PATENT SPECIFICATION

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(19) THE PATENT OFFICE LONDON

(54) A PHOSPHORUS STEEL POWDER AND A METHOD OF MANUFACTURING THE SAME

(71) We, HOGANAS AB, a Company organised under the laws of Sweden, of Fack, 263 01 Höganäs, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to phosphorus steel powder mixtures to be used in powder metallurgy. In addition to iron and phosphorus these powder mixtures can contain other alloying elements common in this technique, such as copper, nickel, molybdenum, chromium and carbon.

The use of phosphorus as an alloying element in powder metallurgy has been known since the nineteen forties. Sintered steel alloyed with phosphorus has substantially improved strength characteristics in relation to non-alloyed sintered steel. Already at an early date there were for this object used mixtures of pure iron powder and ferrophosphorus powder. However, the ferrophosphorus first used had a composition which made it extremely hard and caused a considerable wearing of the tools. This drawback has been reduced to an acceptable degree by using a ferrophosphorus powder having a lower content of phosphorus and thereby reduced hardness see for example Swedish Patent No. 372,293.

However, sintered details manufactured by pressing and sintering such steel powder mixtures sometimes have an unacceptable brittleness. This is revealed for example by the fact that a population of sintered test bars made from these mixtures can comprise individuals having extremely reduced mechanical characteristics especially with regard to impact strength and permanent strain after rupture (break elongation). As the advantage of phosphorus alloyed sintered steels is high strength in combination with very good strain characteristics the above brittleness risks are very serious.

Said brittleness risk has shown up to be present when the ferrophosphorus is of such composition that there is established a liquid phase at the sintering temperature. At the usually used sintering temperatures, 1040°C and above that, this fact provides that phosphorus contents of more than 2.8% in the ferrophosphorus give a sintered material having an increased brittleness risk. The fact that ferrophosphorus having a high phosphorus content is used in spite of this drawback is dependent on the favourable sintering process which is provided by the liquid phase and the favourable distribution of the phosphorus in turn providing for a rapid indiffusion thereof which is obtained because of the fact that the ferrophosphorus provides for a liquid phase.

Thus, the object of the present invention is to solve said problems with regard to the brittleness of sintered steel manufactured from a mixture of iron powder and a ferrophophorus powder having a phosphorus content exceeding 2.8 wt. %. The solution of the problem has proved to reside in the use of a ferrophosphorus powder having a low content of impurities, especially impurities sensititve to oxidation. A further improvement can be obtained if the ferrophosphorus powder also has a small maximum particle size.

A phosphorus steel powder according to the invention for manufacturing sintered details having an extremely small tendency to brittleness ruptures consists of iron or steel powder substantially free from phosphorus, mixed with a ferrophosphorus powder in total containing in all less than 4%, preferably less than 3% impurities which are at the sintering temperature more easily oxidized than the main components iron and phosphorus. Furthermore, the particles of the ferrophosphorus powder shall have a maximum size of 20 μm, preferably a maximum size of 10 μm. The phosphorus content of the ferrophosphorus powder shall exceed 2.8% and in order to reduce the wearing of the tools the phosphorus content shall preferably be less than 17%. If the ferrophosphorus powder is manufactured by grinding a workpiece the phosphorus content should exceed 12% and should preferably be between 14 and 16%. The phosphorus content of the mixture is between 0.2 and 1.5%.

It is often the case that there is a great difference between the particle sizes of the powder components in the mixture leading to an especialy great risk of segregation and thereby of a discontinuous distribution of the powder components. In order to reduce the tendency of the mixture to segregate after the mixing operation 50-200 g of a light mineral oil per metric ton powder can be added during the mixing operation. Thereby the fine alloying particles can adhere to the coarser iron powder particles.

In order to improve the protection against segregation the iron-ferrophosphorus mixture is heated with or without the addition of oil in a reducing atmosphere to a temperature of between 650 and 900°C for a period of 15 min. to 2 hours. Thereby, the powder is loosely sintered together so that a following cautious disintegration has to be carried out in order to restore the original particle size. The powder provided in this way has iron particles with particles of the fine grained ferrophosphorus powder sintered thereto.

The methods described above in order to avoid segregation can be performed to a mixture having more phosphorus powder. The concentrate so obtained can be mixed with the iron powder to provide for the desired phosphorus content in the final product.

The critical contents of the impurities appear from the following examples.

Example 1

Three melts of iron-phosphorus including 15.5-16.5% phosphorus and controlled contents of silicon of 0.02, 0.17, 0.75 and 4.81% and additional impurity contents of ≤0.01% were manufactured and were allowed to solidify. Thereupon, they were ground to a powder from which two size classes were taken out, 0-10 μm and 10-40 μm. These phosphorus powders were mixed with extremely pure iron powder so that the mixture had a phosphorus content of 0.6% whereupon the mixture was compressed to impact strength test bars without indications of fracture having a size of 55 x 10 z 10 mm. The bars were sintered in cracked ammonia at 1120°C for 1 hour. The impact strength was tested at room temperature by means of a Charpy pendulum hammer. The result is shown in Fig. 1 wherein the impact strength (I) relates to the mean value including the standard deviation for seven bars.

The curves clearly show the advantage of the phosphorus powder having partly a small particle size and partly a low silicon content. The silicon content shall be less than 0.5%, preferably less than 0.2%, for giving the impact strength a stable high value. However, the silicon content shall not be too low but exceed 0.05%, preferably exceed 0.1%.

Example 2

Iron-phosphorus alloying powder having aluminium as the only impurity element was manufactured in the same way as according to the preceding example. Three different contents of aluminium were used: 0.015, 0.03, 0.8 and 4.8%. Also powders having two different particle sizes, namely 0-10 μm and 10-40 μm, were manufactured. The further treatment and the return of the results are the same as according to example 1, see Fig. 2.

The same conclusion concerning the particle size can be drawn from this example as from example 1. Also according to this example the toughness is better when the impurity contents are low. A suitable maximum content of aluminium in the iron-phosphorus-alloying powder is 3%, preferably 2%, and a suitable minimum aluminium content is 0.02%.

Example 3

The same tests as according to the above examples were conducted with iron-phosphorus-alloys, this time having manganese as the only impurity element with a content of 0.01, 0.07, 0.68 and 5.0%. The phosphorus content varied between 17.2 and 17.5%. The result appears from Fig. 3.

Once more the example shows the importance of a small particle size of the iron-phosphorus alloying powder. Furthermore, the manganese content should be less than 0.25%, preferably less than 0.15%, and higher than 0.03%, preferably higher than 0.05%.

Example 4

The same tests as according to the above examples were conducted. The phosphorus content of the iron-phosphorus powders was 16.7-17.6% while the only impurity element this time was titanium in the amounts of 0.01, 0.02, 1.0 and 4.4%. The result appears from Fig. 4.

Also this example shows, even if not as striking as the previous examples, that the particle size of the iron-phosphorus-powder shall be low. Also the content of titanium shall be relatively low, less than 3%, preferably less than 2%. If the content of titanium is lowered too much, the brittleness phenomen appears again, for which reason this content shall exceed 0.02%, preferably exceed 0.05%. The following example shows this fact even more clearly.

Example 5

An iron-phosphorus-alloy was manufactured by melting extremely pure raw materials (the same as used according to the previous examples). No artificial impurity elements were added. The alloy was of the following composition: 17.4% P, 0.02% Si, <0.03% Al, 0.01% Mn, 0.01% Mg, 0.01% Ti, balance Fe. The alloy was crushed ground and screened to a powder having a particle size partly less than 10 μm, partly between 10.40 μm. The iron-phosphorus powder was mixed with the same pure iron powder as according to previous examples to a phosphorus content of 0.6%. Impact strength test bars were pressed from the powder mixture, and the bars were sintered in cracked ammonia at 1120°C for a period of 1 hour. The impact strength of the sintered bars was tested according to Charpy. When the particle size of the iron-phosphorus powder was less than 10 μm the mean value of the impact strength for seven test bars was 1.6 kpm (15.7 J) and the standard deviation was 0.8 kpm (7.8 J). The corresponding values for the case of the added iron-phosphorus powder having a particle size between 10 and 40 μm were 0.6 kpm (5.9 J) and 0.4 kpm (3.9 J), respectively.

This example evidently shows that the brittleness risk in connection with phosphorus sintered steel manufactured from a mixture of iron-phosphorus powder and iron powder is great when using extremely pure iron-phosphorus material. Therefore, the total content of impurities which are more easily oxidized than iron and phosphorus at the sintering temperature should exceed 0.1%

Thus, the present invention represents a solution of the problem of brittleness ruptures sometimes appearing in sintered steel manufactured from a mixture of iron powder and ferrophosphorus powder. The solution resides in the fact that the ferrophosphorus powder shall have a content of impurities oxidizable at the sintering conditions which is as low as possible, the total content of such impurities shall preferably however exceed 0.1%. The allowable maximum content of these impurities is 4% and these limits have been defined for allowing contents of certain, especially sensitive impurities.

WHAT WE CLAIM IS:—

1. A phosphorus steel powder for manufacturing sintered articles or mouldings having high toughness, consisting of a steel powder substantially free from phosphorus and having a good compressability, which is intimately mixtured with ferrophosphorus powder having a phosphorus content exceeding 2.8 weight-%, in such an amount that the phosphorus content of the mixture is 0.2 to 1.5%, wherein the total content of impurities which are at the sintering temperature more easily oxidized than the main components iron and phosphorus does not exceed 4%, preferably 3%, and the ferro-phosphorus powder has a maximum particle size of 20 μm, preferably a maximum particle size of 10 μm.

2. A phosphorus steel powder as claimed in claim 1, wherein the content of impurities which are at the sintering temperature more easily oxidized than iron and phosphorus is at least 0.1%.

3. A phosphorus steel powder as claimed in claim 1 or 2, wherein the silicon content is less than 0.5%, preferably less than 0.2%, and exceeds 0.05%, preferably exceeds 0.1%.

4. A phosphorus steel powder as claimed in claim 1 or 2, wherein the aluminium content is less than 3%, preferably less than 2%, and exceeds 0.02%.

5. A phosphorus steel powder as claimed in claim 1 or 2, wherein the manganese content is less than 0.25% preferably less than 0.15%, and exceeds 0.03%, preferably exceeds 0.05%.

6. A phosphorus steel powder as claimed in claim 1 or 2, wherein the titanium content is less than 3%, preferably less than 2%, and exceeds 0.02%, preferably exceeds 0.05%.

7. A phosphorus steel powder as claimed in claim 1, further comprising 0.005-0.02% of a mineral oil for obviating segregation.

8. A phosphorus steel powder as claimed in claim 1, wherein the ferrophosphorus particles are adhered to the steel powder particles by means of sintering for obviating segregation.

9. A phosphorus steel powder as claimed in any preceding claim, in which the phosphorus content is in the range of 12 to 17 weight-%.

10. A method of manufacturing a phosphorus steel powder according to any of the preceding claims, wherein a basic amount of steel powder is intimately mixed with ferrophosphorus powder and the ferrophosphorus particles are adhered to the steel powder particles by adding to the powder to a concentrate possibly with the or loosely sintering the ferrophosphorus particles to the steel powder particles with subsequent cautious disintegration of the cakes thus formed.

11. A method as claimed in claim 10,

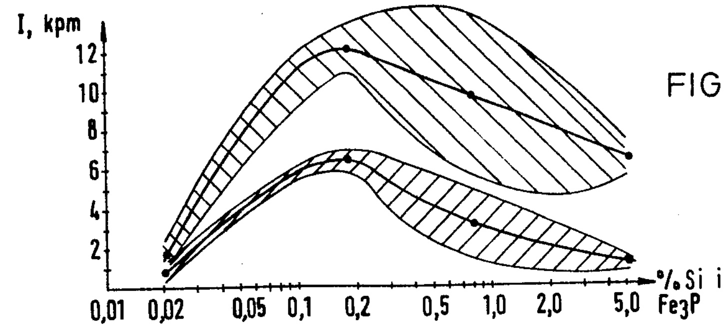

FIG. 1.

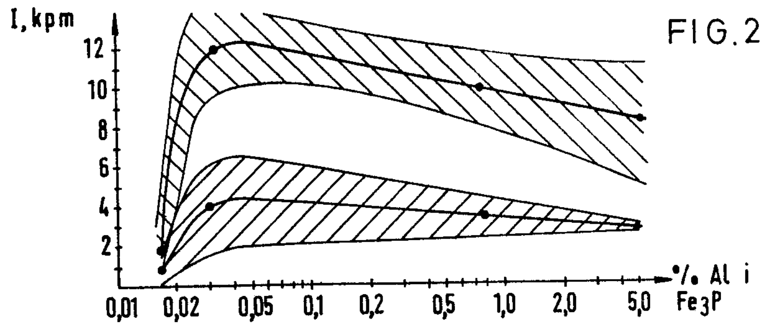

FIG. 2.

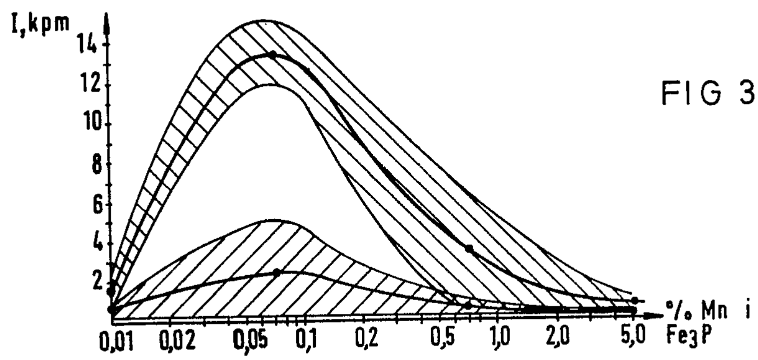

FIG 3.

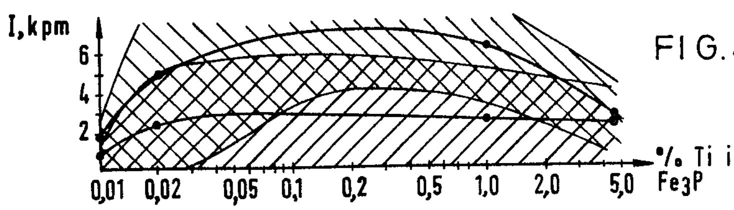

FIG. 4.