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HEAT-RESISTANT ALLOYS

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This invention relates to a method of preparing hard, tough alloys able to preserve their hardness and toughness up to temperatures as high as 1200° C.

The development of gas turbine engines could not be achieved until alloys were available which were sufficiently refractory to heat, that is to say, alloys which, at elevated temperatures, remain tough, undeformable, and resistant to deterioration by oxidation. Even at present any increase in the potentialities of turbine engines such as power, reliable running, duration of service, and low maintenance cost, is closely linked to the improvements which research enables to be made in the possibility of raising the temperature at which materials subjected to certain stresses can be used.

The study of various compositions of alloys of cobalt, nickel, chromium, iron, molybdenum, carbon, etc. has formed the subject of a great deal of investigation. The laws relating heat properties to compositions and to methods of production have been determined, and it can be assumed that the best refractory alloys which can be made from the elements mentioned above are now known. Now the efficiency of turbine engines could be substantially increased still further if the turbines were capable of working at a temperature considerably higher than those which can be tolerated by the best of these latter alloys and which is of the order of 800° C.

It has been suggested that recourse should be had to metallic carbides, which are justly reputed for retaining their toughness at an elevated temperature, and of these, titanium carbide has received particular attention because of its combination of properties. It is indeed remarkable for its low specific weight, substantially equal to 5 g./cm.³ which, in comparison with other refractory alloys, opens the possibility of a considerable reduction in the inertia stresses to which rapidly moving parts are subjected, for its high heat modulus, and for its resistance to oxidation; moreover its cost is moderate, far below that of other refractory carbides which also have the disadvantage of being heavy and oxidizable.

Unfortunately, up to date no one has succeeded in making compact bodies of titanium carbide, which were non-brittle and free from porosity. Fusion takes place at too high a temperature to be considered. Nor is the process of compression and calcination suitable, because the grains of titanium carbide, deprived of all plasticity, only remain in contact at a few points, however great the moulding pressure may be, and the alloy finally obtained is brittle and porous.

Attempts have been made to agglomerate the grains of carbide by conventional methods using a metal of the iron group, and to overheat the product in a vacuum so as to evaporate the bonding metal, but apart from the fact that the operation is difficult and expensive, the actual separation of the bonding metals detracts from the cohesion of the alloy. If the elimination of the bonding metal is incomplete, the plasticity when hot of the

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intergranular cement which is left confers such a capacity for deformation on the material that there is practically no point in substituting these alloys for those consisting of nickel, chromium, cobalt, iron, etc., without titanium carbide.

According to the present invention, a method of preparation has now been discovered, by means of which alloys are obtained having a remarkable combination of mechanical and physico-chemical properties which have not yet been united in a single product, which alloys are suitable for any part which is exposed locally or entirely to an elevated temperature and which is required, under these conditions, to tolerate considerable and prolonged stresses without deformation or deterioration.

The method of preparation, which forms the subject of the invention, relates to alloys of carbon and titanium in which the carbon content comprises between 13 and 18%. In carrying out the process, the raw materials are titanium hydride and pure titanium carbide in which the carbon and the titanium are in equiatomic proportions, the proportion of titanium hydride in the mixture amounting to between 10 and 35%. The two substances are intimately mixed in a suitable proportion in a ball mill; the mixture thus prepared is compressed in a mould of cylindrical or prismatic shape under sufficient pressure to obtain, after extraction from the mould, a block which is sufficiently coherent to be handled without crumbling. The compressed tablets thus obtained are heated slowly in an atmosphere of hydrogen up to about 1,000° C. In the course of this heating, the titanium hydride is dissociated and liberates its hydrogen and, as a result, the compressed tablets break up, at least in those alloys according to the invention which are prepared from the highest proportions of titanium hydride. The tablets are then removed from the furnace, the powder which constitutes them is dispersed by brief crushing and again subjected to compression, though this time in the final shape required, bearing in mind the variations in dimension which will take place during the heating which follows. The shaped parts acquire their cohesion by heating in an atmosphere of hydrogen to a temperature above 1,800° C., a temperature of between 2,000 and 2,200° C., maintained for a period lasting between 10 minutes and one hour, being suitable.

When hydrogen is used as an atmosphere for calcining furnaces, it is difficult to avoid a variation in the composition of the surface regions of the parts, whether decarburization takes place, or cementation (addition of carbon) through the methane which results from the action of the hydrogen on the resistors or crucibles when made of graphite. This disadvantage may be overcome by coating the parts subjected to calcining with a thin layer of aluminium or better still by carrying out the calcining in an atmosphere of rare gas, for example argon. For reasons of economy, the air originally contained in the furnace may be blown out by a current of hydrogen which is retained until the furnace has reached a temperature of 1,000° C. Argon is then substituted for the hydrogen, which is gradually driven out as the temperature rises, the highest temperature being maintained in an atmosphere of substantially pure argon and the small quantities of hydrogen remaining not having any noticeable effect.

The excellent moulding capacity of the powder is unexpected and appears to result from the coating of the grains of carbide with the titanium, resulting from the dissociation of the hydride and from the good distribution of the titanium in the surface layers of the carbide grains. Thus an excellent compactness is obtained

by cold moulding of the powder, and an excellent subsequent calcining.

In alloys having a high carbon content, within the limits of the invention, for example, those which are made from 10% titanium hydride and 90% titanium carbide, the separation of hydrogen which takes place up to 1,000° C. is sufficiently moderate, if heating is carried out slowly, for the compressed tablet subjected thereto to retain its shape, without faults or cracks occurring. It is therefore unnecessary to remove the compressed tablet from the furnace and the heating can be continued up to the temperature necessary for the final cohesion. Needless to say, when a single heating is sufficient, the moulding is done in the final shape, making allowance for shrinkage.

A specific but non-limiting example of preparation according to the invention is given below.

800 g. of pure titanium carbide CTi and 200 g. of titanium hydride are introduced into a ball mill filled with tungsten carbide balls, together with just sufficient volume of petroleum spirits for the pulverulent mass to assume the consistency of cream, the petroleum spirits maintaining the dispersion of the powder during the pulverizing and in particular encouraging the intimacy of the mixture. The pulverization lasts for 10 hours, after which the liquid suspension of the powders is removed from the ball mill; the petroleum spirits are separated by evaporation carried out at about 100°, preferably in an atmosphere of hydrogen. From the dry powder a compressed tablet is made under a pressure of 10 kg./mm.² and in the following operation is gradually heated from room temperature to 1,000° in a furnace traversed by a current of hydrogen. The mass, which has again become pulverulent, is removed from the furnace and the agglomerates which remain are dispersed by blows or by brief pulverization. The powder obtained is placed in a mould of the shape of the desired part, the dimensions of the mould being 13.5% greater than those which are to be obtained finally. For a part of regular prismatic shape, very well shaped homogeneous compressed tablets, having clear limits, are obtained under a pressure of 12 kg./mm.². These compressed tablets are heated under a current of hydrogen in a graphite resistance furnace in such a manner that they are maintained for 20 minutes at 2,050° C.

The parts finally obtained have a density of 4.85 gms./cm.³ and their hardness is 1,500 kg./mm.² Vickers. Their resistance to oxidation is such that they can be in contact with the air for several days at a temperature of 900° without their hardness or their toughness deteriorating, and without undergoing any change other than a slight variation in the tint of the surface which becomes a little less clear. Microscopic examination of the alloy obtained with a magnification of 1,500 diameters, after polishing with diamond powder, and etching with a solution of potassium ferricyanide, shows that it consists of homogeneous fine grains with very fine and sinuous contours. The agglomerating titanium has therefore diffused in the carbide grains in the course of the high temperature calcining, thus leading to a polycrystalline substance without any intergranular binding agent. The impossibility of intergranular slip resulting from this fact and from the sinuous shape of the contours explains why no plasticity appears in the alloy up to very high temperatures, for example 1,400° C. At least 1,800° has to be reached for a certain plasticity to appear, resulting from the relaxation of the interatomic bonds inside the grains.

When parts are manufactured which could not be withdrawn from a mould, or the dimensions of which are too great for a homogeneous compactness to be obtained by moulding, it is possible, after the dissociation of the hydride, to mould the powder in the shape of a prismatic bar, to subject this to calcining at a temperature just sufficient to permit machining into the final shape, and when

this has been done, to proceed to the final calcining at a high temperature. The alloys thus prepared, which have more than about 14% of carbon are perfectly stable structurally at all temperatures.

As a result of their very low density, their hardness and their high modulus of elasticity at a high temperature, and of their resistance to deterioration by oxidation, the alloys prepared form suitable materials for parts such as turbine blades and exhaust valves for internal combustion engines operating at a high temperature and the rapid displacement of which subjects them to heavy stresses. These products can be used for all parts which are required to be tough at a high temperature.

These alloys are much less expensive than the usual alloys having a tungsten carbide base, and can be substituted for them in certain cutting or friction tools.

I claim:

1. A method of preparing hard, tough alloys having a density of less than 5.0 gm./cm.³ and having the property of retaining their hardness and toughness up to a temperature of 1200° C., which comprises intimately combining titanium hydride and titanium carbide into a pulverulent mixture, the carbon and the titanium being in substantially equiatomic proportions, and the percentage of titanium hydride in the mixture lying between 10% and 35%, compressing the pulverulent mixture into briquettes of sufficient cohesion to be handled, heating the briquettes to a temperature sufficient to eliminate hydrogen completely from the hydride, disintegrating the thus-heated briquettes, compressing the particles of the disintegrated briquettes in a mold, and heating the material in a mold in an inert atmosphere to a temperature between 1900 and 2300° C., whereby to form a polycrystalline substance consisting of homogeneous fine grains free from any intergranular binding agent.

2. A method of preparing hard, tough alloys having a density of less than 5.0 gm./cm.³ and having the property of retaining their hardness and toughness up to a temperature of 1200° C. which comprises intimately combining titanium hydride and titanium carbide into a pulverulent mixture, the carbon and the titanium being in substantially equiatomic proportions, and the percentage of titanium hydride in the mixture lying between 10% and 35%, compressing the pulverulent mixture into a mold, heating the material in the mold slowly from room temperature to about 1000° C. to eliminate hydrogen completely from the hydride, and then heating the material in a mold in an inert atmosphere to a temperature between 1900 and 2300° C., whereby to form a polycrystalline substance consisting of homogeneous fine grains free from any intergranular binding agent.

3. A method of preparing hard, tough alloys having a density of less than 5.0 gm./cm.³ and having the property of retaining their hardness and toughness up to a temperature of 1200° C. which comprises intimately combining titanium hydride and titanium carbide into a pulverulent mixture, the carbon and the titanium being in substantially equiatomic proportions, and the percentage of titanium hydride in the mixture lying between 10% and 35%, compressing the pulverulent mixture into briquettes of sufficient cohesion to be handled, heating the briquettes to a temperature sufficient to eliminate hydrogen completely from the hydride, disintegrating the thus-heated briquettes, compressing the particles of the disintegrated briquettes in a mold, heating the material in a mold in an inert atmosphere to a temperature of about 1300° C. and then heating said material to a temperature between 1900 and 2300° C., whereby to form a polycrystalline substance consisting of homogeneous fine grains free from any intergranular binding agent.

4. A method of preparing hard, tough alloys having a density of less than 5.0 gm./cm.³ and having the property of retaining their hardness and toughness up to a temperature of 1200 C., which comprises intimately combining titanium hydride and titanium carbide into a pulveru-

lent mixture, the carbon and the titanium being in substantially equiatomic proportions, and the percentage of titanium hydride in the mixture lying between 10% and 35%, compressing the pulverulent mixture into a mold, heating the material in the mold slowly from room temperature to about 1000° C. to eliminate hydrogen completely from the hydride, heating said material in an inert atmosphere to about 1300° C., and then heating the material in a mold in an inert atmosphere to a temperature between 1900 and 2300° C., whereby to form a polycrystalline substance consisting of homogeneous fine grains free from any intergranular binding agent.

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