

1

2,884,687

WEAR-RESISTANT SINTERED POWDERED METAL

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This invention relates to sintered powdered metals containing titanium-aluminum particles and particularly to such powdered metals having a high degree of wear resistance in either the sintered form or the sintered and worked form.

Various porous metal parts have been employed in industry during recent years, but their use in many applications has been limited because of their relatively low wear resistance. Accordingly, a principal object of the present invention is to provide a novel sintered powdered metal having a high degree of wear resistance due to the presence of titanium-aluminum particles. A further object of this invention is to provide a simple and inexpensive process for forming a sintered powdered metal article containing such particles and having close dimensional tolerances.

These and other objects are attained in accordance with the present invention by the inclusion of a powdered alloy of titanium and aluminum in a powdered metal mix. The resultant product, when sintered, or when sintered and worked to a controlled degree of porosity, possesses excellent wear resistance properties due to the presence of dispersed titanium-aluminum particles. These particles also contribute a substantial degree of score resistance to the sintered powdered metal material. The titanium-aluminum is preferably introduced in the form of a pulverized intermediate alloy, as hereinafter more fully explained.

Moreover, sintered and forged powdered metal parts formed in accordance with our invention, when compared with wear-resistant parts made by conventional manufacturing methods, do not require the expensive machining operations otherwise often necessary to provide the required tolerances. Since little or no machining is necessary, scrap or waste is reduced to a minimum. Such a wear-resistant sintered powdered metal may be used to form piston rings, tappets, gears, valve stem guides, bearings and bearing surfaces, including camshaft thrust bearing plates, etc.

Recently sintered powdered metals have been provided with increased wear resistance by the inclusion of powdered nickel-titanium alloys in the powdered metal mix. This development is disclosed in co-pending patent application S.N. 317,361 filed October 28, 1952, now abandoned, in the name of Alfred L. Boegehold and owned by the assignee of the present invention. However, the use of titanium-aluminum particles in the mix, in accordance with the present invention, affords further advantages over the use of nickel-titanium particles. Titanium-aluminum particles are preferable from an economic standpoint since the average titanium-aluminum alloy, on a weight basis, costs approximately only one-half as much as the typical nickel-titanium alloy. Furthermore, titanium-aluminum has a considerably larger volume than nickel-titanium for the same amount of weight. Of course, titanium-aluminum also does not contain any relatively critical nickel.

On sintering, moreover, titanium-aluminum particles

2

alloy with the powdered metal mix to which they are added to a considerably lesser extent than nickel-containing compounds and tend to remain in substantially the same form in which they are introduced. Maximum wear resistance cannot normally be obtained if these particles alloy to an excessive extent with the base metal of the powdered mix. Another advantage of a sintered powdered metal containing titanium-aluminum particles is that this metal is more susceptible to beneficial cold working and heat treatment.

Other objects and advantages will more fully appear from the following detailed description of a preferred embodiment of our invention.

The part to be manufactured is made by initially thoroughly mixing a finely pulverized alloy of titanium-aluminum with the powdered base metal. Even a relatively minute amount of this alloy powder improves wear and score resistance of the sintered powdered material to an appreciable extent, and the range of this constituent may vary from a small but effective amount to a quantity constituting approximately 25% by weight of the final mix. However, in order to provide the desired combination of economy and strength, particularly impact strength and shock resistance, the titanium-aluminum content preferably should be maintained between about 0.5% and 15% by weight. When more than 25% titanium-aluminum is used, the strength and ductility of the resultant sintered powdered metal article are appreciably reduced. The excessive brittleness of such an article, which reduces its utility for many applications, is evidenced by chipping or cracking of wear test specimens when they are being ground. Optimum properties are usually obtained when the powdered metal mix contains approximately 1% to 10% of the pulverized titanium-aluminum alloy.

Finely divided graphite, preferably 80 mesh or finer, may be mixed with the metal powder and normally improves the quality of the part if it is present in small amounts. Quantities not in excess of approximately 6.5% by weight are generally satisfactory, while a graphite content between about 0.3% and 4% provides superior results in most instances. The inclusion of carbon is especially desirable in powdered iron mixes, but may be omitted for some applications when certain other base metals constitute the predominant constituent in the powdered metal mix.

In view of the above considerations, we have found that a sintered powdered metal article having optimum score and wear resistance properties in accordance with the present invention comprises approximately 1% to 10% by weight of pulverized titanium-aluminum alloy, 0.3% to 4% by weight of carbon, and the balance substantially all powdered iron or other base metal.

Likewise, in order to eliminate the necessity of coating the dies with a lubricant during the briquetting operation, a small but effective amount of zinc stearate powder not in excess of about 2.5% may also be beneficially included in the powdered metal mix. In general, we have found that best results are obtained with a mix having a zinc stearate content between approximately 0.3% and 2%. Other die lubricants, such as stearic acid in powder form, can also be used in place of the zinc stearate. The use of such die lubricants is especially desirable in forming sintered copper base metal articles, for example, while it is not necessary to include a die lubricant in aluminum base powder mixes.

Among the pulverized titanium-aluminum intermediate alloys which may be used, those containing approximately 30% to 90% titanium and 10% to 70% aluminum result in the production of a sintered powdered metal part having satisfactory wear resistance. For best results,

however, a powdered pre-alloy comprising between 30% and 60% aluminum and 40% to 70% titanium is preferred. If the aluminum content of the titanium-aluminum alloy is excessive, the aluminum becomes molten at the sintering temperature, and partial loss of the titanium-aluminum alloy results. Approximately -100 to -400 mesh titanium-aluminum powder is conveniently and preferably employed. Titanium-aluminum particles which are too coarse are somewhat prone to cause scoring.

It will be noted that it is necessary to form particles of titanium-aluminum in order to obtain high wear and score resistance in accordance with the invention. Merely adding titanium and aluminum separately, even if these constituents are added in the aforementioned preferred proportions, normally does not form these particles. It is the alloy of titanium and aluminum, rather than the individual elements, which contributes the desirable properties of wear and score resistance to the sintered powdered metal article.

We have found that the intermediate titanium-aluminum alloy may be formed by preparing a charge of the desired percentages of titanium sponge and aluminum pig, such as commercially available 2S aluminum, the pre-alloy then being pulverized and added to the powdered ferrous base metal. The intermediate alloy mix may also contain small amounts of other metals, such as iron, manganese, silicon, chromium, magnesium and nickel. Normally the approximate maximum quantity of these metals will not exceed approximately 6% manganese, 3% iron, 2% silicon, 1% chromium, 1% magnesium and 0.5% nickel. When converted to percentages of the final sintered powdered metal product, the above silicon and manganese contents, for example, constitute on the average only about 0.3% and 0.9%, respectively. The above percentages of the minor constituents are not critical in most instances, however, and are listed as examples only.

The titanium and aluminum are preferably placed in a graphite crucible, covered, and heated to a temperature between approximately 2700° F. and 2950° F. Inasmuch as titanium is a readily oxidizable and nitridable element, it is desirable to use an inert atmosphere, such as argon, as the melting atmosphere. The formed titanium-aluminum alloy, which solidifies at about 2450° F., may be cooled to room temperature in the crucible. If the titanium-aluminum is to be poured from the crucible, this is preferably done while the temperature of the alloy is between approximately 2500° F. and 2700° F. Cooling and pouring also should take place under an inert atmosphere, the metal preferably being cast under an argon atmosphere as pigs in chilled molds.

Intermetallic compounds, such as TiAl and TiAl₃, are thus formed, and when pulverized and added to the base metal powder, greatly improve the wear resistance of the final sintered product. Mixtures of these titanium-aluminum compounds frequently result, and some of the titanium and aluminum may also be present in the form of a solid solution of titanium and aluminum. Regardless of the exact form in which the titanium-aluminum particles are present in the powdered metal, their presence greatly improves the wear and score resistance of the resultant sintered powdered metal part.

Among the powdered base metals which may be used in practicing the present invention are ferrous metals, zinc, aluminum, magnesium, nickel, copper and lead. Various powdered alloys of these elements, of course, likewise may have their score and wear resistance improved by the inclusion of dispersed titanium-aluminum particles. The usable powdered ferrous metals include iron, steel and powdered alloyed irons. If ferrous base materials are used, commercial iron powders, such as those made by grinding mill scale, deoxidizing and pulverizing, provide excellent results. A steel powder, which may be produced by atomizing very hard steel, grinding and reducing the carbon content of the powder, can also be em-

ployed. Moreover, both electrolytic iron and Swedish sponge iron powders are satisfactory base materials for many powdered iron parts. The size of the base metal powder particles may vary from about -50 to -325 mesh, depending on the material used and the application for which it is designed.

The wear-resistant sintered powdered metal part may be produced by various processes. One highly satisfactory method involves briquetting a mixture of the pulverized titanium-aluminum alloy, and graphite powder, if it is desired to add the latter, and powdered iron, for example, at an appropriate pressure in a die having a contour which is complementary to the surface to be formed. A briquetting pressure between approximately 20,000 and 120,000 pounds per square inch may be employed, depending on the composition of the part and the purpose for which it is to be used. Before briquetting, it is important that the powdered metal constituents be thoroughly mixed in order to provide uniformity of structure and properties to the finished article.

The green briquette is then sintered under suitable conditions of time, temperature and atmosphere into a structure having a controlled degree of porosity. Sintering temperatures between 1900° F. and 2300° F. and sintering times between one-half hour and one hour have proved to be highly satisfactory for powdered ferrous base metal briquettes. These sintering times are not critical, however, and sintering periods as short as four minutes and as long as two hours are satisfactory for various applications. For non-ferrous base powders, such as lead base alloys, for example, the sintering temperature may be as low as about 500° F. Among the non-oxidizing furnace atmospheres which may be employed, dry "Drycolene" gas or a gaseous mixture of "Neutralene" and a small amount of natural gas are satisfactory. For some non-ferrous base powders, such as copper or bronze powders, a dissociated ammonium atmosphere is particularly effective.

It is convenient to prepare "Drycolene" by burning one part of natural gas with approximately ten parts of air, condensing the water vapors, passing the gas through hot charcoal and drying it in activated alumina. The dry Drycolene gas thus is composed of approximately 20% carbon monoxide, 3% hydrogen and 77% nitrogen. The Neutralene atmosphere mentioned above is a closely related gaseous mixture which usually consists of approximately 1.5% carbon monoxide, 1.5% hydrogen and 97% nitrogen. It has proved advantageous to mix about 100 parts of Neutralene with one part of natural gas. Of course, other furnace atmospheres, such as hydrogen, mixtures of nitrogen or hydrogen and methane, etc., can be used, but Drycolene and Neutralene are readily available and each provides a highly effective protective atmosphere.

Following the sintering step, the density and strength of the formed powdered metal part may be increased by hot or cold working, including forging and multiple pressing operations. The forging operation is preferably one of hot forging, and it usually is expedient to forge the briquette before it has cooled after the sintering step. If desired, the sintered briquette may be permitted to cool and then be reheated to a temperature appropriate for forging. Forging temperatures approaching those used for sintering are generally suitable for use in the present invention. Alternatively, desirable physical properties may be obtained by multiple cold pressing of the briquette. The forging or pressing operations, whether hot or cold, increase the tensile strength of the sintered material, especially as the porosity approaches zero. Inasmuch as a very dense structure may permit scoring under severe operating conditions, it is desirable to carefully control the forging so as to provide the formed part with proper porosity. More specifically, therefore, we have usually found it advisable to control forging so as to form a powdered metal article having between approximately

2% and 20% porosity, thereby improving resistance to score.

Following the forging or pressing operation, whichever is employed, the sintered blank may be subjected to an appropriate heat treatment. In the case of a ferrous base metal part, for example, tempering for approximately 30 to 60 minutes at a temperature between about 800° F. and 1100° F. reduces stresses introduced by cold pressing and tempers the martensite formed during rapid cooling after forging. If hot forging has been employed, cooling is preferably accomplished in a die or between plates. In the case of a ferrous base article, the finished product may be advantageously surface treated with an iron-manganese-phosphate coating, such as that provided by the "Lubrite" treatment. Other appropriate surface treatments can be used, of course.

It will be understood that a sintered powdered metal article containing dispersed particles of titanium-aluminum in accordance with this invention may be manufactured under the usual porous metal techniques as disclosed in a number of patents, such as Patents Nos. 1,738,163, 2,097,671, 2,075,444, etc. Also, instead of briquetting the metal powder as hereinbefore explained, it may be molded to shape prior to sintering as suggested in Koehring Patent No. 2,198,702.

Likewise, the powdered metal mix may be merely spread on or otherwise placed in contact with a supporting surface and subsequently sintered. This supporting surface may be a non-porous metal backing strip, such as a steel strip, and the powdered metal may be bonded to the back on sintering. When this latter procedure is used, it may be desirable to first electrodeposit a suitable metal plate on the surface of the back to improve the strength of the bond. This type of process is disclosed in Koehring Patents Nos. 2,187,086 and 2,198,253. After sintering, the composite of spongy powdered metal on the back may be rolled to increase the density of the powdered metal article and then resintered or annealed. Additional rolling and annealing treatments can be employed to further increase the density of the formed article. In this manner a highly wear-resistant sintered powdered metal layer may be formed on a steel back.

All of the above modifications are understood to be within the scope of the present invention, which broadly comprehends the provision of a sintered powdered metal part containing particles of a titanium-aluminum alloy.

Wear and score test apparatus were employed to compare sintered powdered metals formed in accordance with our invention with the same materials devoid of titanium-aluminum particles. In the case of sintered powdered iron, for example, each sample to be tested was machined to prepare a $\frac{1}{8}$ inch by $1\frac{1}{8}$ inch rubbing surface. The specimens were next successively locked in a fixture of the wear test machine and placed in contact with a rotating smooth-surfaced cast iron wheel having a face width of one inch. Increased wear resistance was measured by decreased weight loss in grams and in decreased volume loss in cubic inches, while score resistance was indicated by the load required to cause scoring under prescribed test conditions.

A wear test using this apparatus was conducted in which the specimen load was increased during the $18\frac{1}{2}$ hour period from zero load and automatically adjusted to produce a constant frictional load of 64 pounds. At the end of this test period the sintered and forged specimens formed from a conventional mixture of powdered iron and approximately 2% graphite showed an average weight loss of 0.028 gram. On the other hand, the sintered and forged powdered metal specimens of similar composition but containing the aforementioned preferred amounts of titanium-aluminum particles lost an average of only approximately 0.0053 gram. Likewise, while the conventional powdered iron samples underwent a weight loss averaging about 238×10^{-6} cubic inches, the specimens formed in accordance with the present inven-

tion changed on the average only 18×10^{-6} cubic inches. The results of this test show how greatly the presence of dispersed titanium-aluminum particles increases the wear resistance of sintered powdered metal articles.

Tests also indicate that the presence of the titanium-aluminum particles appreciably increases the anti-friction properties of sintered powdered metals. This property was measured by means of the specimen load required to produce a 64 pound frictional load. Samples formed of sintered powdered iron containing titanium-aluminum particles required an average of about 804 pounds specimen load to produce the 64 pound frictional load as compared with an average of only approximately 568 pounds specimen load when the samples without these particles were tested, thus indicating that the coefficient of friction of such a material is substantially reduced by the presence of the titanium-aluminum particles.

The aforementioned specimens were also subjected to a score test in which the test samples were placed against the aforementioned rotating wheel for 60 minutes under a 502 pound specimen load, and this load was then increased until scoring occurred. The ordinary sintered powdered iron specimens required a load averaging only 502 pounds to produce scoring, but an average load of approximately 801 pounds was required to cause any indication of scoring of the sintered powdered iron containing the titanium-aluminum particles. Hence, the results of this test indicate that the presence of these particles also materially increases the score resistance of sintered powdered metals.

Similar favorable results were obtained by the addition of a pulverized titanium-aluminum alloy to other powdered metals. For example, when this alloy was added to sintered powdered bronze, the beneficial results provided by titanium-aluminum were also evident. In the case of sintered powdered bronze, the samples were prepared as tensile bars briquetted at a pressure of 60,000 pounds per square inch. They were then sintered for 25 minutes in a dissociated ammonia atmosphere at a temperature of 1575° F. and subsequently cooled in this atmosphere. None of the samples were forged. As before, each specimen to be tested was machined to prepare a $\frac{1}{8}$ inch by $1\frac{1}{8}$ inch rubbing surface and the specimens successively subjected to the aforementioned wear test.

A wear test using the above-described apparatus was conducted in which the specimen load was increased to 512 pounds and retained at this figure for a total test period of five hours. At the end of this time the sintered copper base test specimens which did not contain titanium-aluminum particles lost an average of 0.341 gram, while the copper base samples of similar composition but containing the titanium-aluminum particles showed an average weight reduction of only 0.0155 gram. Also, while the latter specimens underwent a volume loss averaging only 2×10^{-5} cubic inches, the average volume of the test specimens not containing titanium-aluminum particles was reduced on the average about 269×10^{-5} cubic inches.

When the various sintered powdered bronze samples were also subjected to the score test and compared, the samples which did not contain titanium-aluminum required a load of only about 590 pounds to produce scoring, but an average load of approximately 791 pounds was required to cause any indication of scoring of the samples containing titanium-aluminum particles.

While the present invention has been described by means of certain specific examples, it is to be understood that other forms may be adopted and are contemplated as being within the scope of the present invention, as defined in the following claims.

We claim:

1. A sintered powdered metal consisting essentially of a titanium-aluminum alloy and at least one base metal selected from the group consisting of iron, zinc, alumi-

num, magnesium, nickel, copper, lead and alloys of said metals, said titanium-aluminum alloy being present in a quantity ranging from a small amount effective to materially increase the wear resistance of the base metal to an amount not in excess of approximately 25%, said titanium-aluminum alloy comprising about 30% to 90% titanium and 10% to 70% aluminum.

2. A highly wear-resistant sintered article made from a powdered metal mix consisting essentially of about 0.5% to 25% by weight of dispersed particles of an alloy of titanium and aluminum, and the balance substantially all at least one metal selected from the group consisting of iron, zinc, aluminum, magnesium, nickel, copper, lead and alloys of said metals, said titanium and aluminum constituting about 30% to 90% and 10% to 70%, respectively, of the titanium and aluminum alloy.

3. A sintered and worked powdered metal characterized by outstanding wear and score resistance, said powdered metal consisting essentially of approximately 0.5% to 15% of a titanium-aluminum alloy and the balance substantially all at least one metal powder selected from the group consisting of iron, zinc, aluminum, magnesium, nickel, copper, lead and alloys of said metals, the titanium and aluminum in said titanium-aluminum alloy constituting about 40% to 70% and 30% to 60%, respectively, of said alloy.

4. A highly wear-resistant sintered powdered metal consisting essentially of about 0.5% to 15% dispersed particles of an alloy of titanium and aluminum, carbon not in excess of 6.5%, and the balance substantially all ferrous base metal, said titanium and aluminum constituting about 30% to 90% and 10% to 70%, respectively, of the titanium and aluminum alloy.

5. A highly wear and score-resistant sintered powdered metal consisting essentially of about 1% to 10% dispersed particles of titanium-aluminum, carbon not in excess of 6.5%, and the balance substantially all copper base metal, said titanium-aluminum comprising 30% to 90% titanium and 10% to 70% aluminum.

6. A sintered powdered metal article characterized by outstanding wear and score resistance, said article being

formed from a powdered mix consisting essentially of about 1% to 10% by weight of powdered titanium-aluminum intermetallic compound containing between 30% and 90% titanium, 0.3% to 4% by weight of finely divided graphite, a small but effective amount of die lubricant not in excess of 2.5% by weight, and the balance substantially all at least one powdered metal selected from the group consisting of iron, zinc, aluminum, magnesium, nickel, copper, lead and alloys of said metals.

7. A highly wear and score-resistant sintered metal article formed from a powdered mix consisting essentially of about 0.3% to 4% finely divided graphite, 0.5% to 15% of titanium-aluminum alloy in the form of particles dispersed throughout said mix, and the balance substantially all powdered ferrous base metal, said titanium-aluminum alloy consisting essentially of 30% to 90% titanium and 10% to 70% aluminum.

8. The sintered metal article set forth in claim 7 in which the titanium-aluminum alloy in the powdered mix has a mesh size between -100 and -400.

9. A highly wear-resistant sintered powdered metal consisting essentially of about 1% to 10% titanium-aluminum alloy in the form of dispersed particles in which titanium constitutes between 30% and 90% by weight of the titanium-aluminum alloy, and the balance substantially all at least one metal powder selected from the class consisting of iron, zinc, aluminum, magnesium, nickel, copper, lead and alloys of said metals.

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