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PROCESS FOR THE MANUFACTURE OF SINTERED ARTICLES

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This invention relates to the manufacture of sintered articles.

It is known to produce sintered articles from compacts made from powders, particularly metal powders, by sintering the compacts in furnaces in which the composition of the atmosphere is controlled.

In normal practice the compacting of the powder is achieved by the use of heavy metallic dies in which the dry powder is subjected to high pressures, in some cases of up to 50 tons per square inch. The compacted article is then transferred to a specially designed furnace having a controlled atmosphere, where it is heated for periods varying from 15 minutes to several hours, at a temperature below, but approaching, with a reasonably safe margin, the melting point of the particular composition.

The atmosphere maintained in the furnace, which is usually of the gas-tight muffle type, is in most cases of a reducing nature, such as hydrogen or cracked ammonia, although in the case of metallic carbides it is normally kept neutral or even slightly carburising.

Although such a method has found considerable practical use in industry, its applications are necessarily limited by the design of suitable dies, capable of withstanding the considerable pressure required, and also by the size of the press which, for articles of more than a few inches of overall dimension, may be required to develop several thousand tons' pressure. The initial cost of the dies is very high, and the press constitutes a major item of capital expenditure, which entails higher production costs.

Furthermore, most sintering furnaces must be of special design and adapted for use with a controlled atmosphere, particularly for the production of articles of ferrous materials which are readily oxidised at elevated temperature.

The role of the cold compacting under the press is, in the first instance, to create by compression a number of points of intimate contact between the particles which are the nuclei of incipient fusion developing at elevated temperature; this effect, however, may be minimised or even cancelled with certain metals or alloys whose particles develop a thin film of strongly adhering oxide, which is only imperfectly reduced by the operating atmosphere and which prevent the metal-to-metal contact, an essential prerequisite of satisfactory bonding by interpenetration of the crystalline lattices. Another effect of the pressure compacting is to reduce the volume of the powder to a stage nearer that of the eventual sintered product. Finally, although it is fragile, the compacted article shows sufficient strength to be handled and transferred to the furnace, provided reasonable care is exercised.

It has now been discovered according to this invention that the above-mentioned disadvantages can be overcome and the advantages hereinafter specified can be obtained if a sinterable inorganic powder, preferably a metal powder, is mixed with a substance which is hereinafter referred to as a flux, which acts as a bonding agent for the particles of the powder in the cold and also during the

sintering as a solvent for films of oxide and other compounds on the surface of the particles which otherwise prevent contact of clean particles and satisfactory interpenetration.

Thus, the process of the present invention for the manufacture of sintered articles comprises mixing a sinterable inorganic powder, preferably a metal powder, with a flux, forming the mixture thus produced into an article of the desired shape, preferably without the use of substantial pressure, and subjecting the article to a temperature sufficient to sinter the particles but insufficient to melt the same.

While the invention is particularly applicable to the treatment of metal powders, it will be understood that it is also applicable to the treatment of other sinterable inorganic powders such as powders of metallic carbides, e. g. tungsten carbide and other so-called "hard metals," metallic silicides and oxides.

Although the flux can be mixed dry with the metal powder and compacted in the usual way, it has been found preferable to utilise it in the liquid form, making a paste of the desired degree of fluidity with the powder. When the flux is a liquid under normal conditions, it can be used as such, or diluted with a suitable solvent. When the flux is a solid, a liquid carrier or solvent must be used.

The liquid carrier or solvent should preferably have a high wetting power and such substances as methyl alcohol, methylated spirit, or other alcohols, and ketones such as acetone, have been found highly satisfactory for that purpose. This does not preclude the use of water or any of the usual solvents.

The substances used as fluxes should preferably have the following general characteristics: they should be soluble in a liquid carrier, they must crystallise or "set hard," if possible, at normal temperature when the liquid carrier evaporates, they should act as solvents to the oxide or other compound which insulates and prevents intergranular contact of the particles of the powder. Finally, it is generally an advantage when the melting point of the flux is reached before the sintering temperature has been attained.

A large number of substances can be utilised as fluxes. Amongst the most satisfactory are: ethyl silicate and most of the organic silicates, a large number of the organo-silicon compounds known as silicones and some water-soluble inorganic silicates, such as alkali metal silicates, e. g. sodium silicate, as well as a number of equivalent derivatives of aluminium such as those in which the aluminium is in the anion, e. g. alkali metal aluminates such as sodium aluminate. These compounds are complete fluxes, in the sense that they combine a "quick-setting" action on the cold powder as well as a fluxing action on the particles during sintering.

Substances whose action is primarily one of fluxing during sintering are: boric acid and borates, ethyl and other organic borates, a number of fluorides, boro-fluorides and silico-fluorides, a large number of metallic halides. Apart from a few exceptions, these latter substances do not set hard from the liquid state and cannot, as a consequence, be used alone for compacting and agglomerating the powder, unless the production of rather fragile compacted articles is not considered a serious drawback.

Furthermore, it is possible to increase the sintering effect of the flux by adding substances which substantially lower the melting point thereof.

For example, in the case of a silica flux, prepared by using ethyl silicate or some equivalent compound, additions of alkali metal hydroxides or compounds forming such oxides or hydroxides, will lower the melting point of the flux by as much as 300° C. Lead compounds, such as lead acetate, will also result in a lowering of the melting point, by formation of a fusible lead silicate.

In effect all substances which combine with the flux with formation of a fusible compound can be used for this purpose, but the selection of this substance is guided by the possible effect on the material to be sintered.

Thus, alkali compounds will not affect iron, steel, nickel, cobalt, or copper powders, but will interfere with powders containing chromium, manganese, molybdenum, tungsten, vanadium or the like, particularly if these metals are present in the free metallic form. If they are present in small concentration in alloy powders containing mainly the non-affected metals, the action of alkali compounds will not be detrimental.

Lead compounds, such as lead acetate, have little or no effect on all the commonly used metal powders and, in that respect, their use is recommended as a safe means of lowering the melting point of a silica flux.

It has been found that a liquid suspension of fine metallic powder in a flux in a liquid carrier can be brought to a remarkable degree of compactness by pouring the mix into a mould and allowing evaporation of the liquid carrier to take place. This compactness can be considerably increased by vibrating the mould and its content on a table having an oscillation frequency of several hundred to several thousand cycles per minute, with a small amplitude. Ultrasonic vibrations can also be used for the same purpose.

Moulds which can be used for shaping the articles can be made from a large variety of substances, which may be absorbent or not, according to requirements. Thus, plaster of Paris moulds can be used with fluxes requiring a rapid and general absorption along the whole surface of contact; the same applies to other porous agglomerated substances. Gelatine-phenol compositions can be used for parts which do not require rapid absorption of the liquid carrier; this applies also to moulds made from low melting-point alloys and metallic moulds in general.

In certain cases, non-absorbent moulds can be fitted with absorbent plugs at selected places, in order to assist the setting of the powder. Thus, in some cases it is desirable, for example, to utilise such an absorbent plug at the lower end of the mould in applications where rapid drying of the sides may lead to surface cracking during solidification of the paste.

The selection of a suitable method of shaping depends almost exclusively upon the shape and nature of the article to be produced and the invention is not limited to the use of moulds. In fact, any method which is applicable to liquid, semi-plastic or plastic substances can be used for the fabrication of the article from the powder.

Thus, according to one embodiment of the invention, rods, bars or tubes are extruded from a semi-plastic composition of flux and powder, by forcing the paste through the die. Blanks of suitable size can be stamped or formed to any required shape by one stroke of a press fitted with a forming die. For small parts of simple design, roller dies can be used.

After moulding or forming, the compacted article is allowed to dry. The powder is then strongly bonded, due to the setting of the flux acting as a cement to the metallic particles. The articles can be handled normally without in any way damaging the shape.

Once the agglomerated article has been dried, it is subjected to a suitable sintering treatment which eventually results in the production of a solid sintered article.

During the sintering operation, the flux serves the dual purpose of dissolving the insulating film between the particles and, particularly in the case of silicate fluxes, of protecting the article to a considerable degree from further oxidation due to an oxidising atmosphere at elevated temperature.

The flux can operate without the help of a reducing atmosphere. For a large number of alloy compositions, and in particular for alloys of high chromium content, a normal or even strongly oxidising atmosphere can be used without danger of internal or even surface oxidation.

This protection is not complete in the case of metals which are readily oxidised, such as iron and ferrous alloys, but it is nevertheless sufficient to permit the use of normal gas fired furnaces or oven furnaces of any type with a bed of charcoal. It is not necessary to utilise gas-tight furnaces with hydrogen or cracked ammonia atmospheres. Most furnaces with a suitable range of temperature can, therefore, be used for the purpose of sintering.

The mechanism of the flux action can be summarised thus:

The molten flux dissolves the insulating compounds between the particles and surrounds all exposed sides of the grains with the exception of the points of actual contact. There is no internal oxidation due to residual air. The points of contact act as nuclei for intercrystalline penetration and this incipient fusion causes gradual contraction of the intergranular spaces slowly forcing out the molten flux, through the porosities, to the surface of the article. Once the flux reaches the surface, it spreads on the article, forming a protective film against further oxidation.

The thermal cycle, time and temperature of treatment, vary greatly according to the nature of the metal or alloy or other powder being used. Thus, temperatures as low as 500° C. can be used for certain types of low melting-point alloys, whilst temperatures of 1550° C. may be required for metals of high melting point, e. g. tungsten and molybdenum. Intermediate temperatures can be used for ferrous alloys, nickel and cobalt alloys and chromium and its alloys.

The sintering may, if desired, be effected in two stages, a higher temperature being employed in the second stage than in the first. The first sintering may be effected by immersing the compacted article in a molten salt bath, e. g. containing a molten alkali metal cyanide, alkali metal chloride or alkaline earth metal chloride, and the second sintering may be effected in an electrode crucible furnace containing in an alkaline earth metal chloride a fusible silicate.

Furthermore, if desired, it is possible to combine the sintering action with the diffusion of metals, such as chromium, silicon, molybdenum or tungsten, e. g. by the processes of United Kingdom Specifications Nos. 646,637 and 646,638.

The following examples illustrate how the process of the invention may be carried into effect:

1. A flux was prepared by diluting 5 ccs. of ethyl silicate with 20 ccs. of methylated spirit, slightly acidified with hydrochloric acid. This flux was thoroughly mixed with fine iron powder (under 240 mesh) to form a fluid suspension, of the consistency of light mineral oil.

A mould, made of a tin-antimony-bismuth alloy, shaped in order to produce a rod, 4" long and ½" in diameter, with an absorbent plug at the lower end, was placed on a vibrating table. The liquid mixture was poured into the mould and allowed to settle for 10 minutes. The mould was then opened and the compacted article was allowed to dry in air for 2 hours. It was then sufficiently solid to be handled without special care.

The article was then introduced into a gas-fired oven furnace of the high speed steel hardening type, on a tray. The bed of the furnace had been covered with charcoal. The temperature was maintained for 2 hours at 1380° C. The article was removed and dipped in water.

Whilst maintaining its shape, the article had markedly contracted. Micro-examination showed normal sintering of the grains, with remarkably few porosities. Silicate inclusions were spheroidised and not numerous. The physical properties of the article were consistent with those of sintered iron powder.

2. A flux was prepared by diluting sodium silicate with water. It was mixed with iron powder as in Example 1 and poured into a mould similar to that used

in Example 1. When the paste was nearly set in the mould, slightly acidified alcohol was poured on top. After removing from the mould, the article was dried in air for 2 hours.

A sintering treatment similar to that of Example 1 was employed.

The article produced showed a normal sintering effect; micro-examination revealed more inclusions and porosities than in the product of Example 1.

3. A flux was prepared by mixing sodium silico-fluoride in a solution of gelatine and water. A liquid suspension was obtained by adding this solution to finely divided powder containing 80% of iron and 20% of nickel.

The mix was poured into a plaster of Paris mould whose surface had been rubbed with soap to prevent adherence of the material. The mix was allowed to dry for several hours. The product was then sintered as in Example 1.

The article produced showed a good sintering effect. There was a small proportion of inclusions and porosities. Surface oxidation was somewhat more marked than in the products of Examples 1 and 2.

4. The ethyl silicate flux of Example 1 was mixed with nickel powder into a thick paste. The paste was squeezed under pressure through a small round aperture, thus producing a rod of small diameter (¼") approximately 4" long. After drying, the rod was given a sintering treatment similar to that of Example 1, but at a temperature of 1320° C.

The diameter of the rod had contracted, the section showed on micro-examination a good sintering of particles, with little or no porosities and very few inclusions. Mechanical properties were consistent with those of sintered nickel powder.

5. A flux was prepared by dissolving cellulose acetate in a large excess of acetone and adding a small quantity of a borax solution in water. A very liquid mix was obtained by mixing the flux with nickel powder. The liquid was then poured into a filter paper thimble and allowed to settle on a vibrating table. The sample was then dried.

The compacted sample, including the filter paper thimble, was given a sintering treatment similar to that of Example 4.

Results were somewhat similar to those of Example 4, but porosities were more frequent and widespread.

6. The ethyl silicate flux of Example 1 was mixed with a powder containing 80% of cobalt and 20% of chromium. The treatment used in Example 1 was followed throughout, but the temperature of sintering was kept at 1340° C.

An excellent sintering effect was obtained and the product was practically free from inclusions and porosities. Physical properties were particularly good.

7. The ethyl silicate flux of Example 1 was mixed with ferro-chrome powder of fine mesh containing: chromium 70%, iron 30%, and carbon less than 0.15%. The method of Example 1 was used throughout.

The sintering temperature was kept at 1400° C., the normal atmosphere of the furnace, without a charcoal bed, was used. The temperature was maintained for 2 hours.

There was no oxidation on the surface, with the exception of a film of less than 0.001". The micro-examination revealed a good sintering effect. The article was rather brittle, but not more so than the equivalent cast alloy.

8. The treatment described in Example 7 was repeated, but with a powder mixture containing 70% of chromium and 30% of nickel.

Here again the sintering was good and oxidation was negligible. The physical properties of the alloy were

markedly superior to those of Example 7. There were very few inclusions and porosities.

9. Example 7 was repeated with a powder mixture containing 65% of chromium and 35% of cobalt.

The sintering effect was good, oxidation was very slight. Physical properties were excellent, in particular, hardness. There were very few porosities and inclusions in the article.

10. A mould was prepared in the shape of an oblong box, 5" x 2" x 3". The bottom was made of a slab of plaster of Paris, the sides of wood. The top was open.

Two mixes were prepared with the ethyl silicate flux of Example 1:

	Percent
(*a*) A mixture of the composition:	
Chromium	60
Cobalt	40
(*b*) A mixture of the composition:	
Iron	70
Cobalt	30

The mould was placed on a vibrating table and mix (*a*) was poured to a depth of approximately ¼". It was allowed to set to a thick paste. Then a similar layer of mix (*b*) was poured. The same operation was then repeated with mix (*a*). The triplex composition was allowed to dry.

It was then subjected to a sintering treatment in an open furnace with a charboal bed, at 1340° C. for 2 hours.

Micro-examination revealed a good layer formation of the two alloys, with satisfactory bonding between the dissimilar compositions. Mechanical properties were good. There was little or no oxidation and few inclusions and porosities.

11. Two mixes were prepared with the ethyl silicate flux of Example 1:

	Percent
(*a*) A mixture of the composition:	
Chromium	40
Nickel	60
(*b*) A mixture of the composition:	
Iron	70
Nickel	30

Mix (*a*) was poured into a plaster of Paris mould similar to that used in Example 3, placed on a vibrating table. When the sides had set to a thick paste, the mould was turned upside down to allow the liquid "core" to drip down, thus leaving a hollow space in the centre of the cast bar. Mix (*b*) was then poured into this cavity and the mould replaced on the vibrating table.

The dried composition was then subjected to a sintering treatment for 2 hours at 1340° C.

Micro-examination revealed a sharply defined boundary between the external part of nickel-chromium alloy and the core of iron-nickel alloy. The sintering was satisfactory, there were few inclusions and porosities.

12. A fluid suspension was prepared from iron powder and the ethyl silicate flux of Example 1. The moulded articles were prepared in the same manner as those of Example 1 but, after drying, they were immersed in a solution of sodium ethylate in alcohol and allowed to dry.

The moulded articles were placed in a steel box in contact with charcoal and heated for 3 hours at 820° C., followed by 3 hours' heating at 1250° C. to produce the sintered articles.

Micro-examination showed that the few silicate inclusions noticed in Example 1 had practically disappeared. The mechanical properties were markedly improved.

13. Moulded articles were prepared as in Example 12, but the immersion in sodium ethylate was replaced by one in a solution of lead acetate in alcohol. The same sintering cycle was used. Results were similar to those in Example 12.

14. Moulded articles were prepared as in Example 1 and were immersed in molten "Neutral Salt" (a mixture of alkali metal and alkaline earth metal chlorides) at

850° C. for 3 hours. They were then removed from the salt and transferred to an oven furnace, placed on trays with charcoal and heated to 1250° C. for 3 hours.

Results were similar to those of Example 1, the porosities and inclusions being slightly more widespread than in the products of Examples 12 and 13.

15. Moulded articles prepared as in Example 1 were immersed in a "Carboneutral" electrode furnace bath (alkaline earth metal chlorides) and maintained at 1300° C. for 3 hours. Results were similar to those of Example 14.

16. Moulded articles prepared as in Example 13 were packed in a chromium diffusion compound (a mixture of ferro-chromium, kaolin, ammonium iodide) in a manner similar to that described in United Kingdom Specification Nos. 646,637 and 646,638. Sintering and diffusion were effected by heating for 3 hours at 850° C. and then for 3 hours at 1200° C.

The articles sintered satisfactorily, the core structure being similar to that of articles prepared by the process of Example 13. There was a deep diffusion of chromium extending to 0.040" to 0.050" from the surface of the articles.

17. A mixture comprising 30% of alumina powder and 70% of chromium powder was prepared and ethyl silicate flux was added. The suspension was poured into a steel mould having the shape of a cylinder 1" diameter x 6" high.

A steel ram was placed at the top end of the cylinder and a pressure of 20 tons per square inch applied to the ram.

A compacted cylinder of chromium/alumina of high density was obtained.

The compacted sample was then heated in a reducing atmosphere to a temperature of 1300° C. for 3 hours.

The resulting sample was extremely hard, was very resistant to oxidation at temperatures up to 1200° C. and was not brittle.

18. A similar experiment was carried out, but with a mixture containing 10% of kaolin powder and 90% of ferro-chromium powder (65% chromium, 0.1% carbon, balance iron). The same ethyl silicate flux was used.

The resulting sample was stronger than that described in Example 17 and had a higher density.

19. The same experiment was repeated, but this time with only alumina powder and ethyl silicate flux.

The sintered alumina compact showed good resistance to impact and behaved satisfactorily from the point of view of thermal shocks. Presumably, aluminium silicate formed by the presence of hydrolysed silica increased the bonding strength of the alumina particles.

20. A mixture comprising 94% of tungsten carbide powder and 6% of cobalt powder was prepared and ethyl silicate flux was added.

The compacted sample was prepared as in Example 17, but the sintering was effected at 1400° C., in a graphite pot, for 2 hours.

The resulting carbide product was less brittle than similar samples obtained from sintered dry powders. The hardness was equivalent.

Similar experiments were carried out with titanium carbide and chromium carbide.

What we claim is:

1. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with a volatile liquid carrier and a flux which is an organic silicon compound selected from the group consisting of silicones and organic silicates which is soluble in said liquid carrier and which acts as a solvent for substances which insulate and prevent intergranular contact of the particles of the powder, forming said paste into an article of the desired shape and subjecting the article to a sintering temperature below the melting point of the powder particles thereof.

2. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with a volatile liquid alcohol and a flux which is an organic silicon compound selected from the group consisting of silicones and organic silicates which is soluble in said alcohol and which acts as a solvent for substances which insulate and prevent intergranular contact of the particles of the powder, forming said paste into an article of the desired shape and subjecting the article to a sintering temperature below the melting point of the powder particles thereof.

3. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with a volatile liquid ketone and a flux which is an organic silicon compound selected from the group consisting of silicones and organic silicates which is soluble in said ketone and which acts as a solvent for substances which insulate and prevent intergranular contact of the particles of the powder, forming said paste into an article of the desired shape and subjecting the article to a sintering temperature below the melting point of the powder particles thereof.

4. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with a volatile liquid carrier and a flux which is an organic silicon compound selected from the group consisting of silicones and organic silicates which is soluble in said liquid carrier and which acts as a solvent for substances which insulate and prevent intergranular contact of the particles of the powder and a substance adapted to reduce the melting point of said flux, forming said paste into an article of the desired shape and subjecting the article to a sintering temperature below the melting point of the powder particles thereof.

5. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with a volatile liquid carrier and a flux which is an organic silicon compound selected from the group consisting of silicones and organic silicates which is soluble in said liquid carrier and which acts as a solvent for substances which insulate and prevent intergranular contact of the particles of the powder, forming said paste into an article of the desired shape and subjecting the article to a two-stage sintering first at a lower and thereafter at a higher temperature, both temperatures being below the melting point of the powder particles.

6. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with a volatile liquid carrier and ethyl silicate as a flux which is soluble in said liquid carrier and which acts as a solvent for substances which insulate and prevent intergranular contact of the particles of the powder, forming said paste into an article of the desired shape and subjecting the article to a sintering temperature below the melting point of the powder particles thereof.

7. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with a volatile liquid carrier and ethyl silicate, extruding said paste through an opening to produce the desired article in the shape of a rod, drying the article by evaporation of said liquid carrier and subjecting the article to a sintering

temperature below the melting point of the powder particles thereof.

8. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with methylated spirit and ethyl silicate, forming said paste into an article of the desired shape and subjecting the article to a sintering temperature below the melting point of the powder particles thereof.

9. A process for the manufacture of sintered articles which comprises forming a paste by mixing a sinterable inorganic powder selected from the group consisting of metal powders and metallic carbide powders with a volatile liquid carrier and a flux which is an organic silicon compound selected from the group consisting of silicones and organic silicates which is soluble in said liquid carrier and which acts as a solvent for substances which insulate and prevent intergranular contact of the particles of the powder, forming said paste into an article of the desired shape and sintering the article at a temperature below the melting point of the powder therein within the range of about 500 to 1550° C.

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