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3,520,680

PROCESS OF PRODUCING STEEL

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17 Claims

ABSTRACT OF THE DISCLOSURE

A process is provided for enhancing the corrosion resistance of stainless steel powder by applying to the powder a coating of tin or a tin alloy of copper or nickel.

This is a division of application Ser. No. 390,462, filed Aug. 18, 1964 now Pat. No. 3,425,813.

This invention is concerned with metal powders for molding purposes, and more particularly with methods for improving the corrosion resistance of stainless steel powder moldings and with novel stainless steel powders which confer such advantages.

In the past, stainless steel powders have been known to be hard and brittle, characteristics which have discouraged their use in powder metallurgy. A substantial advance was made when it was discovered that their molding properties could be greatly improved and green strength enhanced by coating stainless steel powders with copper or nickel by special techniques. It was later found, however, that the moldings prepared from such specially coated powders, like moldings prepared from uncoated stainless powder, lacked the excellent corrosion resistance of stainless steel articles fabricated by conventional, non-powder techniques. Thus, some of the potential advantages sought in employing stainless steel in powder metallurgy failed to be realized.

Now it has been discovered that the corrosion resistance of stainless steel moldings can be strikingly improved by combining the stainless steel powder with tin prior to molding. Not only does tin alone confer this important advantage, but tin combined with nickel or copper is also effective. The moldings prepared in accordance with this discovery are especially resistant to salt-water corrosion.

The powders which lend themselves to such improvement include the austenitic chromium-nickel-iron 300 series stainless steel, such as types 302, 304 and 316, as well as the martensitic 400 series chrome irons. These powders typically average 15 to 45 microns in particle size, some being 100% finer than 325 mesh while others may contain substantial proportions coarser than 200 mesh.

The additives which confer corrosion resistance include substantially pure tin as well as tin in combination with up to 90% of copper, nickel or both. Especially preferred are combinations of 20 to 50% by weight of tin with 80 to 50% by weight of copper, nickel or copper-nickel combinations.

The quantity of additive required, whether it be tin or tin plus copper or nickel, is quite small. Important advantages are achieved with as little as 0.25% additive based on the weight of the stainless powder, and optimum results are generally achieved with no more than about 1.5-2% additive. Indeed, additive levels substantially above 2% will sometimes adversely affect the tensile strength of the molded articles and are therefore preferably avoided.

A number of techniques are appropriate for combining

the stainless steel powder with the additive. Perhaps the simplest procedure involves blending the stainless powder with the powdered additive prior to molding. Thus, tin powder alone or in combination with nickel and/or copper, may be blended intimately with the stainless powder prior to molding to achieve the desired corrosion resistance.

A more complex procedure involves coating the stainless steel powder with the tin or tin alloy at the levels indicated. This method, which assures uniformity and avoids the risk of segregation of the constituents in storage, will often be preferred. An elegant method of preparing such coated powders entails blending the stainless powder with an aqueous dispersion of a reducible tin salt, optionally including reducible copper or nickel salts as well, then separating the water and reducing the salt(s) to elemental metal in an atmosphere of hydrogen.

Reducible salts of tin, copper and nickel which lend themselves best to the aforementioned technique include the chlorides, nitrates, formates, acetates and sulfates of such metals. Stannous chloride, cupric nitrate and nickel nitrate are readily available and appropriate. The quantity of salts should be equivalent to about 0.25 to 1.5% of total elemental tin, copper and/or nickel, based on the weight of stainless powder. The volume of aqueous salt solution or suspension for optimum uniformity will, of course, vary with the particle size of the powder, higher volumes being advisable with the finer powders. Generally at least about 0.025 ml. will be desirable per gram of powder, while volumes in excess of 0.25 ml. per gram offer no added advantage.

After the powder has been combined with the salt dispersion, the water may be removed, suitably by evaporation at elevated temperature or reduced pressure. It is a desirable precaution to stir or agitate the powder during drying to insure uniform deposition.

Where the salts employed for coating include soluble sulfates or chlorides, best results are achieved by precipitating the metal compounds on the stainless powder before separating the water. This permits thorough washing of the coated powder before reduction, to eliminate traces of chloride and sulfur, which may be objectionable in the final product. Precipitation may be effected by addition of alkali, preferably at least about one equivalent, or 10-25% in excess if desired, of alkali per cation equivalent. Any alkali may be employed for this purpose, e.g. sodium or potassium carbonate, bicarbonate or hydroxide. If a hydroxide is used, substantial excess should be avoided to prevent solubilization of the tin compounds. After the precipitation step, the water may be separated from the treated powder by filtration or decanting, and the powder washed and dried.

Reduction of the tin, copper and/or nickel compounds to elemental metal is next effected, by heating the treated powder in a hydrogen atmosphere at a temperature below that which cause sintering. Optimum reduction temperatures and times will vary with the coating composition, the particle size, and the heating capacity of the furnace, and are therefore best determined by experiment. Generally, reduction at a temperature above about 500-600° F. and below about 1600-1800° F. for about 45 minutes to an hour will prove appropriate. After cooling, the product may be subjected to light hammer milling to break up any aggregates which may have formed during processing.

It has been stated above that the novel coated powders produced in this way are useful in molding. Whenever the term "molding" is employed herein and in the appended claims, it is to be understood as embracing all of the various fabricating techniques whereby metal powders are converted into useful coherent aggregates

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by the application of pressure and/or heat. These include the well known techniques of powder rolling, compacting, isostatic pressing, sintering, slip casting and the like.

One preferred technique includes compacting and sintering in accordance with conventional powder metallurgy procedures. To protect the dies, it is customary to add a small quantity of lubricant, e.g. $\frac{3}{4}$ -1% of stearic acid, zinc stearate or the like. The powder is then compacted at high pressure to the desired shape, usually at room temperature and about 30 to 50 tons per square inch pressure. The compacting occurs substantially instantaneously, but the pressure may be applied for about a minute to insure complete flow. The compacted article is then removed from the mold and heated to sintering temperature, suitably at about 2000-2300° F. for from about 15 minutes to an hour. During sintering, the article shrinks and becomes denser, the shrinkage usually being less than about 1%. Where blended, rather than coated powders are employed in the process of the present invention, the conventional compacting and sintering techniques will, of course, be substantially the same.

Other means for carrying out the process of the present invention will be apparent to those skilled in the art. For example, the stainless steel powder may be uniformly coated with copper and/or nickel, and then blended with particulate tin prior to compacting and sintering. Alternatively, tin-coated stainless steel powder may be blended with particulate copper and/or nickel, or with particulate copper-nickel alloy.

The pressed, sintered products which result possess outstanding corrosion resistance. Conventional stainless steel articles prepared by powder metallurgy techniques corrode within minutes when exposed to salt water, rusting and throwing down brown sediment. The products produced in accordance with the present invention, however, remain bright, and the salt water remains water-white and clear for many hours or days in this very severe test.

The following examples are provided for illustrative purposes and should not be construed as limiting the invention, the scope of which is indicated by the appended claims.

EXAMPLE 1

Stannous chloride dihydrate, 9.72 grams, is dissolved in 30 ml. water, whereupon some white precipitate forms. The resulting suspension is mixed with 500 grams Type 304 stainless steel powder, and the mixture is dried one hour at 400° F. and screened through 100 mesh.

The solid thus obtained is divided into two portions. These are heated in a furnace under a hydrogen atmosphere for one hour at 1800° F. and 1200° F., respectively, to obtain two powders each uniformly coated with 1% tin.

The powders are compacted at 50 tons per square inch, applied for one minute at room temperature, and then sintered at 2100° F. for one hour, to form test bars about $\frac{1}{4} \times \frac{1}{4} \times 3$ inches.

For corrosion testing, each bar is exposed for 24 hours in a 250 ml. beaker containing 80 ml. of a solution of 5 g. sodium chloride in 95 ml. distilled water. Control bars, prepared from uncoated stainless steel powder and from stainless steel powder coated with 1% copper or 1% nickel show almost immediate staining upon immersion, and exhibit rusting within 24 hours. The bars prepared from tin-coated powder show negligible staining after 24 hours, and the immersed metal remains rust-free in 48 hours' exposure.

The copper- and nickel-coated powders are prepared in the same manner as the tin-coated powder, with substitution of aqueous cupric nitrate and nickel carbonate for the stannous chloride solution.

EXAMPLE 2

Stannous chloride dihydrate, 258 grams, is dissolved

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in 715 ml. water and added to 30 pounds of Type 304 stainless steel powder. These ingredients are mixed for 3 minutes, and then a solution of 133 grams of sodium carbonate in 350 ml. hot water is added to precipitate the tin salt. After two minutes' additional stirring 1000 ml. water is added and the slurry is filtered and washed with three 2500 ml. portions of water. The resulting damp solid is dried at 500° F. in a rotating tube furnace and heated at 1200° F. under hydrogen for $\frac{3}{4}$ hour to obtain stainless steel powder uniformly coated with 1% tin. Properties of the coated powder are as follows:

Apparent density: 3.54 grams per cc.

Sieve analysis—	Percent
100 mesh -----	1.1
150 mesh -----	4.4
200 mesh -----	13.0
270 mesh -----	23.8
325 mesh -----	57.7
Through 325 mesh -----	100.0

This product is molded as in Example 1 to form test bars resistant to salt-water corrosion in a test of 10 days' duration. Other properties of the sintered bars are as follows:

Density—6.67 grams per cc.
Change in length on sintering— -0.66%
Tensile strength—43,300 p.s.i.
Elongation, percent in 1 inch—15.0
Rockwell hardness—B-35

The experiment is repeated, substituting equivalent proportions of stannous and stannic sulfate for the stannous chloride, and an equivalent proportion of potassium carbonate for the sodium carbonate, with substantially the same results.

EXAMPLE 3

Stainless steel powder, 200 grams, is wetted with a solution of 0.38 g. stannous chloride dihydrate and 6.73 g. cupric nitrate trihydrate in 17 ml. water. Next, a solution of 3.45 g. sodium carbonate in 13 ml. hot water is added, followed by 10 ml. water. After stirring, the mixture is filtered, and the damp solid is washed with 200 ml. water and dried at 385-400° F. for one hour.

The solid thus obtained is reduced in hydrogen at 800-1200° F. for $\frac{3}{4}$ hour to obtain stainless steel powder having a 1% coating of an alloy of 10% tin in copper. This product is compacted at 50 tons per square inch and sintered at 2300° F. for one hour. In the previously outlined salt water corrosion test, the immersed metal remains stain- and rust-free for the duration of a 216-hour test, whereas another bar, also sintered at 2300° F., and prepared from stainless steel powder coated with 1% copper, exhibits rusting of the immersed end and ferric hydrate precipitation in the solution within 72 hours.

The experiment is repeated, substituting equivalent proportions of cupric formate, acetate and sulfate for the cupric nitrate, with substantially the same results.

EXAMPLE 4

The procedure of the previous example is repeated, with substitution of 1.24 grams of the stannous chloride, 5.05 grams of the cupric nitrate, and 3.12 grams of the sodium carbonate for the previously specified quantities, to obtain a powder uniformly coated with 1% of an alloy of 33% tin in copper.

Test bars are compacted at 50 tons per square inch and sintered at 2100° F. In the salt-water corrosion test, the immersed metal remains clean and rust-free for the duration of a 216-hour test.

Properties of the coated powder, prepared as described, are as follows:

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Apparent density: 3.84 grams per cc.

Sieve analysis—	Percent
100 mesh -----	-----
150 mesh -----	1.0
200 mesh -----	8.3
270 mesh -----	12.7
325 mesh -----	22.8
Through 325 mesh -----	55.2
	100.0

Properties of the sintered bars are as follows:

Density—6.60 grams per cc.
Change in length on sintering— —0.48%
Tensile strength—40,100 p.s.i.
Elongation, percent in 1 inch—13.5
Rockwell hardness—H-85

EXAMPLE 5

The procedure of Example 4 is repeated with the omission of the sodium carbonate addition and the filtration step, to prepare a coated powder like that of the previous example. After reduction at 800–1200° F. as before, the product is subjected to a light hammer-milling to break up aggregates. The resulting powder is compacted and sintered as in the previous example, and the moldings exhibit corrosion resistance comparable to the products of that example.

Properties of the coated powder, prepared as described, as follows:

Apparent density: 3.80 grams per cc.
Sieve analysis on—

	Percent
100 mesh -----	---
150 mesh -----	2.3
200 mesh -----	7.7
270 mesh -----	14.8
325 mesh -----	23.6
Through 325 mesh -----	51.6
	100.0

Properties of the sintered bars are as follows:

Density—6.64 grams per cc.
Change in length on sintering— —0.49%
Tensile strength—41,200 p.s.i.
Elongation, percent in 1 inch—15.0
Rockwell hardness—H-87

EXAMPLE 6

The procedure of Example 3 is repeated, with substitution of 1.24 grams of the stannous chloride, 6.76 grams of nickelous nitrate hexahydrate and 3.35 grams of the sodium carbonate for the previously specified ingredients and quantities, to obtain a powder uniformly coated with 1% of an alloy of 33% tin in nickel. Test bars are molded as before, with 0.75% stearic acid incorporated as lubricant. The products exhibit substantially enhanced corrosion resistance in comparison with bars molded from nickel-coated stainless steel powder.

The experiment is repeated, substituting equivalent proportions of nickel acetate and nickel sulfate for the nickel nitrate, with substantially the same results.

EXAMPLE 7

A solution of 24.8 grams stannous chloride dihydrate and 101 grams cupric nitrate trihydrate in 200 ml. water is poured into a solution of 71 grams sodium carbonate (25% excess) in 200 ml. water. After stirring, the suspension is filtered and the cake washed with 950 ml. water and dried overnight at about 225° F. The dry solid is reduced at 800–1200° F. for ¾ hour to obtain an alloy powder containing about 33% tin in copper.

One percent by weight of this powder is blended with stainless steel powder, and the mixture is compacted at 50 tons per square inch and sintered at 2100° F. for

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one hour. In a salt-water corrosion test of 192 hours' duration, the immersed metal remains stain- and rust-free.

Portions of the stainless steel powder are also blended with 0.25, 0.5 and 2% by weight of the tin-copper alloy, and these mixtures are compacted and sintered as before to form corrosion-resistant moldings. These experiments are repeated, substituting pure copper and tin powders in equivalent proportion for the alloy powder, and excellent salt-water corrosion resistance is again obtained.

EXAMPLE 8

Following the procedures of Example 2, stainless steel powders uniformly coated with 0.5% and 1.5% tin are prepared, and found to have the following properties:

	0.5% tin	1.5% tin
Apparent density-----	3.62	3.43
Sieve analysis on—		
100 mesh -----	-----	-----
150 mesh -----	1.1	1.1
200 mesh -----	4.1	4.8
270 mesh -----	11.0	16.3
325 mesh -----	23.1	23.9
Through 325 mesh -----	60.7	53.9
	100.0	100.0

These powders are compacted at 50 tons per square inch and sintered at 2300° F., to form test bars which remain clean and rust-free after 10 days' exposure in the previously described corrosion test. Other properties of the sintered bars are as follows:

	0.5% tin	1.5% tin
Density, g./cc.-----	6.78	6.79
Change in length on sintering, percent-----	-1.05	-1.37
Tensile strength, p.s.i.-----	46,400	52,700
Elongation, percent in 1 inch-----	21.4	24.0
Rockwell hardness-----	B-40	B-40

EXAMPLE 9

Following the procedures of Example 3, the following uniformly coated stainless steel powders are prepared:

Wt. percent coating:	Coating composition
0.25 -----	100% tin.
0.25 -----	50% tin-50% nickel.
0.25 -----	50% tin-50% copper.
1.0 -----	50% tin-50% nickel.
1.0 -----	20% tin-80% nickel.
1.0 -----	50% tin-50% copper.
1.0 -----	20% tin-80% copper.
1.0 -----	50% tin-25% copper-25% nickel.
1.5 -----	50% tin-50% nickel.
1.5 -----	20% tin-80% nickel.
1.5 -----	50% tin-50% copper.
1.5 -----	20% tin-80% copper.

These powders are compacted at 50 tons per square inch and sintered at 2300° F. to prepare moldings of excellent resistance to salt-water corrosion.

EXAMPLE 10

Moldings corresponding in composition to those of Example 9 are prepared by blending the appropriate proportions of tin, nickel and copper powders with stainless steel powder, followed by compacting at 50 tons per square inch and sintering at 2300° F. The moldings obtained exhibit outstanding resistance to salt-water corrosion.

EXAMPLE 11

Cupric nitrate trihydrate, 9.3 grams, is dissolved in 27 ml. water and poured over 500 grams of stainless steel powder. The mixture is stirred, dried at 210° C., and screened through 100 mesh. The dry, screened powder is reduced under hydrogen for 30 minutes at 1800° F., cooled under hydrogen for 30 minutes, milled and screened through 100 mesh.

The resulting copper-coated powder (0.5% copper) is blended with 0.5% of 325 mesh tin powder, compacted

into test bars at 50 tons per square inch, sintered for one hour at 2100° F. and cooled for 30 minutes. When exposed for 24 hours to 5% salt solution as described in Example 1, the test bars remain corrosion-free. Similar results are obtained with nickel-coated stainless steel powders blended with tin powder, and with tin-coated stainless steel powder blended with copper powder or with nickel powder.

What is claimed is:

1. A process for improving the corrosion resistance of stainless steel powder moldings which comprises combining said powder prior to molding with from about 0.25 to 2% by weight of an additive consisting essentially of at least 10% tin and up to 90% by weight of at least one alloying element selected from the group consisting of copper and nickel.
2. The process of claim 1 wherein said additive is substantially pure tin.
3. The process of claim 1 wherein said additive contains from about 20 to 50% by weight of tin.
4. The process of claim 1 wherein said additive is blended in particulate form with said stainless steel powder.
5. The process of claim 1 wherein said additive is coated on said stainless steel powder.
6. The process of claim 1 wherein a portion of said additive is coated on said stainless steel powder and the remainder of said additive is blended in particulate form with said coated powder.
7. A process for preparing stainless steel moldings of enhanced corrosion resistance which comprises combining stainless steel powder with from about 0.25% to 2% by weight of an additive consisting essentially of at least 10% by weight of tin and up to about 90% by weight of at least one alloying element selected from the group consisting of copper and nickel, compacting said combined powder at high pressure, and heating said compact to sintering temperature.
8. The process of claim 7 wherein said stainless steel powder is coated with said at least one alloying element, and wherein particulate tin is blended with said coated powder.
9. A process for improving the corrosion resistance properties of stainless steel molding powder which comprises the steps of blending said powder with an aqueous dispersion of a reducible tin salt in an amount equivalent to from about 0.25 to 1.5 weight percent tin based on the weight of said stainless steel powder, separating the water, and reducing said salt to elemental tin in an

atmosphere of hydrogen at elevated temperature below the sintering temperature.

10. A process for improving the corrosion resistant properties of stainless steel molding powder which comprises the steps of blending said powder with an aqueous dispersion of a reducible tin salt additionally containing at least one salt selected from the group consisting of reducible copper salts and reducible nickel salts, the total weight of said tin, copper and nickel salts being equivalent to about 0.25% to 1.5% by weight of cations of said salts based on the weight of said stainless steel powder, separating the water, and reducing said salts to elemental metals in an atmosphere of hydrogen at an elevated temperature below the sintering temperature of said powder.

11. The process of claim 10 wherein said salts are selected from the group consisting of chlorides, nitrates, formates, acetates and sulfates.

12. The process of claim 11 wherein said tin salt is stannous chloride.

13. The process of claim 11 wherein said copper salt is cupric nitrate.

14. The process of claim 11 wherein said nickel salt is nickelous nitrate.

15. The process of claim 10 wherein said water is separated by evaporation.

16. The process of claim 10 wherein said water is separated after precipitating said salts upon said stainless steel powder by addition of at least about one equivalent of alkali per cation equivalent.

17. The process of claim 16 wherein said alkali is sodium carbonate.

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