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ALUMINOTHERMIC METHOD AND ARTICLES
OF MANUFACTUREJohn Howard Deppeler, Weehawken, N. J., as-
signor to Metal & Thermit Corporation, New
York, N. Y., a corporation of New JerseyNo Drawing. Application April 8, 1943,
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11 Claims. (Cl. 75-27)

This invention relates to alumino-thermic methods and articles of manufacture, and it comprises a process of manufacturing metals and alloys, such as alloy steels, which comprises introducing into a bath of molten metal, for example into the usual ladle used in foundry practice, a plurality of highly compressed pellets of a thermit mixture under conditions producing ignition of the thermit, said pellets usually containing a thermit adapted to furnish alloying constituents to said molten metal and having such density, specific surface and heat conductivity as to be capable of being heated throughout to ignition temperatures by means of the heat derived from the molten metal, ignition of the pellets being followed by a substantially instantaneous reaction of high metal transfer efficiency, furnishing metal as well as a substantial quantity of heat to the molten metal bath. My invention also includes the said thermit pellets as articles of manufacture.

This application is a continuation-in-part of my copending application, Serial No. 313,973, filed January 15, 1940. In this prior application, I disclosed and claimed my process and product as applied to chromium, titanium, and silicon thermit. The present application is directed to the use of thermit containing at least one difficulty-reducible metal oxide in quantity sufficient to cause the thermit to require substantial preheating before undergoing reaction. In its specific aspects the present invention involves the use of zirconium, beryllium and boron thermit in addition to those disclosed in said copending application.

The so-called alumino-thermic process has been used industrially for somewhat over 40 years, during which time it has become well established in certain fields such as in the welding of steel rails, the welding and reclamation of all types of steel equipment and to a somewhat smaller extent in the making of small castings and in the manufacture of carbide-free metals and alloys. Thermit mixtures have also been employed to a considerable extent in foundry practice for the production of special alloys and for purifying iron. Certain special uses for the thermit reaction have also been developed, such as the commonly used method for increasing temperatures in the ladle in foundry practice, wherein a can containing a briquetted thermit mixture is secured to the end of a poling rod and inserted under the surface of the metal in the ladle, the resulting thermit reaction supplying heat to the metal.

Loose thermit mixtures have a tendency to become segregated owing to the different gravities of their constituents and, largely for the prevention of this segregation, it has been proposed frequently to briquet such mixtures. As an illustration, reference may be made to the two patents to Pacz, Nos. 1,562,041 and 1,562,042, in which it is proposed to employ large briquets weighing several pounds. It is proposed that one of these briquets be ignited by means of a blast lamp and placed in a crucible, other briquets being added in such fashion as to maintain the ignition and to supply the required amount of metal to the bath.

The thermit briquets which have been actually used in the art have all been lightly compressed and of large size. They have been incapable of being ignited and reacted efficiently by mere introduction into a bath of molten metal. For this reason, either they have been provided with pockets of ignition powder, have been ignited with a blast lamp or by contact with ignited thermit, or they have been held beneath the surface of the molten metal, as described in the early patent to Goldschmidt et al., No. 733,957, for example.

If the attempt should be made to introduce thermit briquets of the above described type into a bath of molten metal, for example into a ladle of molten iron or steel, it would be found that these briquets would float on top of the metal, that ignition would take place, if at all, merely at the surface of the briquets in actual contact with the molten metal, resulting in the disintegration of the briquets and the loss to the slag of the bulk of the metal oxide contained in the briquets. Some of the aluminum would go into solution in the metal bath and this might even spoil the entire charge. Even when a briquet of this type is held beneath the surface of the metal, it has been found that ignition takes place slowly from the outside inwardly and that there is a considerable loss of metal oxide to the slag. In the method of increasing temperatures in the ladle as described above, for example, it has been found necessary to provide pockets of ignition powder in the thermit briquets in order that satisfactory reaction efficiencies may be obtained.

I have discovered that, if a thermit mixture is compressed into relatively small pellets or buttons under high pressures, the heat conductivity of the thermit is increased to such an extent that upon contact with a bath of molten metal, the pellets are preheated as a whole to ignition temperatures, resulting in ignition and a substantially instantaneous reaction with negligible loss of metallic oxide to the slag.

Pellets made according to my discovery comprise a thermit mixture and advantageously a small amount of a binder compressed under pressures not substantially less than 100 pounds per square inch, and having a smallest dimension not substantially exceeding one-half inch. Said pellets desirably have a heat conductivity sufficiently high for the pellets to become preheated throughout and ignited upon contact with a bath of molten metal at a temperature of about 2100° F. or above, such ignition resulting in a substantially instantaneous reaction of high metal transfer efficiency. When used as herein described, such pellets furnish metal to the metal bath with but small loss to slag; all as more fully herein-after set forth and as claimed.

It is usually advantageous to employ a binder in making the pellets of my invention for the reason that there is less tendency for the pellets to disintegrate during reaction. But if sufficiently high pressures are employed, it is possible to dispense with the use of binders. It is important that any binder which is employed be non-hygroscopic and it is further desirable that the binder be heat-conducting rather than heat-insulating. I have obtained excellent results with a Celluloid binder and with resinous binders, such as urea-formaldehyde or Bakelite molding powders, maleate resins, or one of the phthalates.

The pressures required to produce the desired high heat conductivity of the pellets varies to some extent with the type of thermit, with the binder employed, and with the size of the pellets. With thermit which react without pre-heating, lower pressures are required since the aluminothermic reaction takes place more quickly and instantaneous preheating to ignition temperatures is not as important. But with chromium, silicon, titanium, boron, beryllium, and other thermit, which react only upon substantial preheating, pressures of upwards of 100 pounds per square inch are usually required for the production of the desired heat conductivity in the pellets. If heat as well as pressure is applied during the pelleting operation, the pressures can be reduced somewhat. Temperatures approaching the melting point of aluminum can be used, and this greatly assists in compacting the thermit and increasing its heat conductivity. Of course, no harm is done if the pellets are compressed to an extent which is greater than that which is required to give the desired heat conductivity whereas, if the pressures which are applied are too low, the efficiency of the reaction is reduced and all of the desired results may not be achieved. I have discovered that pressures of not substantially less than 100 pounds per square inch give the desired properties and for the reasons stated at least such pressure should be used for best results in producing the pellets of this invention.

The size and shape of the pellets of this invention are important owing to the fact that the pellets, upon contact with a bath of molten metal, must acquire ignition temperatures substantially instantaneously throughout their mass. This means that the pellets must quickly acquire a temperature corresponding substantially to the temperature of the metal bath even though they contact with said bath on one face only. All parts of the pellets must reach ignition temperatures before the ignition at any one point has progressed sufficiently far to cause disintegration. For this reason, the pellets preferably should be of substantially uniform thickness, i. e. flat discs, 5

squares, etc. Obviously the smaller the pellets and the better their heat conductivity, the more completely this result is realized. The smallest dimension of the pellets in general determines the distance through which the heat of the bath must pass during preheating of the pellets. Flat discs having diameters of several inches may be employed provided their smallest dimension is not substantially over one-half inch. This ensures that the heat of the metal bath will quickly penetrate through the discs. On the other hand, if the pellets are spherical, I have found that the maximum diameter which can be employed, in the case of thermit requiring preheating, is about three-fourths inch. The specific surface, i. e. surface per unit of volume, is the important factor. For this reason, the disc form is usually more advantageous than the spherical form. I have obtained excellent results with pellets one-half inch in diameter and a substantially uniform thickness of about one-quarter inch. It would be impossible to obtain practical efficiencies using the large briquets of the prior art, regardless of the pressures used in compacting them, providing that these briquets should be merely added to a molten bath, (as may the pellets of the present invention), without the use of extraneous means for producing ignition and reaction.

My invention can be explained in somewhat more detail by reference to the following examples in which compositions are given for several thermit mixtures which have been found valuable in actual practice.

1. Chromium thermit

A suitable formula for this type of thermit is 100 parts by weight of Cr_2O_3 mixed with $35\frac{1}{2}$ parts of pulverized aluminum. One hundred parts of this thermit, to which have been added 10 parts of a resinous binder and $\frac{1}{2}$ part of a lubricant are then run through a pelleting machine operating at a pressure of about 100 pounds per square inch and producing pellets having dimensions of about $\frac{1}{2}$ by $\frac{1}{4}$ inch.

2. Titanium thermit

This thermit is formed by mixing 100 parts of ilmenite, 33.8 parts of pulverized aluminum and 5 parts of powdered Celluloid as a binder. This mixture is moistened slightly with a Celluloid solvent and passed through a pelleting machine operating at a pressure of about 500 pounds per square inch to produce pellets having dimensions of about 1 by $\frac{1}{4}$ inch.

3. Titanium thermit

Another titanium thermit can be produced by mixing 100 parts of ilmenite, 25 parts of Fe_2O_3 , $38\frac{1}{2}$ parts of pulverized aluminum and 5 parts of cellulose acetate, this mixture being passed through a pelleting machine producing pellets having dimensions of $\frac{1}{2}$ by $\frac{1}{4}$ inch.

The purpose of the iron oxide in the above titanium thermit mixture is to increase the speed of the reaction and, therefore, its efficiency, owing to the fact that titanium oxide reacts with aluminum only with difficulty.

4. Manganese thermit

A manganese thermit can be produced by mixing 100 parts of Mn_2O_3 with 29 parts of aluminum and 3 parts of pulverized Celluloid. This mixture is pelleted under the application of heat and pressure after being moistened with a Celluloid

solvent. A pure manganese is produced upon the ignition of this thermit which is highly valuable for alloying with cast iron or steel.

5. Silicon thermit

A silicon thermit can be produced by mixing 100 parts of SiO_2 and 65.4 parts of aluminum together with 17 parts of a resinous binder and 1 part of a lubricant. This mixture is pressed in a pelleting machine at a pressure not substantially less than 100 pounds per square inch to produce pellets having a smallest dimension not exceeding $\frac{1}{2}$ inch. These pellets when added to a molten steel bath having a temperature not substantially below 2100°F . will react to produce silicon which will thereby enter the steel bath.

6. Boron thermit

A boron thermit can be produced by mixing 100 parts of B_2O_3 and 77.5 parts of aluminum together with 18 parts of a resinous binder and 1 part of a lubricant. This mixture is pressed in a pelleting machine at a pressure not substantially less than 100 pounds per square inch to produce pellets having a smallest dimension not exceeding $\frac{1}{2}$ inch. These pellets, when added to a molten steel bath having a temperature not substantially below 2100°F . will react to produce boron which will thereby enter the steel bath.

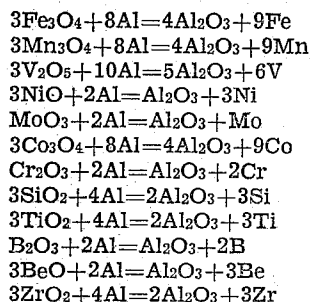
7. Beryllium thermit

A beryllium thermit can be produced by mixing together 100 parts of BeO and 71.8 parts of aluminum together with 17 parts of a binder and 1 part of a lubricant. This mixture is pressed in a pelleting machine at a pressure not substantially less than 100 pounds per square inch to produce pellets having a smallest dimension not exceeding $\frac{1}{2}$ inch. These pellets, when added to a molten copper bath, having a temperature not substantially below 2100°F . will react to produce beryllium which will thereby enter the copper bath.

The binder which is used in the above specific examples can, of course, be replaced by other binders such as sugar, bitumens, shellac, nitrocellulose, cellulose acetate, or natural or artificial heat setting resins, such as urea-formaldehyde, maleate resins, phthalates, or Bakelite molding powders. When thermoplastic binders are employed, it is not necessary to use a solvent provided that the pellets are heated while being formed. Alkali metal silicate solutions can be used but these are likely to be hygroscopic. The thermit mixture can be mixed with the binder while the latter is in the form of a solution if desired, as will be understood by those skilled in this art.

The alumina slag produced in the use of my pellets floats on top of the molten metal and can be readily removed. Within reasonable limits any desired quantity of the thermit metal can be added in this fashion without decreasing the temperature of the bath, owing to the fact that the heat of the aluminothermic reaction is, of course, transferred to the bath, this being greater than the heat required for preheating the thermit pellets. I have found this to be true of thermit of all types, even the difficultly ignitable thermit which normally require preheating to high temperatures prior to ignition and reaction, such as titanium, zirconium, silicon, boron, beryllium, and chrome thermit, for example. The wide range of thermit mixtures which are useful in this in-

vention may be judged by a consideration of the following equations of reaction of some of the known thermit all of which are applicable:



The first of the above equations represents the reaction which takes place in the well-known iron thermit reaction which is used to produce superheated molten steel for welding operations. This type of reaction takes place without preheating of the thermit. A large amount of heat is evolved by the reaction. The last six reactions do not propagate in the cold and the corresponding thermit mixtures require substantial preheating in order to obtain propagation of the reaction throughout the mass. The nearer the preheat to the temperature which would cause a spontaneous reaction of the entire mass, the greater the efficiency of the reaction in reducing the oxide to metal.

In practice the preheating of difficultly-ignitable thermit mixtures is a time consuming operation which requires a large amount of technical skill. Even with the best practice which has been developed thus far, the amount of metal obtained from the metal oxide in the most efficient of these reactions is not more than about 70 per cent of the theoretical amount available.

The above equations correspond only to what might be called pure thermit. But it is common in the art to produce mixed thermit. In fact, metallic vanadium and molybdenum are usually produced in the form of ferrovanadium and ferro-molybdenum by the use of vanadium and molybdenum thermit mixed with iron thermit. It is also common practice to mix the difficultly reducible oxides with iron oxide which then supplies heat and increases the efficiency of the reactions. In the case of titanium oxide, for example, in order to obtain reasonable efficiency, it is necessary to employ a mixed iron-titanium thermit and also to preheat it to as high temperatures as possible.

The present invention has eliminated the above preheating difficulties owing to the fact that, when my pellets are introduced into the ladle, for example, the heat from the molten metal supplies the preheat required and this heat becomes distributed substantially instantaneously and uniformly throughout the pellets which are thereby preheated to ignition temperatures. A substantially instantaneous reaction is produced and this reaction returns the preheat to the molten bath. This solves many of the problems involved in introducing alloying metals of difficultly-reducible oxides into molten iron and steel, for example.

Under present practice, there is no economical way of introducing chromium or titanium into the ladle in foundry practice. The addition of ferro-chrome, for example, cools the charge too greatly. If the usual chrome thermit should be introduced into the ladle, the bulk of the chromic oxide would be lost to the slag. This is true even

though the thermit should be preheated. If an iron-chromium thermit should be employed, containing sufficient iron oxide to ignite satisfactorily, the iron resulting from the thermit reaction would greatly exceed the chromium added to the ladle and would spoil the charge. But if a chrome thermit is formed into relatively small pellets under high pressures, in accordance with the present invention, and if these pellets are introduced into the ladle, it has been found that these pellets readily ignite and react substantially instantaneously with but small loss to the slag. And the thermit reaction which occurs supplies heat to the charge rather than cooling it. The thermit pellets can be shoveled into the ladle in suitable amount and the reaction is completed immediately. This appears to be the first practical method of producing chromium or titanium alloys directly in the ladle, without any loss of heat and with a high reaction efficiency.

Alumino-thermic reactions involve two valuable products, (1) the superheat derived from the heat of reaction of the thermit and (2) the resulting metal. The present practice in which ferro-chrome, ferro-titanium, etc., are produced in separate alumino-thermic processes, crushed to suitable size and then added to molten iron or steel, involves the loss of the superheat. The steel is cooled by the addition and this, of course, results in a loss of reaction efficiency. The quantity of metal which can be added is limited by the fact that the molten metal becomes sluggish from the loss of heat and cannot be readily poured. It is evident that the present invention eliminates these difficulties by providing a method of adding both of the alumino-thermic products to the metal bath. A larger proportion of alloying elements can be added and the temperature of the bath is increased by the thermit reaction during the process rather than being cooled.

While I have described what I consider to be the best embodiments of my invention, it is evident that various modifications can be made in the procedures and compositions described without departing from the purview of this invention. The specific examples illustrate the pelleting of pure thermit and mixtures of difficultly-ignitable thermit with iron thermit. It is evident that the invention is likewise applicable to mixed thermit in general. If desired or if convenient, the pellets of my invention can be preheated before being added to the ladle, for example. Preheating is not required but when expensive oxides are incorporated in the thermit, this operation does increase the efficiency of the resulting reaction to some extent. Other modifications of this invention which fall within the scope of the following claims will be immediately evident to those skilled in this art.

What I claim is:

1. In the manufacture of metals and alloys, the process which comprises contacting a bath of molten metal, having a temperature not substantially below 2,100° F. with highly compressed pellets of a thermit comprising at least one reducible metal oxide and aluminum as a reducing agent, and up to 15% of a binder, said thermit requiring a substantial amount of preheat for reduction of said metal oxide to metal, said pellets having a smallest dimension not substantially exceeding $\frac{1}{2}$ inch, having a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and having a heat conductivity such

that, upon contact with said metal bath, they react substantially instantaneously with a high metal transfer efficiency.

2. In the manufacture of metals and alloys, the process which comprises contacting a bath of molten metal having a temperature not substantially below 2,100° F. with highly compressed units of thermit containing at least one difficultly-reducible metal oxide selected from a class consisting of chromium, silicon, zirconium, titanium, boron and beryllium oxides, as its chief component which is reduced to metal in the thermit reaction; said thermit units containing aluminum as a reducing agent and up to 15% of a binder, and said pellets having a smallest dimension not substantially exceeding $\frac{1}{2}$ inch; a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and heat conductivity such that, upon contact with said metal bath, they react substantially instantaneously with a high metal transfer efficiency.

3. As new articles of manufacture, pellets comprising a highly compressed thermit containing at least one reducible metal oxide and aluminum as a reducing agent, and up to 15% of a binder, said thermit requiring a substantial amount of preheat for reduction of said metal oxide to metal, said pellets having a smallest dimension not substantially exceeding $\frac{1}{2}$ inch, having a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and having a heat conductivity such that, upon contact with a metal bath, having a temperature not substantially below 2,100° F. they react substantially instantaneously with a high metal transfer efficiency.

4. As new articles of manufacture, pellets comprising a highly compressed thermit containing at least one difficultly-reducible metal oxide selected from a class consisting of chromium, silicon, zirconium, titanium, boron and beryllium oxides as its chief component which is reduced to metal in the thermit reaction; said thermit pellets containing aluminum as a reducing agent and up to 15% of a binder, and said pellets having a smallest dimension not substantially exceeding $\frac{1}{2}$ inch, a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and a heat conductivity such that, upon contact with a molten metal bath having a temperature not substantially below 2,100° F., they react substantially instantaneously with a high metal transfer efficiency.

5. As new articles of manufacture, pellets comprising a highly compressed thermit containing at least one difficultly-reducible metal oxide selected from a class consisting of chromium, silicon, zirconium, titanium, boron and beryllium oxides, as its chief component which is reduced to metal in the thermit reaction; said thermit pellets containing aluminum as a reducing agent, and up to 15% of a binder, and said pellets having a density corresponding to that produced by a pressure not substantially less than 100 pounds per square inch applied at temperatures approaching but not exceeding the melting point of aluminum; a smallest dimension not substantially exceeding $\frac{1}{2}$ inch and being characterized by having a heat conductivity such that, upon contact with a bath of molten metal at a temperature not substantially below 2,100° F., they react substantially instantaneously and with a high metal transfer efficiency.

6. In the manufacture of metals and alloys, the process which comprises contacting a bath of molten metal having a temperature not substantially below 2,100° F. with highly compressed units of thermit containing chromium oxide as its chief component which is reduced to metal in the thermit reaction; said thermit units containing aluminum as a reducing agent and up to 15% of a binder, and said pellets having a smallest dimension not substantially exceeding ½ inch; a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and heat conductivity such that, upon contact with said metal bath, they react substantially instantaneously with a high metal transfer efficiency.

7. In the manufacture of metals and alloys, the process which comprises contacting a bath of molten metal having a temperature not substantially below 2,100° F. with highly compressed units of thermit containing titanium oxide as its chief component which is reduced to metal in the thermit reaction; said thermit units containing aluminum as a reducing agent and up to 15% of a binder, and said pellets having a smallest dimension not substantially exceeding ½ inch; a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and heat conductivity such that, upon constant with said metal bath, they react substantially instantaneously with a high metal transfer efficiency.

8. In the manufacture of metals and alloys, the process which comprises contacting a bath of molten metal having a temperature not substantially below 2,100° F. with highly compressed units of thermit containing boron oxide as its chief component which is reduced to metal in the thermit reaction; said thermit units containing aluminum as a reducing agent and up to 15% of a binder, and said pellets having a smallest dimension not substantially exceeding ½ inch; a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and heat conductivity such that, upon contact with said metal bath, they react substantially instantaneously with a high metal transfer efficiency.

9. As new articles of manufacture, pellets comprising a highly compressed thermit containing chromium oxide as its chief component which is reduced to metal in the thermit reaction; said thermit pellets containing aluminum as a reducing agent and up to 15% of a binder, and said pellets having a smallest dimension not substantially exceeding ½ inch, a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and a heat conductivity such that, upon contact with a molten metal bath having a temperature not substantially below 2,100° F., they react substantially instantaneously with a high metal transfer efficiency.

10. As new articles of manufacture, pellets comprising a highly compressed thermit containing titanium oxide as its chief component which is reduced to metal in the thermit reaction; said thermit pellets containing aluminum as a reducing agent and up to 15% of a binder, and said pellets having a smallest dimension not substantially exceeding ½ inch, a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and a heat conductivity such that, upon contact with a molten metal bath having a temperature not substantially below 2,100° F., they react substantially instantaneously with a high metal transfer efficiency.

11. As new articles of manufacture, pellets comprising a highly compressed thermit containing boron oxide as its chief component which is reduced to metal in the thermit reaction; said thermit pellets containing aluminum as a reducing agent and up to 15% of a binder, and said pellets having a smallest dimension not substantially exceeding ½ inch, a density corresponding to that produced by an applied pressure not substantially less than 100 pounds per square inch and a heat conductivity such that, upon contact with a molten metal bath having a temperature not substantially below 2,100° F., they react substantially instantaneously with a high metal transfer efficiency.

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