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[54] METHOD OF MAKING TOOLS BY IMPREGNATING A STEEL SKELETON WITH A CARBIDE, NITRIDE OR OXIDE PRECURSOR

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[57] ABSTRACT

Method of making tools by compressing, e.g., steel particles into a porous skeleton, having high temperature strength and being penetrated by a continuous network of pores of total volume below 50 percent and by filling at least part of the pores with a non-metallic material that is substantially undeformable and harder than the skeleton at temperatures up to about 650° C.

24 Claims, No Drawings

METHOD OF MAKING TOOLS BY IMPREGNATING A STEEL SKELETON WITH A CARBIDE, NITRIDE OR OXIDE PRECURSOR

The present invention relates to method and process of tool and die making by compressing powder or the like and sintering this intermediate product subsequently.

In many areas of engineering there is a great need for particularly formed and shaped parts of very high strength, particularly at high temperatures. This is particularly true in the aerospace industry but also for gas turbines, and in the field of hot working and forming of heavy metal or the like. Parts that undergo mechanical wear and tear, particularly at temperatures above 650° C are often made by cast alloys as well as by hot forgeable alloys using as basic component nickel or cobalt.

Another known method for making form parts of high hot strength or high temperature resistance and high hot hardness uses metal powder as raw material and frequently high melting oxides are added. The powder or mixture of powders is then compressed into porous blocks or billets, which are subsequently sintered to obtain high density. Sintering is to occur at high temperatures. Alternatively, hot pressing or hot extrusion is used for forming and condensing the parts to be made. In either case, it is deemed desirable to obtain a product having a high density. The non-metallic parts, and preferably also the metal powder, should be very fine in order to obtain a finally dispersed and essentially uniform distribution of the inclusion. As with present day knowledge, this is believed to result in parts of high strength.

It is also known to provide a frame or skeleton from thin metal fibers, preferably thinner than 0.1 mm diameter, by means of chromium diffusion treatment. Chromium is caused to be included in these fibers and subsequently this skeleton is dipped into ceramic dross, i.e., a watery suspension of a ceramic compound. Such a method is disclosed, for example, in German Patent No. 1,227,663. However, this method is very expensive and time-consuming, because of the long periods needed for diffusion, and also the drying period is quite long. Furthermore, it is required that the skeleton itself is relatively porous in order to make sure that the solid particles of the suspension do in fact penetrate deeply into the fibers. Moreover, the water of this ceramic suspension must be removed subsequently. To increase density further, sintering of the ceramic components is required, whereby the metallic component becomes already liquidous.

The present invention is based on development and investigations that have been conducted independently from the foregoing and were particularly directed to the making of tools and dies to be used for hot working. It is important that the material worked with is considerably cheaper than the known alloys on nickel and cobalt basis. These developments have led to the result that, for example, a porous die or mold for extrusion, e.g., of steel pipes, and having a nitrogen content of about 1 percent could be made from chromium steel powder, having a longer service life than known dies and molds. Moreover, the product (e.g., pipe) had a better surface texture when such particular die was used. The improvement was particularly noticeable when compared with known type of steel dies that have been used in the past for extrusion and were made on bases of melting metallurgy, without pores. Other tests, however, led to the conclusion that in many cases it is not sufficient to obtain a high hot strength at temperatures above 650° C but it was found that the strength at lower temperatures, even down to room temperature, is also of considerable influence on the light of such a die.

It is an object of the present invention to provide process and method for tool and die making that results in a tool or die which is very hard and has a high wear resistance, particularly for temperatures above 650° C, but also for temperatures below that value. The known materials do not have that property or only to a very unsatisfactory degree. For example, tool steel and martensitic aging steel as used to an increasing extent, are very hard at temperatures up to about 550° C, but their strength decreases rapidly above that temperature. Above 550° C one uses exclusively the usually austenitic alloys having nickel or cobalt basis as was mentioned above but it was also stated above, that these alloys do not have the sufficient strength at lower temperature, and that was found to be detrimental for overall wear and life.

In accordance with the present invention, it is suggested to make tools or dies to be used for hot forming of metal, such as a press or rolling mandrel or a die of an extrusion molding machine or the like in the following manner. The tool or die is made as a skeleton with a penetrating and all-pervading network of pores but at a total volume of pores less than 50 percent, preferably about 20 to 30 percent. Metal to be used here is to have high hot strength and high temperature resistance. The pores are to be filled with a non-metallic, an-organic material as completely as possible, and having significant hardness particularly below 650° C, so as to render the tool practically undeformable. The mechanical properties, such as hardness, strength, wear-resistance or the like, are determined in the lower temperature range predominantly by the non-metallic component, while for temperatures above 650° C, the metal component of the skeleton determines predominantly these properties. The particular tool or die, made in that manner, particularly with a total pore volume of less than 50 percent, has these pores filled with non-metallic material either completely or only in zones of the tool engaging later the material to be worked; these zones may have a depth of about 5 to 10 mm, as filled with the non-metallic inclusion, while the remainder (interior) of the tool, has a relative density of 90 percent and above. The raw material, from which to make the tools or dies, may be comprised of small particles of any form, such as flakes, shavings, powder, fibers, cuttings or the like. These particles are compressed and sintered, and the resulting porous part has the shape of the tool or die to be made. As a consequence, a metallic body is produced penetrated by a continuous, all-pervating network of pores, and that is actually the basis for defining the body as a skeleton. It is this a random type frame and support microstructure made of material of high temperature resistance.

A heat resisting steel alloy that could be used in accordance with the invention has composition shown in the following table.

TABLE A

		% (by weight) (range)	Preferred Example
Carbon	max.	0.5	0.05
Silicon		0.2 – 2.0	1.4
Manganese		0.3 – 15	0.6
Chromium		10 – 25	13
Nickel		4 – 20	13
Tungsten	up to	10	1.4
Vanadium	up to	2	1
Iron	remainder		remainder
The following elements could be added to further increase hot strength:			
Niobium	up to	2	—
Molybdenum	up to	3	—
Boron		0.03	—
Zirconium		0.03	—

One can also use chromium steel alloys having a relatively high nitrogen content, an example thereof is shown in Table B.

TABLE B

		% (by weight) (range)	Preferred Example
Carbon	max.	0.5	0.02
Silicon		0.2 – 2.0	0.7
Manganese		0.3 – 15	1.3
Chromium		10 – 25	25
Nickel		4 – 20	13.5
Tungsten	up to	10	3.3
Vanadium	up to	2	—
Nitrogen		0.2 – 3.0	1.62
Iron	remainder		remainder

A heat resisting nickel alloy may, for example, be made in accordance with Table C.

TABLE C

		% (by weight) (range)	Preferred Example
Carbon		<0.3	0.2
Silicon	up to	2	0.35
Manganese	up to	4.0	0.7
Chromium	up to	22	17
Molybdenum	up to	20	17.5
Tungsten	up to	8	4.2
Cobalt	up to	18	—
Titanium	up to	4	—
Aluminum	up to	5	—
Iron	up to	20	3
Nickel	remainder, at least	40	57

A heat resisting cobalt alloy may be made in accordance with Table D.

TABLE D

		% (in weight) (range)	Preferred Example
Carbon		<0.60	0.55
Silicon	up to	1	0.7
Manganese		0.5 – 3	2.4
Chromium		10 – 22	21
Nickel		10 – 20	11.5
Tungsten	up to	15	15
Molybdenum	up to	4	—
Niobium	up to	4	—
Iron	up to	4	remainder
eventually some Nitrogen	remainder,		
Cobalt	at least 22		44

After having explained various compositions to be used as raw material, we proceed now to the description of making the skeleton or frame. This, however, follows basically known procedures. The metal particles are poured into a mold and condensed subsequently. It is usually of advantage to sinter the pressed form so that the metal parts engage more intimately so as to establish an integral body. In combination with sintering, or separately therefrom, the porous skeleton may be particularly treated in order to increase the hot strength and heat resistance; for example, there may be provided carbonization, nitrating or cold working. In many cases, as will be shown more fully below with reference to the preferred embodiment of the invention, it may be of advantage to condense the metal parts when still relatively soft and to increase hardness of the resulting skeleton body after its production.

The relative density of the skeleton is variable over a large range and may actually range from about 4 percent, if shavings are used, up to 90 percent for very fine powder or the like. Preferably, the relative density ranges from 60 to 85 percent. The metallic skeleton body has in each of these cases a network of pores which are more or less interconnected and penetrate the body throughout. They are now to be filled so that, in effect, a second network be produced, which, in turn, is penetrated by the metallic skeleton. This second and, in fact, coherent network of filler material is produced by infiltration, impregnating or the like. This may be combined with an annealing process, for example, upon sintering the metal skeleton body, but impregnation could be carried out in a separate process. The melted, i.e., liquified, material that is to penetrate the pores of the skeleton, may have already the final composition or it is an intermediate product that reacts chemically with some element of the skeleton body so that, in fact, the final product is composed of a second non-metallic, inorganic network that has become integral with the porous skeleton as originally produced.

As means for obtaining this penetration, one may use preferably silicate, water glass, glass, enamel or the like. In addition, other salts, such as chlorides or aluminates, can be used. Molten metal or a metal alloy can be used also for impregnation, such as aluminum, magnesium, individually or an aluminum silicon alloy or an aluminum titanium alloy.

These impregnating metals penetrate the pores of the skeleton body and are changed into non-metallic compounds within the pores. For example, these metals are caused to react with carbon, oxygen and/or nitrogen, so as to produce carbides, oxides or nitrides. These reactions require some annealing. The reaction material (carbon etc.) must be present in the pores. For example, carbon or nitrogen may be present prior to impregnation in the metal part of the skeleton, or oxygen may be formed on the surface of the pores, for example, as an oxide skin of the metal of the porous skeleton body. Still alternatively, the skeleton can be treated with a watery solution from which salt or an oxide thereof has precipitated, and the oxygen thereof will react subsequently with metal caused to penetrate the pores.

Including the reaction material in or on the pores of the skeleton is also applicable if the skeleton body is subsequently impregnated with silicate, e.g., for improving the wettability or for reducing viscosity of the principle impregnating material, or the softening point after impregnating is to be increased.

The tool is to be used at a temperature, generally, that is below the melting point of the non-metallic material that penetrates the pores of the skeleton; however, for a short period of time, operating temperature may be somewhat above that melting point, particularly if the strength of the metallic skeleton is sufficient to sustain that hot temperature. In this case, actually the heat of fusion serves as local heat sink and the improved thermal conduction facilitates withdrawal and transfer of heat from the surface of the tool that is subjected immediately to the hot working temperature.

The non-metallic material in the network of pores must not react chemically, at least not strongly react chemically, during subsequent use with material worked by the tool or die, nor must subsequent exposure of the tool or die to a working material cause the removal of the non-metallic material from the pores in the metallic skeleton.

The tool made in accordance with the present invention differs from the form parts made in accordance with known impregnating methods. it should be mentioned that impregnating a porous metal skeleton with a liquidous metal such as copper is known, however, in that case, two intertwining metal networks are produced. Also, it is known to penetrate metallic skeletons with grease or oil or with watery solutions, but penetration and impregnation in this case has an entirely different purpose. The resulting form parts are not comparable in any way with the tools made in accordance with the present invention.

In the following example, the preferred embodiment of practicing the invention will be described. It is, however, an example only and is not to be understood as limiting the inventive concept. The example is particularly to be described for making a die to be used for extruding pipes or tubes from steel billets. 24/14 CR/NI steel powder or sawdust shavings of such material (see Table B above) are at first compressed and condensed to obtain an annular body with a relative density about 70 percent. That annulus was sintered and subjected to a treatment with nitrogen so that its nitrogen content was little above 1 percent. Texture and microstructure consisted actually almost completely of so-called non-genuine nitrogen perlite or nitrogen pearloid having a finely laminated texture composition of chromium nitrate Cr_2N and an austenitic base. That body had high temperature resistance and hot strength. This annulus constituted the skeleton and was placed into a vacuum furnace, above a supply of silicate (water glass), and was heated together therewith to a temperature of 1,000° to 1,050° C using a nitrogen atmosphere at about 600 torr (or about 116 pounds per square inch). The viscosity of the silicate was sufficiently low for that temperature.

After having reached the desired temperature range, the furnace was evacuated and the skeleton was dipped into the molten silicate. Again, the furnace was filled with nitrogen at a pressure of 700 torr. The annulus remained submerged in the molten silicate for about 10 minutes, while molten, low viscosity silicate penetrated the pores of the annulus. Thereafter, the annulus was removed from the silicate but not from the furnace. Heat was maintained in the furnace for about 10 minutes longer, before being turned off. This, then, completed the making of a die to be used for extrusion molding.

For particular cases it was deemed advisable to impregnate the annulus only for a surface layer thickness of about 5 to 10 mm depth, and only these portions that will come into contact with the extruded material and with lubricant. This restriction was obtained by compressing the interior of the annulus prior to impregnating to obtain a relative density of 90 to about 95 percent leaving, therefore, little porous structure in the interior of the annulus, while lower relative densities were maintained in these particular surface portions. Only these surface layer portions were then sufficiently porous to receive, and to be penetrated by the silicate.

The invention is not limited to the embodiments described above but all changes and modifications thereof not constituting departures from the spirit and scope of the invention are intended to be included.

I claim:

1. Method of making a tool comprising the steps of compressing and sintering chromium-nickel-steel particles to obtain a porous skeleton of not more than 50 percent pore volume; sintering the skeleton; nitrating the skeleton to obtain chromium-nitride with at least 1 percent N in the skeleton; impregnating the skeleton with molten silicate to fill at least some of the pores and annealing the skeleton in a nitrogen atmosphere.

2. Method as in claim **1,** providing surface zones of the skeleton with a relatively high porosity for a depth of about 5 to 10 millimeter, the interior having relative density of at least 90 percent, and filling only the surface zones with said molten material.

3. The method of making a tool comprising the steps of making a skeleton by compressing steel particles such as powder or flaky shavings to form a porous skeleton penetrated by a continuous network of pores of total volume not exceeding 50 percent, said steel particles containing at least one element selected from the group consisting of carbon, nitrogen and oxygen;

dipping the skeleton into a molten material selected from the group consisting of silicates, metals and metal alloys having an affinity to said carbon, nitrogen and oxygen to form respectively a carbide, nitride or oxide, for a period sufficient to cause the molten material to penetrate the pores; and

annealing the penetrated skeleton to cause formation of the carbide, nitride or oxide as *a* filler, filling at least part of the pores, said carbide, nitride or oxide being substantially undeformable and harder than the steel skeleton at temperatures up to about 650°C.

4. Method as in claim **3,** providing the porous metal alloy with an approximately uniform distribution of pores and a pore volume of about 20 to 30 percent.

5. Method as in claim **3,** providing surface zones of the skeleton with a relatively high porosity for a depth of about 5 to 10 millimeter, the interior having relative density of at least 90 percent, and filling only the surface zones with said molten material.

6. Method as in claim **3,** the filler being formed by dipping the skeleton into one of the materials selected from the group consisting of molten aluminum, magnesium, aluminum-silicon alloys and aluminum-titanium alloys.

7. Method as in claim **3,** the skeleton made by compressing and sintering particles comprising up to 0.5

percent C; 0.2 – 2.0 percent Si; 0.3 to 15 percent Mn; 10 – 25 percent Cr; 4 to 20 percent Ni; up to 10 percent W; and up to 2 percent V, the remainder being iron, all percentages by weight, the pore volume being about 20 to 30 percent.

8. Method as in claim **7,** wherein the particles further include up to 2 percent Nb, up to 3 percent Mo, up to 0.03 percent BZr, the iron content being lower accordingly.

9. Method as in claim **8,** the filler made by dipping the skeleton into a molten material selected from the group consisting of silicate, Mg; Al; Al-Si alloys; or Al-Ti alloys for impregnation; and annealing the impregnated skeleton.

10. Method as in claim **3,** the skeleton made by compressing and sintering particles comprising up to 0.5 percent C; 0.2 to 2.0 percent Si; 0.3 to 15 percent Mn; 10 to 25 percent Cr; 4 – 20 percent Ni; up to 10 percent W; up to 2 percent V; 0.2 to 3.0 percent N, the remainder Fe.

11. Method as in claim **10,** the filler made by dipping the skeleton into a molten material selected from the group consisting of silicate; Mg; Al; Al-Si alloys; or Al-Ti alloys for impregnation; and annealing the impregnated skeleton.

12. Method as in claim **3,** the skeleton made by compressing and sintering steel particles comprising up to 0.3 percent C; up to 2 percent Si; up to 4.0 percent Mn; up to 22 percent Cr; up to 20 percent Mo; up to 8 percent W; up to 18 percent Co; up to 4 percent Ti; up to 5 percent Al; up to 20 percent Fe; the remainder Ni, but at least 40 percent.

13. Method as in claim **12,** dipping the skeleton into one of the molten materials selected from the group consisting of silicate; Mg; Al; Al-Si alloys, and Al-Ti alloys for impregnation; and annealing the impregnated skeleton.

14. Method as in claim **3,** the skeleton made by compressing and sintering steel particles comprising up to 0.60 percent C; up to 1 percent Si; 0.5 – 3 percent Mn; 10 – 22 percent Cr; 10 – 20 percent Ni; up to 15 percent W; up to 4 percent Mo; up to 4 percent Nb; up to 4 percent Fe; N not exceeding a few percent; remainder Co, at least 22 percent.

15. Method as in claim **14,** dipping the skeleton into one of the molten materials selected from the group consisting of silicate; Mg; Al; Al-Si alloys; and Al-Ti alloys for impregnation; and annealing the impregnated skeleton.

16. The method as in claim **3,** including the steps of providing the surfaces of the pores of the skeleton with a layer that includes oxygen; impregnating the pores with a metal which upon annealing reacts with said layer; and annealing the impregnated skeleton to fill the pores with the oxide of the metal.

17. The method as in claim **3,** wherein the steel of the particles compressed include at least one of the elements selected from the group consisting of carbon and nitrogen for the formation of carbide and nitride.

18. The method as in claim **3,** wherein the formation of the skeleton includes sintering, the sintering being combined with said annealing.

19. Method of making a tool comprising the steps of compressing chromium-nickel-steel particles such as powder or flaky shavings to obtain a porous skeleton penetrated by a continuous network of pores of a total pore volume below 50 percent;

sintering the skeleton; and

filling at least part of the pores with a molten material selected from the group consisting of silicate, a salt such as a chloride and an aluminate.

20. Method as in claim **19,** wherein the chromium-nickel-steel comprises up to 0.5 percent C; 0.2 – 2.0 percent Si; 0.3 to 15 percent Mn; 10 – 25 percent Cr; 4 to 20 percent Ni; up to 10 percent W; and up to 2 percent V, the remainder being iron, all percentages by weight, the pore volume being about 20 to 30 percent:

21. Method as in claim **20,** wherein the chromium-nickel-steel also includes up to 2 percent Nb; up to 3 percent Mo, up to 0.03 percent BZr, the iron content being lower accordingly.

22. Method as in claim **19,** wherein the chromium-nickel-steel comprises up to 0.5 percent C; 0.2 to 2.0 percent Si; 0.3 to 15 percent Mn; 10 to 25 percent Cr; 4–20 percent Ni; up to 10 percent W; up to 2 percent V; 0.2 to 3.0 percent N, remainder Fe.

23. Method as claimed in claim **19,** wherein the chromium-nickel-steel comprises up to 0.3 percent C; up to 2 percent Si; up to 4.0 percent Mn; up to 22 percent Cr; up to 20 percent Mo; up to 8 percent W; up to 18 percent Co; up to 4 percent Ti; up to 5 percent Al; up to 20 percent Fe; remainder Ni, but at least 40 percent.

24. Method as in claim **19,** wherein the chromium-nickel-steel comprises up to 0.60 percent C; up to 1 percent Si; 0.5 – 3 percent Mn; 10 – 22 percent Cr; 10 – 20 percent Ni; up to 15 percent W; up to 4 percent Mo; up to 4 percent Nb; up to 4 percent Fe; N not exceeding a few percent; remainder Co, at least 22 percent.

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