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(54) Method to obtain coatings on mechanical parts by P/M techniques.

(57) Method to obtain coatings on mechanical parts by P/M techniques be means of a paste composed by a binder and metal and/or ceramic powders comprising operations of slowly adding to the paste an additive formed by a solution of free or complex ions preferentially metallic ones in a polar solvent; homogenizing the paste mixture and the additive; applying of the product obtained that way on the surface of a substrate to coat; removing the binder by a first stage of slow heating (a) and a second stage of fast temperature (b) increase. The mentioned additive is chosen among those that do not produce precipitates under atmospheric pressure below 80º C; they precipitate between 80 and 120º C; and their precipitates are stable below 200º C.

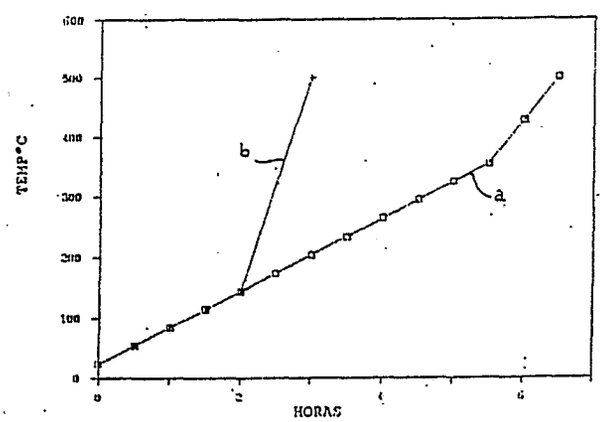

FIG. 1

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METHOD TO OBTAIN COATINGS ON MECHANICAL PARTS BY P/M TECHNIQUES

This invention applies to a method to obtain coatings on mechanical parts by P/M (Powder Metallurgy) techniques by means of a paste conventionally applied on the required surface of a substrate to coat. This paste is set up by a binder and metallic and/or ceramic powders.

Powder Metallurgy offers unique advantages, as for instance to obtain materials composed by a metallic matrix with non metallic inclusion or selflubricating materials with oil containing prorosity. For this and other reasons, several P/M methods have been developed to obtain coatings on substrate parts.

The most common method to apply coatings on substrate parts is the single-axis pressing of two powder layers of different composition which form parts composed by two differente materials after sintering. The limit in this case is the impossibility of filling a die and densifying powders over non flat surfaces, for instance on spherical and conical surfaces.

Another application method is the injection moulding of a plastified mixture in a cavity where the substrate part is an insert or part of the mould. This method is especially suitable to large series.

A paste like product can be also applied by forming a sheet from which shapes are cut and sticked to the substrate part.

In fact, coatings can be obtained by any method for paste application, as for instance a brush, smoother, centrifugation etc.

Several methods are known to obtain a paste composed by a binder and metallic or ceramic powders or mixtures of both, as for example the methods describred in article 5 of the publication "Progress in Powder Metallurgy" volume 42, 1986.

The binder ratio varies according to the powder grain size or according to the specific powder surface. The binder may be of wax basis, being formed, for instance, by wax and petrolatum or of polymeric basis, being formed, for instance by polymetylmetacrilate dissolved in toluene or of water based, formed, for instance, by a solution of cellulosic glue or by a combination of various.

The materials of the substrate part have only the limitation of being compatible with the temperature and atmosphere used when sintering the coating.

The pastes may be also used for manufacturing parts without substrate, i.e. totally formed by the coating material, by means of coating a substrate of the required shape and detachable after sintering, as for instance graphite.

Binder forming always comprises a thermal treatment stage for binder removal before sintering the powders. This stage is the most critical of the process, since faults easily appear, as for instance distortion of the part shape of cracks and craters on the surface. To avoid these defaults a very slow warmup and a very long process duration are necessary, resulting in a high cost, and consequently in a necessary limitation of the process to very specific applications.

It is obvious that the binder composition influences the shaping properties of the paste and the coating behaviour during thermal treatment.

Pastes based on wax are very plastic at room temperature, consequently they are easily formable. However, as the temperature increases, its viscosity reduces and, therefore, they tend to flow and distort during the removal stage.

Pastes based on cellulose or water solved polysaccharides harden with temperature and retain well the shape during binder removal, but they have poor formability and its viscosity at room temperature is very affected by solvent losses during storage or handling.

Thermoplastic polymers with solvents also harden when heating and solvent evaporation, but they soften again when temperature further increases. They are easily conformable, but they are affected by distortion during removal and variable viscosity with solvent losses.

The known processes use to combine the mentioned basic compositions, for instance a wax with one polymer and one solvent or plasticizer in order to compensate advantages and disatvantages. Besides, all known pastes require slow heating, as we already stated, to avoid internal pressures by vapors or decomposition gases caught inside the pastes which generate craters and cracks when reaching the surface.

The minimum temperature to assure total removal of a organic type binder is 500º C and the most favorable atmosphere is oxidant. The total process with usual heating speeds of 0,5º C per minute has a duration of 9 to 10 hours and results in very rusty parts. This oxidation is used to furnish a cementing skeleton among the particles as the binder is disappearing. However, it is negative for the sintering stage in major or minor degree, according to the alloy elements, since the oxide reduction requires high temperatures and longer exposure times to reducing atmospheres. In addition, the dimensional change in sintering depends upon the oxidation degree and in the case of bronzes very much.

As we have already seen, coatings of this type need a slow heating speed at the critical binder removal stage. In order to avoid distortions, cracks

or craters coatings are very thin (between 10 and 50 microns) or they are conceived for very concret applications, as for instance the coating described in the US license No. 4.596.692 from Morishita and others, or they use a specific and concret binder as mentioned in the US licence No. 4.491.559 from Kennametal Inc. which contains metal particles of tungsten carbide.

As already stated parts can be entirely made from pastes suitable for coatings, as those manufactured according to the US Patent No. 4.626.406 from Inco Alloys International Inc. However, these pastes present a serious obstacle consisting in the binder removal stage which must be carried out by a very slow temperature increase taking days and in some cases even weeks. Therefore, in such cases it is a question of very concret application processes.

Surprisingly it has been found out that the method subject to this invention allows coatings which admit a fast temperature increase from the moment of removing the water based vehicle or the polar solvent without outflow nor distortion after the binder removal has been finished. The coating obtained according to the method subject of this invention shows an excellent homogeneity and after debinding a suitable strenght for hadling on trays, pallets and trucks without more care than usual in manufacturing plants. Coating pastes obtained according to this invention allow fast heating from 120º C approximately and without shape distortions, cracks or craters and in a reducing, neutral or oxidant atmosphere and even in vacuum.

Basically the coating accordingly the invention allows shorter debinding and is more flexible on alloy elements oxigen affinity than the methods known until now.

Essentially the method according to the invention is characterized by performing the operation after the conventional paste is obtained, of slowly adding at atmospheric pressure and at a temperature ranging between 10º and 50º C an additive formed by a solution in a polar solvent, preferably of metallic free or complex ions; homogenizing the paste mixture and the additive by mechanical agitation; application of the product obtained in that way on the surface of the substrate part to coat, by any known way; performing of a first binder removal stage, by conventional application of heat until nearly 120º C by a temperature increase of approximately 0,5º C per minute, and a second and last binder removal stage with faster temperature increase. Then the part is ready to be submitted to the known coating sintering operations and finishing.

According to another invention feature, the mentioned additive is closen among those which do not produce precipitates at atmosphere pressure below 80º C. They precipitate between 80 and 100º C and their precipitates are stable below 200º C.

According to another invention feature, the mentioned additive is chosen in such a way that its free metal ions are compatible with the alloy of the metal and/or ceramic powders which form part of the conventional paste to which the additive is added.

In order to better clarify the invention below three examples of realization of the method are given:

EXAMPLE 1:

Spherical bronze 70% Sn, particle size ranging between 250 and 125 microns was mixed with a binder formed by 80% petrolatum and 20% of Hoechst wax tipe C in a proportion of 93% powder and 7% binder. This paste was applied on a cylindrical surface of P/M steel parts 2% copper, density 6.8 g/cc, forming a 1.2 mm thickness. Then binder cycles were tested in an oven with air atmosphere with different heating speeds. In this way the cycle represented in figure 1, curve a, was determined as the shortest and still free of distortions and cracking. An identical paste to the previous one was prepared but adding 2% of an additive formed by 17% of copper sulphate and 83% of water. Tests to determine the shortest cycle were performed and the cycle represented in figure 1, curve b, was obtained. It is noted that the presence of the additive according to this patent allows the reduction of binder removal practically to half the time.

EXAMPLE 2:

A mixture of atomized iron powder with particle size below 100 microns and atomized nickel powder with particle size below 50 microns in a proportion of 96% iron and 4% nickel was prepared. This mixture was then mixed with a binder formed by 80% petrolatum and 20% Hoechst wax type V in a proportion of 90% to 10%. The obtained paste was conformed as in the previous examples and submitted to removal cycles producting in all cases a coating overflow. To this paste was added 1% of an additive formed by 40% in weight of iron ammonic oxalate and 60% water.

The parts coated with this additivated paste were submitted to a removal cycle represented in figure 1, curve b, without producing distortions, cracking nor craters.

EXAMPLE 3:

Spherical bronze 90% Cu-10% Sn with a particle size ranging between 300 and 100 microns was mixed with a binder formed by 58,3% in petrolatum, 1,8% in wight of sodium alginate and 39,9% of water in a proportion of 85% powder and 15% binder. This paste was applied on the cylindrical surface of test parts with 1.5 mm thickness. By the same methodology of example 1, the thermal cycle represented in figure 1, curve a, was determined as the shortest to avoid cracks. In the same test a paste identical to the previous one was prepared but by adding 1.5% of an additive formed by 17% in weight of copper sulphate and 83% of water. In the test to determine the shortest cycle, the cycle represented in figure 1, curve b, was obtained. Once again the presence of additive allows reducing the removal time.

After widely describing the invention's nature as well as the way of putting it into practice, it is stated that everything that does not alter, change or modify the basic principle may be submitted to detail variations.

Claims

1.- Method to prepare coatings by P/M (Powder Metallurgy) techniques on mechanical parts by means of a paste which is conventionally applied on the substrate part surface, the paste being formed by a binder and by metallic and/or ceramic powders characterized because after obtaining the mentioned conventional paste following operations are being carried out:

- Slowly adding at atmospheric pressure and temperature ranging between 10 and 50º C an additive formed by a solution in polar solvent of complex ions preferantially metallic;
- homogenizing of the paste mixture and additive by mechanical agitation at atmospheric pressure or applying vacuum for a period ranging 3 and 60 minutes;
- applying of the product obtained this way on the surface of the substrate part to coat in any known way;
- perfoming the first binder removal stage by conventional application of heat to nearly 120º per minute; and
- performing the second binder removal stage by heating and fast increase of temperature, then the part being ready to be submitted to the known sintering and finishing operations.

2.- Method to prepare coating according to claim 1, characterized because the mentioned additive is chosen among those which do not produce precipitates at atmospheric pressure below 80º C; they precipitate between 80 and 120ª C; and their precipitates are stable below 200º C.

3.- Method to prepare coatings according to claims 1 and 2 characterized because the mentioned additive is chosen in such a way that their free metallic ions are compatible with the alloy system of the metallic and/or ceramic powders which form part of the conventional paste to which additive is added.

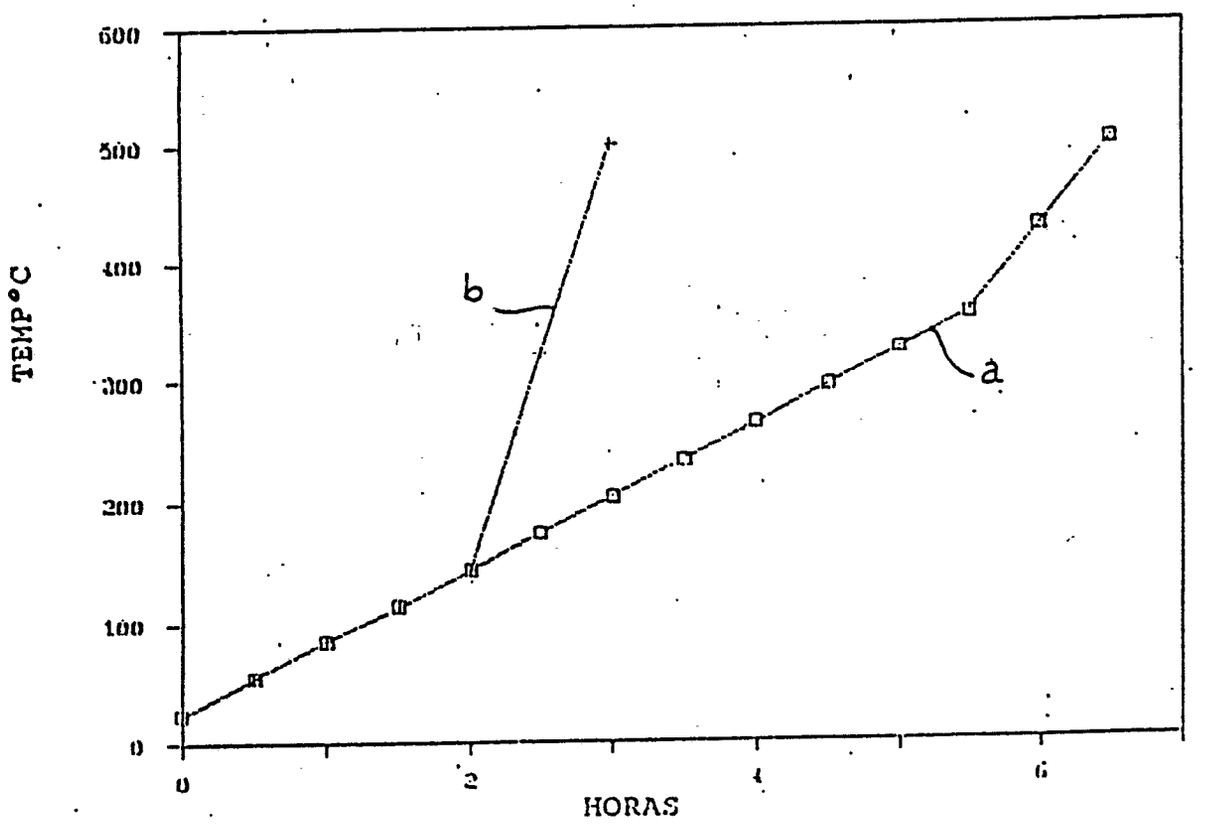

FIG. 1

European Patent Office

EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 89500102.2

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE - A1 - 3 628 363 (MTU) * Claims 1-4,7,9; column 3, line 56 - column 4, line 25 *	1	C 23 C 24/08 B 22 F 7/04
D,A	US - A - 4 626 406 (JON M. POOLE) * Column 1, lines 20-31; column 2, line 43 - column 3, line 63; table 3; claims 1,2 *	1	
A	US - A - 4 371 589 (JOSHUA B. WARNER) * Abstract *	1,3	
A	DE - B - 1 185 901 (DR. H.C. HANS VOGT) * Claims 1,4 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 23 C 24/00
C 22 C 32/00
B 22 F 7/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	17-01-1990	DUNGLER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
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