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METHODS FOR THE REDUCTION AND SINTERING OF BODIES CONTAINING REDUCIBLE METAL COMPOUNDS

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The invention is for improvements in and relating to the reduction and sintering of bodies containing or consisting of reducible metal compounds.

One object of the invention is to enable the reduction and sintering of such bodies to be performed without formation of cracks or fissures in the bodies. Another object is to adapt this improved method of reduction and sintering for the production of articles of predetermined shape and size, finished or semi-finished, direct from reducible metal compounds.

According to the U. S. patent specifications Nos. 2,386,072 and 2,386,073 blocks are prepared from ores or metal oxides in the powdered form, embedded in carbonaceous material, heated and reduced to iron sponge. The British specification No. 3926/1897 describes the production of finished articles direct from the ore. The ore is pressed to shape and the bodies thus obtained are reduced and sintered in a reducing gas atmosphere.

According to the methods disclosed in the U. S. Patent specifications the reducible material is embedded in and is on all sides supported by the carbonaceous material. The mechanical pressure of the reduction agent acts on the glowing, porous mass which during the reduction has such a high temperature as to assume a very plastic state and therefore under the pressure of the surrounding reduction agent is somewhat compressed. It is therefore hardly possible for cracks to be formed in the body, and even if such cracks are formed they are without significance, as iron sponge is being produced which is to be subjected to further treatment.

It is different with the method disclosed in the British specification. In this case any cracks formed in an early stage of the reduction are not closed up by any external mechanical pressure but remain open. This applies of course to the sides and the top of the body. Cracks at the bottom on the other hand may be closed up under the pressure of the material above.

It has, however, been found that this difficulty in carrying out the reduction, particularly in a gas atmosphere, may be overcome if the following procedure is adopted. The reduction is carried out in two or more steps in each of which the temperature is increased and for a

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predetermined period of time maintained within predetermined limits for permitting the escape of the gases evolved by the reduction process to take place so slowly as to avoid formation of cracks in the body being treated.

Investigations of the relationship of time to temperature have shown that for each oxide (oxides of the same metal but in different stages of valency behave as different oxides) there are specific temperature ranges in which the evolution of gas during the reduction reaches a point where distortion of the body being treated is liable to occur.

The drying and the reduction of the bodies may be effected in a continuous process. The reduction is carried out at temperatures which are far below the temperatures used for the production of metals by the usual melting methods.

The manner in which the reduction is carried out therefore is of the greatest importance for the success of the process. In order to illustrate this the reduction of iron oxide (magnetite ore) will be described in detail. It is assumed that finely divided magnetite ore is compressed to a body having substantially the shape and dimensions of the final article to be produced. The compact is dried at a temperature of 80 to 200° C. and can then be heated comparatively quickly to a temperature between 425 and 475° C. At this temperature (the prereduction temperature) and the reduction velocity for

$\text{Fe}_2\text{O}_3 \rightarrow \text{FeO}$ (magnetite ore = $\text{Fe}_3\text{O}_4 = \text{Fe}_2\text{O}_3$, FeO)

is fairly high but not so high that the reaction products formed burst the very brittle mass. If now the temperature is quickly raised above this point the reduction velocity increases to such an extent that the mass no longer retains its shape but numerous cracks are formed. Therefore, after reaching the temperature 425 to 475° C. this temperature must be maintained for a predetermined period of time which depends on the dimensions of the body. The temperature may then be raised, but only very gradually, up to 500° C., and after that more quickly to a temperature of about 600 to 650° C. At this temperature a new reduction process sets in which is very lively and accompanied by the evolution of large quantities of gas, as FeO is reduced to

Fe. Also in this case the temperature must at first be kept constant, at approximately 600 to 650° C., and can then be raised slowly up to about 700° C. From this point the temperature may be raised more quickly to the temperature, 1000 to 1250° C., at which the final reduction and an appreciable sintering of the mass occurs. This sintering is accompanied by shrinking and an increase of the strength properties.

It is of the greatest importance that the reduction closely follows a predetermined temperature-time scheme which depends on the nature of the reducible metal compound, the dimensions of the body being treated etc. The bodies which are passed into the furnace must when they pass out of the furnace finally reduced and sintered be free from cracks in order that the subsequent treatment may be carried out successfully.

The consumption of energy corresponds to approximately 500 kilograms of coal per ton iron (according to Wiberg's method for the production of iron sponge). In this figure the energy consumption for maintaining the reduction temperature as well as the amount of reduction agent required for the reduction itself is included.

This description relating to iron ore applies generally to any other reducible oxide, but the temperatures vary from case to case and so may also the time periods. Thus for example copper oxide requires considerably lower reduction temperatures than iron oxides.

If different reducible oxides are present in comparatively large amounts it may be necessary to keep the temperature constant or raise the temperature very slowly in many different steps. It is also necessary to have regard to the different valencies of the different oxides. In most cases, however, oxides requiring reduction temperatures substantially different from that of the main body are present only in small amounts, and in such cases it has been found unnecessary to take the conditions of reduction of these oxides into consideration. In such cases it is thus possible to conduct the process considering only the nature of these oxides which constitute the main body of the material being treated.

As reducing agent may be used reducing gases from an external source, and in a continuously working furnace these gases preferably are conducted in opposite direction to that in which the bodies being treated are passed through the furnace. In some cases, however, particularly if the bodies to be treated have large sectional areas which render the diffusion of the reducing gases through the porous mass difficult or even impossible, it is preferable to mix a solid reducing agent, for example carbon, carbonaceous products, tar etc., with the material to be reduced. In such cases it may be preferable to use an amount of carbon which is sufficient also to carburize the product subjected to final reduction and final sintering, so that a product having the desired carbon content is obtained. The reduction may also be carried out by using both methods.

It is also possible to produce alloyed semi-manufactured or finished products by reducing mixtures of oxides or other reducible compounds. Also in these cases the reduction is generally carried out at a temperature below the melting point of the metal having the lowest melting point. On the other hand it is not always possible to adhere to this rule if a component having a particularly low melting point is present.

The reduction as above described may be carried out in chamber furnaces, bell furnaces or furnaces of the type in which the goods is continuously passed through the furnace. When using chamber furnaces the temperature may with advantage be controlled by means of programme regulators. The continuous furnace is particularly advantageous for the production of profiles, bands, tubes etc. of great lengths.

A continuous furnace preferably suitable for the process of the invention should have a number of different zones, i. e. one zone permitting a comparatively slow increase of the temperature from about 70 to 80° C. to about 200° C. for drying the body being treated. The temperature can then be raised comparatively quickly to the point corresponding to the first point of inflection on the curve obtained by plotting the data obtained by a thermal analysis of the reduction process of the material to be treated (in the following this point will be referred to as "the first reduction maximum", whereas the temperature at which the reduction process $\text{FeO} \rightarrow \text{Fe}$ becomes more lively will be called "the second reduction maximum"). The temperature corresponding to the first reduction maximum is maintained constant for such a period of time that the evolution of gas which accompanies the reduction proceeds quietly, so that bursting of or the formation of fissures in the mass is avoided. The temperature is then raised, at first very slowly and then more quickly, until the second reduction maximum is reached. When this temperature has been reached there follows a zone in the furnace in which the temperature is maintained constant, and then the temperature may again, at first slowly and then comparatively quickly, be raised to the desired end temperature at which the reduction and sintering is completed. The process described above apply to the reduction of iron ore with hydrogen. If other reducing agents or combinations of different reducing agents are employed other temperatures will have to be used but the principle remains the same.

As final product after the reduction a porous metal body of low strength and having a pore volume of the order of 30 to 70% is obtained. Such metal articles may in some cases be used as they are; they can with advantage be used as gas or liquid filters.

An important application field of the method of the invention is, however, the production of compacts. For this purpose the reduction in steps is followed by presintering and final reduction in a further step at a still higher temperature, and then follows compacting and final sintering.

The compacting operation may consist of such a working of the porous material as forging, pressing, hammering, rolling and so on in the hot or cold state. In the case of steel for example it is possible to continue heating the body reduced at a temperature of 1000° C. in the same furnace in which the sintering is carried out to a temperature suitable for rolling and pass the body from the furnace straight to a rolling mill, a hammering machine or the like, so that the body is immediately compressed to the compact state. Then follows an annealing treatment or final sintering at a temperature of 1000 to 1250° C., and a material is obtained having a pore volume of 3 to 5% and a strength which is not appreciably different from that of molten and rolled steel. As the desired result is obtained by means of one or at the most two rolling operations or one or two forging operations the energy consumption is only 30% of

that required for the normal reducing rolling of castings.

It is of importance that the final reduction takes place at such a high temperature as to carry the sintering of the material to such a point that the strength of the material is sufficient for compression directly after the sintering process.

The invention also comprises a method for the production of articles of predetermined shape and dimensions direct from reducible metal compounds, using the reduction method above described. This method consists in preparing from the powder of the reducible metal compound a body having substantially the shape of the finished article, drying the body, reducing the metal compound in two or more stages in each of which the temperature is increased and for a predetermined period of time maintained within predetermined limits so as to permit escape of the gases evolved by the reduction to take place so slowly as to avoid formation of cracks in the material, completing the reduction and pre-sintering at a still higher temperature, compacting to final shape and resintering.

From the U. S. patent specifications Nos. 2,386,072 and 2,386,073 referred to above it is known to produce iron sponge from ores and oxides in the powdered form by mixing the powder with a binding agent, forming a compact mass, surrounding the formed body with a carbonaceous material, and for a period of time of 4 to 5 hours, heat to reducing temperature (approximately 1100° C.), the reduction being effected by means of reducing gases generated by the carbonaceous material.

The method of the present invention differs from the known methods just described in that it is a question of producing articles of final shape and sintered to completion, not iron sponge, that the reduction is not effected by packing in a solid reducing agent but in a free gas atmosphere, by means of a reducing agent contained in the body being treated or by both methods, that the reduction takes place in two or more steps in each of which the temperature is increased and according to a predetermined scheme, and that the reduction and sintering is followed by compacting and final sintering. It may be added that when employing the methods disclosed in the U. S. patent specifications the rate of diffusion of the reducing gases formed during the heating is limited and that therefore the production by these methods of bodies having thick walls is rendered difficult and uneconomical.

The British specification No. 3926/1897 relates to the production of bars and articles of final form direct from the ore. The ore is finely divided, mixed with water or tar and coal dust, and from the paste thus obtained are moulded the articles to be made. The objects are heated in a reducing atmosphere to a temperature below the melting point of the metal of which the objects will be made up. The method of the invention differs from the known method in that the reduction is carried out in two or more steps and the sintering in two steps between which is interposed a compacting operation.

Generally speaking, powder metallurgical methods are known according to which metal powder is produced one way or the other, is pressed to shape and sintered. From these methods the invention differs in that articles of final shape are made in a continuous process direct from the raw material.

The method described above for the production

of articles of final shape direct from the raw material may be used for the production of semi-manufactured articles such as bars, sheet metal, tubes and the like, and for the production of finished articles.

The raw material may consist of highly concentrated ores, pure oxides, sulphides, calcined pyrites and so on. The powder is moulded into bodies having the shape of the final article to be produced. The moulding may be effected by compressing the dry powder but it is preferable to bring the powder into a more or less plastic paste by means of a suitable process. Thus it has been found that by adding 3 to 15% of coal tar finely divided and highly concentrated magnetite ore which in itself is very short and absolutely unplastic acquires very good plastic properties. In another case it was found possible to plastify a powdered iron oxide by adding a very small amount of freshly precipitated iron hydroxide. Calcined pyrites could be plastified by adding 2% of manganic hydroxide. By adding freshly precipitated iron hydroxide to a mixture of copper oxide and iron oxides a sufficiently plastifying effect was obtained. Also other oxihydrates and other plastifying methods may be used.

The energy consumption for the plastification is very small and corresponds at most to 50 kilograms per 1000 kilograms of metal.

The moulding to bars, tubes, bands, profiles etc. may be effected by compression in press dies as in the plastic industry or by extrusion as in the production of plastic masses or in the extrusion of easily mouldable metals. The plastic mass may also be rolled out in rolling mills. Thus for example the plastic mass may be extruded on a carrier of ordinary paper which is passed between two rollers. This method is particularly suitable for the production of band or sheet. The carrier of paper can be disregarded as it is carbonized during the subsequent heat treatment. Whatever method is used for shaping the plastic masses the compression pressures required are low and in any case are less than 3 tons per square centimeter. The energy consumption is therefore small and does not exceed a value corresponding to 25 kilograms of coal per ton of metal.

The drying, reduction, pre-sintering, compression and final sintering then is carried out as above described. The drying operation may, however, be carried out in some other way, for example at least partially in porous moulds. The pre-sintering is generally effected at a temperature which is 50 to 150° C. below the final sintering temperature, and the final sintering is generally carried out at a temperature which is not lower than 80% of the absolute melting temperature of the metal concerned.

When producing profiles, bands, tubes, etc. in continuous lengths it may be preferable to admix the reducing agent, the whole amount or a portion thereof, in the solid state with the mass to be reduced (large cross sections), or in some cases (small cross sections) to reduce only by means of reducing gases.

If the compression, forging, hammering, rolling etc. is carried out in immediate continuation of the pre-sintering operation there is no risk of oxidation of the interior of the metal product, as the interior of the porous metal body is filled with reducing gases which during the working are pressed out through the pores.

The shrinking during the combined reduction and sintering process has generally been found

to be of the order of 10 to 20% of the original dimensions of the formed body. In the subsequent compression operation the volume of the object was reduced by a further 40 to 50%.

Below is a summary comparison of the energy consumptions required for the production of band steel according to the usual melting method and according to the powder metallurgical method of the invention above described. For the conversion of coal to kilowatt-hours it has been assumed that 1 kilogram coal corresponds to 3 kilowatt-hours when the coal is used for generating heat. For the sake of simplicity the same conversion figure has been used for the carbon required for the reduction of ore or iron oxides to metal.

The figures indicate kilowatt-hours per ton Fe.

Production by melting

	Kilowatt-hours per ton
Production of pig-iron	2,100
Production of open hearth iron or electro-steel from pig-iron and scrap iron	600
Heating of castings and semi-manufactured products to rolling temperature ..	500
Rolling	200
Total, Fe	3,400

Powder metallurgical production

	Kilowatt-hours per ton
Plastifying the raw materials	150
Reduction, sintering and heating to rolling temperature	1,500
Rolling	75
Total, Fe	1,725

It thus appears that a properly conducted powder metallurgical process can save from 45 to 50% of the energy consumption required for accomplishing the same result by the methods now in use. And yet the heavy and troublesome transportations of semi-manufactured products required in steel works and rolling mills have not been taken into consideration. On the other hand the raw material for the powder metallurgical production must be subjected to a thorough concentration, and these two amounts are assumed to cancel out each other, if anything the advantage is to the new method described.

The invention will be illustrated by the following examples without being limited thereby.

Example 1

Powdered iron ore was mixed with 3% coal tar and compressed at a pressure of 4 tons per square centimeter to cylindrical compacts. The compacts were dried at a temperature of 200° C. and then allowed to cool. The compacts were then heated in a continuous furnace in a hydrogen atmosphere to 500° C. at a rate of heating of 5° C. per minute. The temperature was then raised so as to reach 600° C. at the end of approximately 30 minutes and at this temperature the compacts were reduced during a period of time of 3 hours. The temperature was then raised as quickly as possible to 1250° C.; this temperature was maintained for 30 minutes. The compacts were allowed to cool and the total shrinking of the ore volume was found to be 2% and the porosity about 50%. The reduced compacts were repressed in the original die to a specific weight of 7.0 grams per cubic centimeter and sintered at a temperature of 1250° C. for a period of time of

one hour. The tensile strength was then found to be 18 kilograms per square millimeter.

Example 2

Compacts prepared as in Example 1 were slowly heated to a temperature of 580° C. in an atmosphere of 50% H₂ and 50% CO to which had been added 0.5% gaseous nitrogen-containing substances for preventing precipitation of carbon. The compacts were reduced at this temperature for a period of time of 3 hours and the temperature was then during a period of time of 2 hours raised to 1250° C. After cooling the compacts had a specific weight of 5.5 kilograms per cubic centimeter and a tensile strength of 10 kilograms per square millimeter.

Example 3

Highly concentrated iron ore was ground to a particle size of less than 0.3 millimeter and intimately mixed with 20% of a 10% wax emulsion to a plastic mass. The water in the emulsion was evaporated and after treatment in a kneading machine a powder having good flow properties was obtained. It also had good plastic properties when subjected to high pressure. As a result of the good flow properties the determination of the amount required for the dies was easy.

The powder was formed by extrusion into a tube having an internal diameter of 25 millimeters, a wall thickness of 12.5 millimeters and a length of 1 meter.

The drying and the reducing sintering was carried out as in Example 2. After final sintering the tube was taken directly to a hammering machine and compressed hot over a mandrel having a diameter of 23 millimeters and the hammer heads so adjusted that the outer diameter of the tube was reduced to 36 millimeters. In this way a tube was obtained having a length of 2 meters, a density of 7.6 and a tensile strength of 28 kilograms per square millimeter.

What we claim is:

1. In a process for producing an article of predetermined shape from powdered material consisting essentially of Fe₂O₃, the steps comprising compacting said powdered material at a pressure of not over about 3 tons per square centimeter into a body having substantially the shape of the article to be produced, heating the compacted body at a rate not exceeding 5° C. per minute to a temperature of about 600° C. in an atmosphere consisting essentially of a reducing atmosphere, and maintaining it at said temperature for a sufficient length of time for a substantial part of the gas evolved at said temperature to escape during the reduction of the valency involved without causing cracks in the body, and then heating to a temperature in the range of 1000 to 1250° C. in an atmosphere consisting essentially of a reducing atmosphere for a sufficient length of time to complete the reduction of the oxide and for at least presintering to take place.

2. In a process for producing an article of predetermined shape from powdered material consisting essentially of Fe₂O₃ with a small amount of freshly precipitated iron hydroxide, the steps comprising compacting said powdered material at a pressure of not over about 3 tons per square centimeter into a body having substantially the shape of the article to be produced, heating the compacted body at a rate not exceeding 5° C. per minute to a temperature of about 600° C. in an atmosphere consisting essentially

of a reducing atmosphere, and maintaining it at said temperature for a sufficient length of time for a substantial part of the gas evolved at said temperature to escape during the reduction of the valency involved without causing cracks in the body, and then heating to a temperature in the range of 1000 to 1250° C. in an atmosphere consisting essentially of a reducing atmosphere for a sufficient length of time to complete the reduction of the oxide and for at least presintering to take place.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
896,060	Kuzel -----	Aug. 11, 1908
1,040,699	Ladoff -----	Oct. 8, 1912
1,111,698	Liebmann -----	Sept. 22, 1914
1,902,090	Musso -----	Mar. 21, 1933
2,065,618	Sherwood -----	Dec. 29, 1936
2,166,207	Clark -----	July 18, 1939
2,315,302	Volterra -----	Mar. 30, 1943