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CORROSION RESISTANT POWDER METAL PARTS

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ABSTRACT OF THE DISCLOSURE

A method of providing a powder metal article subjected to a corrosive halogen ion containing environment with corrosion resistance thereto, which comprises the steps of: pressing metal powder into a green compact; sintering the green compact in a substantially non-oxidizing atmosphere, thereby forming a sintered article; substantially impregnating and coating the sintered article with an aqueous alkali metal silicate solution; curing the solution at a temperature of at least about 300° F. to drive off the water radical of the solution, and render the article porous and the silicate impregnant and coating water insoluble; and placing the article into service in a corrosive halogen ion containing environment.

A pressed and sintered porous powder metal article coated both externally and internally along porous passages with a cured alkali metal silicate coating having an average thickness of at least 15 microinches and which is capable of withstanding a 5% aqueous sodium chloride spray solution, without showing signs of rusting, pitting or staining at normal visual levels, for a period in excess of 100 hours, in accordance with testing procedures established by ASTM designation B117–64.

This application is a continuation-in-part of now abandoned copending application Ser. No. 762,968, filed Sept. 26, 1968.

The invention relates to a method of providing a powder metal article subjected to a corrosive halogen ion containing atmosphere with corrosion resistance thereto and to a pressed and sintered porous powder metal article which is resistant to a corrosive halogen ion containing environment.

The use of powder metal articles has grown at a very rapid rate in recent years. Largely responsible for this, is the recognition that powder metal articles can combine the economic advantages of mass production for both simple and complex configurations. Today, powder metal articles are continuing to find new markets as replacements for articles machined from conventional wrought and cast materials.

A shortcoming of powder metal articles is that they possess a lower resistance to corrosion than do articles of the same chemical composition in wrought or cast form. Although it is not entirely certain, it is believed that the lower corrosion resistance of powder metal articles is due to the retention of corrosive substances in the pores of the article.

Prior to the present invention, there was considerable belief that the pores of a powder metal article had to be permanently filled to avoid corrosion. This is clearly seen from an article entitled Impregnation of Powder Metallurgy Parts by Wilson N. Pratt, which appeared on pp. 122–123, vol. 133, No. 2 of Steel magazine.

We have discovered that the corrosion resistance of powder metal articles, to halogen ion containing environments; e.g., chlorine ion containing environments, can be substantially improved without destroying the porous nature of the article. Moreover, we have discovered that

porous powder metal articles covered both externally and internally along porous passages, with a cured alkali metal silicate coating, can withstand a 5% aqueous sodium chloride spray solution, without showing signs of rusting, pitting or staining at normal visual levels, for a period in excess of 100 hours, in accordance with testing procedures established by ASTM designation B117–64.

It is accordingly an object of this invention to furnish a method of providing a powder metal article subjected to a corrosive halogen ion containing environment with corrosion resistance thereto.

It is a further object of this invention to furnish a pressed and sintered porous powder metal article which is resistant to a corrosive halogen ion containing environment.

The method of the present invention provides a powder metal article subjected to a corrosive halogen ion containing environment; e.g., a chlorine ion containing environment, with corrosion resistance thereto. It comprises the steps of: pressing metal powder into a green compact; sintering the green compact in a substantially non-oxidizing atmosphere, thereby forming a sintered article; substantially impregnating and coating the sintered article with an aqueous alkali metal silicate solution; curing the solution at a temperature of at least about 300° F. to drive off the water radical of the solution, and render the article porous and the silicate impregnant and coating water insoluble; and placing the article into service in a corrosive halogen ion containing environment. Pressing, sintering, coating and impregnating can be accomplished by any of the conventional prior art processes. Illustrative processes include double-action pressing, sintering in hydrogen (by far the most advantageous sintering atmosphere), and immersion and vacuum immersion coating and impregnating. Curing takes place at temperatures of at least 300° F. Temperatures in the range of 600 to 900° F. are, however, presently preferred. At curing temperatures less than about 600° F., there is a tendency for the silicate to redissolve and turn white, and at curing temperatures above about 900° F., there is a tendency for the silicate to soften and for the coating and impregnant to become discontinuous. Curing may be effected in from 1 to 10 minutes or more, depending upon the bulk of the article being treated, the thermal properties of the heating equipment, the thickness of the coating and impregnant, and other interrelated variables.

The aqueous alkali metal silicate solution contains sufficient alkali metal silicate to provide a cured silicate impregnant and coating having an average thickness of 15 to 1000 microinches and preferably 35 to 600 microinches, and can contain wetting agents which lower the surface tension of the solution and provide more uniform coating, as well as corrosion inhibitors which further enhance corrosion resistance. Illustrative alkali metal silicates include sodium silicate and potassium silicate, with sodium silicate being preferred. Typical wetting agents include "Wetanol" (Glyco Products, Inc., New York, N.Y.) and typical corrosion inhibitors include sodium oxalate, sodium phosphate and sodium aluminate. The amounts of wetting agents and corrosion inhibitors varies depending upon the desired results.

The article of the present invention is a pressed and sintered porous powder metal structure, coated both externally and internally along porous passages with a hard, non-organic alkali metal silicate coating having an average thickness of from 15 to 1000 microinches and preferably from 35 to 600 microinches. An average thickness of at least 15 microinches is necessary to insure adequate corrosion resistance from halogen ion containing environments. Coatings having an average thickness in excess of 1000 microinches can interfere with the appearance of the metal, may not be adequately "cured" and are more

susceptible to efflorescence or bleeding of a white deposit. The article of this invention is capable of withstanding a 5% aqueous sodium chloride spray solution, without showing signs of rusting, pitting or staining at normal visual levels, for a period in excess of 100 hours, and preferably in excess of 500 hours, in accordance with testing procedures established by ASTM designation B117–64. The term, normal visual levels, relates to all that can be observed without the aid of microscopes and other magnifying or special equipment.

The following examples are illustrative of the invention.

Atomized, pre-alloyed Type 304L and 316L stainless steel powders were prepared. The powders had the composition, and particle size distribution and properties, respectively shown below in Tables I and II.

TABLE I

Alloy	Composition (wt. percent)								
	C	Mn	P	S	Si	Cr	Ni	Mo	Fe
Type 316L (Lot 182)	0.03	0.13	----------		0.89	17.37	14.00	2.37	Bal.
Type 304L (Lot 236)	0.025	0.082	0.014	0.011	0.58	17.65	12.20	------	Bal.

TABLE II

Alloy	Mesh (wt. percent)			Hall flow (seconds/ 50 g.)	Apparent density (g./cu. cm.)
	−100/+200	−200/+325	−325		
Type 316L†(Lot 182)	23.0	27.6	49.4	30.6	2.62
Type 304L (Lot 236)	23.2	28.7	48.1	25.6	2.97

Twenty gram samples of the powders were double-action pressed into ¼ inch thick green compacts in a one-inch diameter die and subsequently sintered at 2300° F. for two hours. Compacting pressure of 30 and 40 tons per square inch were used to produce the green compacts and hydrogen, dissociated ammonia and vacuum atmospheres were used during sintering. After sintering, the densities of the samples were between 77 and 80% of their theoretical density of 7.90 g./cu. cm.

The samples were coined at their original compacting pressure after sintering, to obtain higher densities, and subsequently re-sintered for 2 hours at 2300° F. in the same atmosphere in which they were originally sintered. After re-sintering, the samples had densities between 83 and 89% of their theoretical density.

Several of the samples (samples A through E) were given a room temperature salt immersion test with a 5% aqueous sodium chloride solution. Samples A and B were Type 316L stainless steel and samples C, D and E were Type 304L stainless teel. The samples were not given a cured alkali metal silicate coating. Their condition after specific time periods of exposure to the salt is reported below in Table III. Table III additionally sets forth their porosity and the atmosphere in which they were sintered.

TABLE III

Sample	Sintering atmosphere	Percent porosity	Sample condition
A	NH_3	16.0	Stains and rust spots after 4 hours.
		20.6	Rust spot after 4 hours, stains after 8 hours.
B	H_2	11.6	Stains after 32 hours, rust after 74 hours.
		20.6	Stains after 4 hours, rusting after 120 hours.
C	NH_3	23.3	Rust spots and stains after 4 hours.
		27.7	Stained after 4 hours, rusted after 8 hours.
D	H_2	12.0	Rust stains after 4 hours, pitting after 144 hours.
		23.5	Do.
E	Vacuum	11.0	Staining from edge after 4 hours, general surface rust after 32 hours.
		23.0	Stain and pitting after 4 hours.

A study of Table III reveals that none of the samples were free of rusting, staining and pitting after 100 hours of testing regardless of composition, porosity and sintering atmosphere.

Powder metallurgists have suggested that sintered stainless steel powder metal parts may be made corrosion resistant by heating them for 20 to 30 minutes in air at temperatures between 750° and 930° F. To study the effectiveness of this approach, six samples (samples F through K) were heated in air at 850° F. for 25 minutes and then given the same salt test that was given to samples A through E. Samples F, G and H were Type 316L stainless steel and samples I, J and K were Type 304L stainless steel. None of the samples were given a cured alkali metal silicate coating. Their condition after specific time periods of exposure to the salt is set forth below in Table IV. Table IV additionally sets forth their porosity and the atmosphere in which they were sintered.

TABLE IV

Sample	Sintering atmosphere	Percent porosity	Sample condition
F	NH_3	16.0	Rust spots and stains after 4 hours.
		20.6	Do.
G	H_2	11.5	Stains and rust spots after 16 hours.
		20.6	Stains after 8 hours, pitting after 32 hours.
H	Vacuum	11.0	Rust and pits after 74 hours.
		21.2	Rust and pits after 98 hours.
I	NH_3	23.3	Rust stain after 4 hours, rust spots after 8 hours.
		27.7	Rust stain after 4 hours, rust spots after 16 hours.
J	H_2	12.0	Pit and rusting after 74 hours.
		23.5	Rust spots after 120 hours.
K	Vacuum	11.0	Localized pits after 74 hours, rusting after 98 hours.
		23.0	Rusting after 32 hours.

A comparison of Table IV with Table III reveals that heating the samples in air for 25 minutes at 850° F. did not materially affect their corrosion resistance.

Six additional samples (samples L through Q) were cleaned, dip coated and impregnated in an aqueous alkali metal silicate solution, cured and given the same salt test as were samples A through K. Samples L, M and N were Type 316L stainless steel and samples O, P and Q were Type 304L stainless steel. Cleaning involved the steps of degreasing in clean acetone to remove surface contamination, drying at 200° F., soaking in a 50% aqueous solution of ammonium hydroxide, rinsing in distilled water and drying under a vacuum at 300° F. Coating and impregnating involved the steps of immersing the samples in sodium silicate solution containing about 19 weight percent solids in water with 0.1% by weight of "Wetanol," wetting agent, and mechanically withdrawing the samples at a steady rate to insure constant wet film thickness. Curing involved heating at 200° F. for 30 minutes, heating at 400° F. for 30 minutes and heating at 600° F. for 30 minutes. The condition of the samples after specific time periods of exposure to the salt is reported below in Table V. Table V additionally sets forth the porosity of

the samples and the atmosphere in which they were sintered.

TABLE V

Sample	Sintering atmosphere	Percent porosity	Sample condition
L	NH_3	16.0	Rust spots and stains after 4 hours.
		20.6	Rust spots after 8 hours.
M	H_2	11.6	No attack, slight surface stain from edge after 1,000 hours.
		20.6	A few small pits, stains on surface from edge after 1,000 hours.
N	Vacuum	11.0	Rust spots after 4 hours.
		21.2	Rust spots and stains after 4 hours.
O	NH_3	23.3	Rust spots and stain after 4 hours.
		27.7	Rust spots after 4 hours.
P	H_2	12.0	Slight stain from edge after 1,000 hours.
		23.5	Do.
Q	Vacuum	11.0	Fine rust spots after 4 hours, bleeding after 32 hours.
		23.0	Stain after 4 hours, rusting after 8 hours.

A study of Table V clearly shows the excellent corrosion resistance obtained by following the teachings of the present invention and the importance of hydrogen sintering. Samples M and P, the samples sintered in hydrogen, were in good condition after 1000 hours of exposure to the salt and were free from staining, pitting and rusting after 100 hours of exposure. On the other hand, samples L, N, O and Q, the samples sintered in a vacuum or in dissociated ammonia, were not free from staining, pitting and rusting after exposure periods of far less than 100 hours.

An additional group of six samples (samples R through W) were prepared and tested in the same manner as were samples L through Q with the exception that these samples were vacuum coated and impregnated rather than simply being dip coated and impregnated. More specifically, samples R through W were submerged in a tray of coating solution for one hour, in a chamber drawn under vacuum and kept in the solution until atmospheric pressure was reached, after the vacuum was released subsequent to the one hour period. Samples R, S and T were Type 316L stainless steel and samples U, V and W were Type 304L stainless steel. The condition of the samples after specific time periods of exposure to the salt is reported below in Table VI. Table VI additionally sets forth the porosity of the samples and the atmosphere in which they were sintered.

TABLE VI

Sample	Sintering atmosphere	Percent porosity	Sample condition
R	NH_3	16.0	Rust spots after 74 hours.
		20.6	Rust spots after 32 hours.
S	H_2	11.6	No attack, very slight surface stain from edge after 1,000 hours.
		20.6	Do.
T	Vacuum	11.0	Some staining after 74 hours, edge rust after 98 hours.
		21.2	Some staining after 98 hours, bleeding rust after 216 hours.
U	NH_3	23.3	Rust spots after 8 hours.
		27.7	Rust spots after 16 hours.
V	H_2	12.0	No attack, very slight stain from edge after 1,000 hours.
		23.5	Do.
W	Vacuum	11.0	Rust spots and stains after 34 hours.
		23.0	Rust spots and stains after 74 hours.

A study of the results of Table VI confirms the findings discussed above with regard to Table V. More specifically, they clearly show that excellent corrosion resistance is obtained by following the teachings of the present invention and by employing hydrogen sintering atmospheres during the method of the invention. In addition, they show that the corrosion resistance of the samples with greater porosity was as good or better than that for the similarly treated samples with the lower porosity levels. Furthermore, a comparison of Table VI with Table V shows that somewhat better results are obtained when vacuum coating and impregnating is used rather than simple dip coating and impregnating.

Another set of six samples (samples AA through FF) were prepared and tested in the same manner as were samples R through W with the exception that the coating solution had 25 grams of sodium oxalate, a corrosion inhibitor, added to each liter thereof. Samples AA, BB and CC were Type 316L stainless steel and samples DD, EE and FF were Type 304L stainless steel. The condition of the samples after specific time periods of exposure to the salt is reported below in Table VI. Table VII additionally sets forth the porosity of the samples and the atmosphere in which they were sintered.

TABLE VII

Sample	Sintering atmosphere	Percent porosity	Sample condition
AA	NH_3	16.0	Rust spots after 120 hours.
		20.6	Slight stain after 144 hours, pitting after 168 hours.
BB	H_2	11.6	No attack, very slight surface stain from edge after 1,000 hours.
		20.6	Do.
CC	Vacuum	11.0	Slight stain after 8 hours, edge rust after 216 hours.
		21.2	Slight stain after 16 hours, rusting after 168 hours.
DD	NH_3	23.3	Slight stain after 74 hours, rust spots after 120 hours.
		27.7	Slight stain after 74 hours, rust spots after 144 hours.
EE	H_2	12.0	Pit and rust stain after 74 hours.
		23.5	Very slight stain from edge after 1,000 hours. No attack.
FF	Vacuum	11.0	Rust near edges on surface after 240 hours.
		23.0	Rusting on edge after 144 hours, surface rusting after 216 hours.

A study of the results of Table VII shows that a corrosion inhibitor improves the corrosion resistance to some degree but is not as important a factor as is the alkali metal silicate. Moreover, Table VII reveals that sintering atmospheres other than hydrogen, such as a vacuum or dissociated ammonia, can produce satisfactory results under particular conditions even though they are not as effective as hydrogen.

The above and following examples were directed to stainless steel embodiments despite the fact that the invention is believed to be adaptable to a wide variety of metals, including other alloy steels and carbon steels, as stainless steel probably constitutes the most important use for the invention. Moreover, testing was performed in a corrosive chlorine ion containing environment as the chlorine ion is the most often encountered halogen ion. Furthermore, each sample had approximately one to two mils removed from one surface, with a belt grinder, and additional material removed with a series of successively finer grit papers through 200 grit, to simulate wear. The opposite sides of the samples were retained in the as-sintered condition. All samples were cleaned in 50 percent ammonium hydroxide solution to remove grinding contaminants, and subsequently rinsed in distilled water and dried.

Additional vacuum sintered samples were given a 5% aqueous sodium chloride spray test for one thousand hours in accordance with the procedures established in ASTM designation B117–64. The samples were both Type 316L and Type 304L stainless steel. One group of the samples was left uncoated, another was coated and impregnated with alkali metal silicate, as were samples L through Q and R through W, and another was vacuum coated and impregnated with a solution containing about 29 wt. percent "Quram 220" (Philadelphia Quartz Co., Chester, Pa.) organic ammonium silcate and 0.1 wt. percent "Wetanol." Organic ammonium silicate has a quaternary ammonium ion as the cation, which unlike an alkali metal cation, volatilizes during curing, thereby leaving almost pure silica.

The results of the testing are as follows:

TYPE 316L STAINLESS STEEL

(A) Uncoated

(1) Large pits and rust bleeding on ground surfaces of samples with porosity of 14% and greater.

(2) No rusting on ground surface of sample with 10.4% porosity.

(3) Discoloration, pitting and rust bleeding on unground surfaces of samples with 10.4 to 19.5% porosity.

(B) Coated and impregnated with ammonium silicate

(1) Several large pits and heavy rust bleeding on ground and unground surfaces of samples with 10.4 to 19.5% porosity.

(C) Coated and impregnated with alkali metal silicate

(1) Some surface discoloration but no rust on both the ground and unground surfaces of samples with 10.4 to 19.5% porosity.

TYPE 304L STAINLESS STEEL

(A) Uncoated

(1) Large pits and bleeding on ground and unground surfaces of samples with 13.6 to 27.1% porosity.

(B) Coated and impregnated with ammonium silicate

(1) Large pits and heavy rust bleeding on both ground and unground surfaces of samples with 13.6 to 27.1% porosity.

(C) Coated and impregnated with alkali metal silicate

(1) Some small pits and light rust bleeding on both ground and unground surfaces of samples with 13.6 to 27.1% porosity.

A study of the above results shows that ammonium silicate is not effective for providing a powder metal article with corrosion resistance to a halogen ion containing environment and that samples coated and impregnated with alkali metal silicate and sintered in a vacuum stand up reasonably well to a 5% aqueous sodium spray test, despite the fact that they would have greater corrosion resistance if they had been sintered in hydrogen.

From the above paragraphs it will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific examples thereof will suggest various other modifications and applications of the same. It is accordingly desired that in construing the breadth of the appended claims they should not be limited to the specific examples described herein.

We claim:

1. A method of making a powder metal article comprised of steel to be subjected to a corrosive halogen ion containing environment with corrosion resistance to said environment, which comprises the steps of: pressing steel powder into a green compact; sintering said green compact in a substantially non-oxidizing atmosphere, thereby forming a sintered article; substantially impregnating and coating said sintered article with an aqueous alkali metal silicate solution; curing said solution at a temperature of at least about 300° F. to drive off the water radical of the solution and render said article porous and said silicate impregnant and coating substantially water insoluble, said cured silicate having an average thickness of at least 15 microinches.

2. A method according to claim **1** wherein said green compact is sintered in a hydrogen atmosphere.

3. A method according to claim **1** wherein said solution is cured at a temperature of from 600 to 900° F.

4. A method according to claim **1** wherein said aqueous alkali metal silicate solution is an aqueous sodium silicate solution.

5. A method according to claim **1** wherein said sintered article is impregnated and coated by immersing said article in said aqueous alkali metal silicate solution.

6. A method according to claim **5** wherein said sintered article is impregnated and coated in a vacuum.

7. A method according to claim **1** wherein said aqueous alkali metal solution contains a corrosion inhibitor additive.

8. A pressed and sintered porous powder metal article comprised of steel and capable of withstanding a 5% aqueous sodium chloride spray solution, without showing signs of rusting, pitting or staining at normal visual levels, for a period in excess of 100 hours, in accordance with testing procedures established by ASTM designation B117–64; said article being coated both externally and internally along porous passages with a cured alkali metal silicate coating having an average thickness of at least 15 microinches.

9. An article according to claim **8** wherein said cured alkali metal silicate coating has an average thickness of from 15 to 1000 microinches.

10. An article according to claim **9** wherein said cured alkali metal silicate coating has an average thickness of from 35 to 600 microinches.

11. An article according to claim **8** wherein said metal is stainless steel.

12. An article according to claim **8** wherein said article is capable of withstanding a 5% aqueous sodium chloride spray solution, without showing signs of rusting, pitting or staining at normal visual levels, for a period in excess of 500 hours, in accordance with testing procedures established by ASTM designation B117–64.

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