesh, while the iron is prepared to pass 40 mesh. The iron is preferably prepared by the sponge iron process by heating a mixture of 100 parts of —10 mesh magnetite and 60 parts of 20 mesh coal under reducing conditions at temperature of about 1050° C. for six hours, cooling the charge out of contact with air, and then crushing to —40 mesh and removing the excess carbon and other substances from the iron by suitable concentrating treatment, such as magnetic separation.

A mixture is then made as follows (parts by weight):—

	Parts
40 mesh titanium carbide	100
40 mesh iron metal	400
Sodium silicate solution 1.30 sp. gr.	75
Total	575

This charge is thoroughly mixed to a consistency suitable for pressing by using only enough binder to serve as bond, and the charge is then pressed into briquettes of suitable size and dried to expel the water.

In use in treating molten metals, the briquettes of any suitable size are added at the desired point in the process, usually at the ladle, in an amount sufficient to accomplish desired results.

The grain or granule size of raw materials used in process of making the briquettes may vary widely as also the proportions of titanium carbide and iron. In this example the product contained approximately:

	Percent
Titanium	15.13
Carbon	3.78
Iron and other compounds	75.72
Sodium silicate bond	5.37
	100.00

The titanium carbide might be materially increased or lowered, if a product richer or leaner in titanium were desired.

Zirconium carbide briquettes may be similarly produced by the methods of Example A.

A zirconium carbide iron briquette would have the following approximate composition when made from zirconium carbide (100 parts by weight), iron (431 parts by weight) and 75 parts of sodium silicate solution (sp. gr. 1.3).

	Percent
Zirconium content	15.8
Carbon	2.20
Iron and others	76.9
Sodium silicate bond	5.1

An example of my methods of making a titanium carbide briquette by the use of an alkali zirconium silicon citrate as a bond is now given.

Example B.—100 parts of titanium carbide (—40 mesh) and 400 parts of iron metal particles (—40 mesh) are dampened with 35 parts of the citrate of sodium zirconium silicate solution such as is set forth in my pending application for patent Serial No. 623,605 filed July 20, 1932, which has approximately the following composition:

	Percent
Silicon (calculated as SiO_2)	4.07
Zirconium (calculated as ZrO_2)	7.96
Titanium (calculated as TiO_2)	0.02
Iron (calculated as Fe_2O_3)	0.01
Carbon (C)	8.21
Sodium (calculated as Na_2O)	5.95
Water	73.78
	100.00

This charge is mixed well to form a damp mixture, and is then pressed into form and dried; an addition of water may be made to the charge if required.

A titanium carbide iron briquette made from above proportions of titanium carbide and iron using 35 parts of the citrate compound would have the following composition after drying:

	Percent
Titanium	15.8
Iron	78.4
Carbon	3.9
Citrate bond	1.9
	100.00

The following is an example using zirconium oxychloride as a bonding material.

Example C.—A charge is made up containing the following ingredients:

	Parts by weight
Titanium carbide (—40 mesh)	100
Metallic iron (—40 mesh)	400
$ZrOCl_2+3H_2O$	20
	520

The charge is mixed with just enough water to form a paste, and then the mass is stiffened by addition of a suitable precipitant for the zirconium, such as, ammonia or phosphoric acid. The stiffened charge is then formed into shape and dried to form a coherent briquette.

Such briquette would contain approximately the following:

	Percent
Titanium	15.9
Iron	78.4
Carbon	3.9
Balance. ZrO_2, etc. bond	1.8
	100.00

The following example is given to illustrate the production of a titanium carbide-zirconium carbide briquette.

Example D.—A charge is made up of approximately the following ingredients:

	Parts by weight
Titanium carbide (—40 mesh)	50
Zirconium carbide (—40 mesh)	50
Metallic iron (—40 mesh)	415.5
1.3 sp. gr. sodium silicate solution	75
	590.5

The charge is mixed to damp consistency and pressed into shape and dried.

The composite briquette will have the following approximate composition:

	Percent
Titanium	7.35
Zirconium	8.16
Iron and others	76.40
Carbon	2.85
Sodium silicate	5.24
	100.00

The titanium carbide referred to in the foregoing examples is produced by reduction of titanium oxide (TiO_2) in presence of carbon in an electric furnace, having only enough carbon in the charge to form TiC. Some carbon of course will come from the electrodes and furnace lining material and the initial charge should be so proportioned as to allow for this. During the run in an electric arc type furnace, the contact with air should be avoided in order to prevent the absorption of nitrogen with resultant formation of nitrogen compounds. The charge is cooled in the furnace in which it was formed, and is then cleaned from foreign material, unreduced charge, etc., and is thereafter crushed and pulverized to suitable fineness, 40 mesh for instance. Such titanium carbide has approximately the following analysis: Titanium 79%; carbon 19% and other compounds 2%.

Zirconium carbide is made in substantially the same manner by using either zircon ($ZrSiO_4$) or ZrO_2 as the starting material. Such zirconium carbide has approximately the following analysis: Zirconium 86%; carbon 12%; and other compounds 2%.

I do not wish to confine my methods to the cold or low temperature forming of the briquettes, since a mechanical mixture of the titanium carbide and iron powder could be heated in a reducing atmosphere to a temperature sufficiently high to cause the iron to sinter and thus bond the titanium carbide particles and iron without employing a bonding material.

Again a low melting point metal, such as zinc, tin, etc. might be incorporated in small amounts, and by heating the mixture to, or slightly above, the melting point of the soft metal a bonding of my briquettes may be effected.

I do not wish to be limited to the press method of producing the briquettes, because suitable mixtures could be extruded into rods of any suitable size and shape, dried and hardened in any suitable manner. Suitable products could be made by hand-shaping to the desired size and shape.

Though I have described the formation of briquettes of titanium carbide and/or zirconium carbide mixed with iron, other metals besides iron might be used in the briquette as I have indicated, and such briquette could be used in alloying with or otherwise treating a bath of molten metal such as is used together with the titanium and/or zirconium carbide briquette for scavenging effects.

I claim as my invention:—

1. A method of making metallurgical scavengers containing a carbide of a metal of the group consisting of titanium and zirconium mixed with another metal as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, and then briquetting same.

2. A method of making metallurgical scavengers containing a carbide of a metal of the group consisting of titanium and zirconium mixed with iron as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, and then briquetting same.

3. A method of making metallurgical scavengers containing a carbide of a metal of the group consisting of titanium and zirconium mixed with another metal as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, forming briquettes of said mixture, and drying same.

4. A method of making metallurgical scavengers containing a carbide of a metal of the group consisting of titanium and zirconium mixed with iron as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, forming briquettes of said mixture, and drying same.

5. A method of making metallurgical scavengers containing titanium carbide mixed with another metal as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, and then briquetting same.

6. A method of making metallurgical scavengers containing titanium carbide mixed with iron as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, and then briquetting same.

7. A method of making metallurgical scavengers containing zirconium carbide mixed with another metal as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, and then briquetting same.

8. A method of making metallurgical scavengers containing zirconium carbide mixed with iron as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, and then briquetting same.

9. A methood of making metallurgical scavengers containing titanium carbide and zirconium carbide mixed with another metal as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, and then briquetting same.

10. A method of making metallurgical scavengers containing titanium carbide and zirconium carbide mixed with iron as major ingredients thereof, which comprises intimately mixing said ingredients in finely-divided form with a bonding agent to form a coherent mass of moldable consistency, and then briquetting same.

11. A method of making metallurgical scavengers having a relatively low carbon content and containing titanium carbide mixed with iron as major ingredients thereof, which comprises intimately mixing 100 parts of finely-ground titanium carbide and 400 parts of finely-ground iron moistened with about 75 parts of sodium silicate solution (sp. gr. 1.30) to form a coherent

mass of moldable consistency, and then briquetting same.

12. A method of making metallurgical scavengers having a relatively low carbon content and containing zirconium carbide mixed with iron as major ingredients thereof, which comprises intimately mixing 100 parts of finely-ground zirconium carbide and 431 parts of finely-ground iron moistened with about 75 parts of sodium silicate solution (sp. gr. 1.30) to form a coherent mass of moldable consistency and then briquetting same.

13. A briquette consisting of a coherent mechanical mixture of finely-ground carbide of a metal of the group consisting of titanium and zirconium, another metal and a bonding agent.

14. A briquette consisting of a coherent mechanical mixture of finely-ground carbide of a metal of the group consisting of titanium and zirconium, iron and a bonding agent.

15. A briquette consisting of finely-ground carbide of a metal of the group consisting of titanium and zirconium and iron bonded together by sodium silicate.

16. A briquette consisting of finely-ground titanium carbide, zirconium carbide, and iron bonded together by sodium silicate.

17. A briquette consisting of finely-ground titanium carbide and iron, said carbide comprising one molecule of carbon to one molecule of titanium and a bonding agent.

18. A briquette consisting of finely-ground zirconium carbide and iron, said carbide comprising one molecule of carbon to one molecule of zirconium and a bonding agent.

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