United States Patent Office

3,142,894

Patented Aug. 4, 1964

3,142,894

SINTERED METAL ARTICLE AND METHOD OF MAKING SAME

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No Drawing. Continuation of application Ser. No. 774,166, Nov. 17, 1958. This application Aug. 31, 1962, Ser. No. 220,854

20 Claims. (Cl. 29—182.5)

This invention relates to sintered powdered metal articles and structures adapted for operation in relatively high temperature applications, as high as or even higher than 1200° F.

It particularly relates to sintered articles and structures of this kind, for instance seal and bearing structures characterized by substantial dimensional and physical stability at such high temperatures for substantial periods of time and operative at these temperatures and at lower temperatures, including ambient temperatures under oxidizing, reducing and neutral atmospheric conditions without external lubrication. Moreover, our invention is concerned with the novel compositions and methods for obtaining these features.

The present application is a continuation of co-pending application Serial No. 774,166 now abandoned filed November 17, 1958.

It has heretofore been proposed as, for example, in the patents to Calkins 1,974,173 and 1,940,294 to make sintered powdered products of compositions essentially of iron particles, powdered copper, and small amounts less than 2% of powdered graphite. These compositions after mixing are conventionally compacted in molds at pressures of between 25,000 to 50,000 p.s.i. and then sintered at about 2100° F. in a reducing or non-oxidizing atmosphere and then cooled in such atmosphere. Customarily it has also been the practice to incorporate quantities of lubricant such as oil or soap in the composition after sintering. These compositions produce porous structures containing substantial amounts of coarse pearlite and considerable ferrite (Fe) having use as internally lubricated bearing materials, at low temperatures. However, they lack the wearing properties and the physical and dimensional stability essential for use as bearing materials or seals at temperatures in the order of 900° F. to 1200° F. Furthermore, such materials are not capable of providing good wearing properties without lubrication under any conditions.

It has also been proposed in the British patent No. 719,146 to Deventer to consolidate a cold mixture of very fine particles of iron, copper, and between 2 to 10% graphite at a pressure of 1000 atmospheres (about 15,000 p.s.i.), and to then subject the compact to a pressure of 3500 atmospheres (52,500 p.s.i.) in a furnace heated at 960° C. (1760° F.) and to then cool the material to a temperature of 150 to 300° C. while being maintained under this high pressure. It is specifically stated that the material is "fritted and not sintered," while the pressure is maintained, until the mixture becomes coherent. The patentee suggests that the product provides a bearing surface which needs no lubrication at elevated temperatures (not stated) but which, from the uses suggested by the patentee, to wit, piston rings, bearings, crosshead checks are applications not involving temperatures much above 400° F. Due to the low temperature of heat treatment in the Deventer process, which for all purposes may be denominated as a hot pressing process, during which no liquid phase sintering or carburizing occurs, the resulting product is essentially composed of ferrite and graphite and

is substantially free of pearlite, hematite, magnetite, wüstite and carbides, one or more of which it will be seen are essential to the present invention. Moreover, the Deventer product is substantially weaker than those of Calkins and hence can be used only under conditions of light stress. It also obtains no advantage whatever from a liquid phase copper and when used at elevated temperatures as high as 1200° F. the pores of this material become rapidly filled with oxidation products producing swelling and dimensional changes. Moreover, its tensile strength is then only about 1600 p.s.i.

It is further proposed in the patent to Lenel 2,187,589 to treat with steam, air, carbon dioxide or oxygen at 1,050° F. a porous, sintered iron article fabricated from iron or iron compositions including graphite, copper, nickel, or manganese and in particular a mixture of 98 parts sponge iron, 2 parts graphite and 1½ parts zinc stearate or stearic acid, to obtain a corrosion-resistant film or layer of oxide which will prevent corrosion of the product at normal temperatures by the action of the atmosphere or water vapor. It is stated that a film of magnetic iron oxide will form a better corrosion-resistant and adherent film than red iron oxide.

The patentee is concerned with the corrosion aspects of porous iron products at ambient temperatures. There is no recognition of the advantages to be obtained by iron oxide formation in a sintered product in conjunction with adequate amounts of graphite from the standpoint of providing a wearing surface for seals or bearings to be subjected to operation at high temperatures in the order of 1200° F. and higher. Nor is it recognized that oxide formation prior to use facilitates the making of a product having substantial dimensional stability in subsequent high temperature use.

There are many applications where a material is required to serve, for example, as either a seal or bearing at high temperatures above 900° F., in the order of 1200° F. to 1400° F. and where the parts at these temperatures must have substantial strength, must be dimensionally stable and/or must resist wear by rubbing. Moreover, due to the high temperatures of operation, and in many instances the configuration of the parts involved, lubrication is not possible. A case in point is the regenerator of a gas turbine engine. In such an installation it is essential that the hot exhaust gases and ambient temperature incoming air be sealed from each other as they enter and leave the regenerator. The temperature of the oxidizing gases involved in such an operation covers a range of between 1200° F. to 1400° F. Moreover, the regenerator surface is not flat. Hence, the seal must be flexible enough to conform under spring loading, to its particular contour or any changes therein during operation. Since lubrication is not possible, the seal must be made of a material that will operate satisfactorily for many hours (preferably above 500) under the stated conditions. A further example is the regenerator center bearing. This part is required to function as a bearing under oxidizing conditions at the indicated temperatures without lubrication while at the same time resisting wear by rubbing and being substantially dimensionally stable. Similar requirements are essential in the case of missile parts except, however, that there, dimensional stability is not of greatest importance because of the limited service expected.

The known products discussed above will not provide the desired features and parts made from unprotected graphite alone have no strength whatever at the stated temperature under extended exposure due to catastrophic oxidation.

It is therefore the main object of our invention to provide a powdered metal article or product comprising a sintered compact of powdered ferrous metal and graphite

with or without copper in which the ferrous metal is preferably substantially pure iron powder but may be a powdered alloy of iron, and which product will exhibit substantial strength, a high degree of dimensional stability and resistance to substantial stressing when exposed to heat, especially temperatures above about 900° F. and as high as about 1200° F. and even higher, for substantial periods of time and that will, depending upon treatment, have an oxidized grain structure characterized by the appearance of substantial amounts of one or more surface oxides from the group consisting of magnetite, wüstite and hematite between and around particles of ferrite and partially decarburized and/or spheroidized pearlite.

Another object is to provide a powdered metal article or product as in the preceding object, such as a seal or bearing and the like comprising a sintered compact of powdered ferrous metal with or without copper and/or alloying metals, that includes graphite in amount sufficient to minimize wear during the breaking-in period by serving as a lubricant during such period and that will promote wear resistance and control the wear rate at the mating surface during service both by dry film lubricant action and by its modifying effect on the surface oxides to form those providing a compensating growth.

A further object is to provide an article or product as in the preceding objects which requires no external lubrication even at high temperatures.

It is also an object to provide a novel process by which products of the character recited in the preceding objects may be obtained.

A particular object is to improve the dimensional stability of sintered iron powdered metal articles and products in high temperature service by subjecting the products following treatment at the sintering temperature to cooling in a reducing atmosphere to a temperature below that which will produce catastrophic oxidation which temperature may be ambient temperature, and preferably during this cooling cycle which may also include holding at such a temperature or, following reheating in air after completing this cooling cycle, in either event, from a temperature between 1050° F. to 2150° F., cooling the product in an oxidizing atmosphere such as air, steam or oxygen to a temperature at which non-uniform cooling thereafter outside the furnace will not promote warpage from thermally induced stresses.

These and other objects and advantages of our invention will be apparent from the following description.

We have now discovered and believe that the dimensional instability of prior products referred to above is primarily due to a growth in the particle structure occasioned by the after formation especially at high temperatures above 900° F., of substantial amounts of the iron oxide (Fe_3O_4) known as magnetite and/or the iron oxide (FeO) known as wüstite during oxidation at such high temperatures. This condition appears to follow decarburization of the pearlite and cementite produced in sintering and the subsequent oxidation to magnetite of the ferrite thus formed or present. This condition can be substantially avoided and a substantially dimensionally stable product be obtained by providing in the sintered matrix prior to subjection of the products to high temperature service an oxidized grain structure providing substantial amounts of desirable oxides from the group of magnetite, wüstite and hematite over, between and around particles of ferrite and partially decarburized and/or speroidized pearlite so as to produce a surface layer or layers thereof. Moreover, through the provision of sufficient graphite to control break-in wear and to control further oxidation we have found that this substantially stable condition once obtained can be substantially preserved in service.

Further, we have found that the poor wearing properties evident in the prior structures are due to their inherent composition of pearlite and/or ferrite which permits wear of the soft iron by smearing and galling. This condition

can be inhibited by the presence of substantial amounts of oxide at the wearing surface of the article, a feature of our invention which is found to act as a wear-controlling agent. It reduces the wear rate in service at the mating surfaces and provides a structure requiring no external lubrication. The preferred oxide is usually identifiable at the wear interface as a smooth black shining non-abrasive surface.

We have discovered that the foregoing advantageous products and novel grain structure is possible of attainment prior to service use by a number of procedures of which a few hereafter described will be by way of example, all, however, involving oxidizing of the sintered matrix under prescribed controlled conditions.

Thus the compacted ferrous metal composition will be sintered under reducing conditions, generally at atmospheric pressure at a temperature between 1900° F. and 2300° F., high enough to obtain a bond between the ferrous particles and render any copper present, in the fluid phase. The temperature employed will depend upon the nature of the ferrous particles making up the compact. For example, where the ferrous particles are of substantially pure iron sintering will preferably be carried on at a temperature between 2000° F. and 2050° F. for best results.

The sintering treatment produces a relatively dense ferrous structure or matrix of integrally bonded ferrous particles whose grain structure is characterized by large particle areas of pearlite and ferrite or cementite. When present, the copper aids to improve the bond between the ferrous particles.

The hot sintered matrix is now cooled in a reducing atmosphere such as dry hydrogen or cracked gas to a temperature at which the atmosphere may be changed to an oxidizing atmosphere such as air, steam, or oxygen, which temperature will be one dependent upon the character of ferrous particles in the composition, the density of the matrix, the time at such temperature, and the rate of subsequent cooling.

In all cases the combination of temperature, time and rate of cooling will be employed to avoid catastrophic oxidation. For most operations the temperature will fall in the range 1050° to 2150° F. with a cooling rate where a thermal oxidation treatment is employed of between 50° F. to 500° F. per hour, the higher the temperature the higher the cooling rate. Also where isothermal oxidation treatment is employed the rate of cooling will preferably be greater. Where the ferrous particles are, for example, of substantially pure iron a good temperature will be about 1500° F. with a cooling rate of at least about 100° F. per hour.

The still hot matrix is now substantially uniformly further cooled in the oxidizing atmosphere from this temperature at the controlled rate down to a temperature where further cooling of a non-uniform character, such as cooling outside a furnace, will not produce warpage due to thermal stressing. This temperature will generally be between about 300° F. to 500° F. Uniform cooling to ambient temperature is preferred.

In many cases it may be preferred for manufacturing reasons and ease of handling the parts to initially cool the hot sintered matrix in the reducing atmosphere to a temperature below that where the change from a reducing to an oxidizing atmosphere would take place as described above and which temperature may be as low as ambient temperature. In such event the matrix will be reheated in air or a reducing atmosphere to the aforesaid atmosphere change-over temperature and then substantially uniformly cooled as described above in an oxidizing atmosphere as where no reheating was involved. In some cases rapid reheating may be essential, in which case induction heating is preferred. The recooling rate will be determined by the factors previously described to which may be added the reheating time and atmosphere in which reheating takes place.

The described cooling of the matrix in an oxidizing atmosphere will reduce the amount of pearlite by decarburization and promote substantial internal oxidation throughout 30 to 60% of the cross-sectional area of the part to produce a particle growth of iron oxide as represented by one or more of magnetite (Fe_3O_4), wüstite (FeO), and hematite (Fe_2O_3). The resulting product will be stable to changes in dimension when subjected to heating in service, especially to high temperatures above about 900° F. and up to about 1200° F. and even higher and will exhibit excellent wearing properties in such use. The iron oxide will generally constitute 5% to 20% by volume of the internally oxidized areas. For optimum strength and dimensional stability this volume should preferably be at least about 10%. Where optimum stability is not of greatest importance this percentage may be as low as 2%.

We have further discovered that when graphite is incorporated in the composition in the proper amount either locally or throughout the same so as to be present in the as-sintered wearing surface, it serves to minimize initial wear by acting as a lubricant during the breaking-in period. Moreover, where the sintered product has also been given the dimensional stabilizing oxidizing treatment of the invention, such graphite both at the wearing surface and throughout the structure inhibits a modification of the desired oxide present as a result of such treatment. Furthermore, there is evidence that it promotes the formation of additional iron oxide, (magnetite) and/or wüstite (FeO). The additional magnetite and/or wüstite formed during service further reduces the wear rate at the mating surfaces by providing a compensating growth without incurring dimensional instability. Furthermore, the graphite at the wearing surfaces minimizes galling wear by acting as a dry-film lubricant in low temperature service below about 900° F.

Although the dimensional stability features of our invention and the processing making this possible have broad application to products of sintered powdered iron per se, it is preferred for reasons already described and hereafter expanded that the composition of the products of our invention consist essentially of iron, copper and graphite. The amounts of each to be used will depend somewhat upon the size and complexity of the part to be made, the green strength of the compact, and the service the finished product is to encounter. In general, in order to obtain the maximum novel benefits of the invention, the ingredients of such preferred composition are preferably kept substantially within the following range:

	Percent by weight
Copper	1½ to 6
Graphite	6 to 15
Iron	Balance

The upper limit of graphite is limited by the green strength required of the compact. Amounts should not be used in excess of that required to produce a compact that will stay together during the in-process handling and sintering, generally without use of extraneous binders, using only a wetting agent, such as kerosene, which will distill out long before sintering occurs. This amount of graphite is usually approximately 15% by weight.

In certain cases as where large or complex shapes, such as turbine seals, are to be made it is found that the spring-out after elastic compression of the graphite in the briquetting die may cause a change in green shape of the piece or even prevent its ejection from the die. In these cases an upper limit of 12% by weight of graphite is preferred.

We have further found that the use of about 10% graphite will give about ½% spring-out in forming and about ½% shrinkage on sintering, creating an approximate balance with resultant exactness in the size of the product. By using this amount of graphite it is possible to make the dies substantially size-for-size, according to the dimensions of the finished product as shown by print. This is a distinct advantage from a production standpoint.

As previously described, it is desirable to have sufficient graphite present such that additional magnetite is formed during service at high temperatures. Without any graphite present, the pre-oxidizing treatment of the invention will produce sufficient iron oxide to prevent substantial dimensional instability, the control of which is an important feature of our invention, but such will not prevent modification of the oxide in service at high temperature with consequent loss of wear resistance. The presence of adequate graphite is needed to promote the formation of additional magnetite desirable for wear control.

We have found that at least about 6% graphite is required in the composition to provide the desired control at the wearing surface under oxidizing conditions at temperatures in the range 900° F. to 1200° F. At lower temperatures the graphite oxidizes to CO and CO_2 at a much slower rate, therefore a greater quantity of graphite is needed for such service.

In general, we have found that the use of about 10% graphite will give the best combination of green strength, sintered strength, and high temperature, and break-in period wear properties.

Examples of commercial graphite powders we can use are Dixon 8485 graphite, a natural graphite made by Joseph Dixon Crucible Company, Jersey City, New Jersey, and Asbury F. G. graphite, a natural graphite made by Asbury Graphite Mills, Asbury, New Jersey, both of which contain about 95% carbon and 5% inert material. By preference, the graphite will be in fine powdered form, preferably of a size to pass through a 325 mesh screen. When of this size it will readily distribute uniformly in the composition when wetted by kerosene and blended with iron powders of 200 to 325 mesh. Larger size graphite may be used but such will affect uniformity and tend to produce soft areas in the wearing surface which will be swept out in the wearing process. The Dixon graphite is of such fineness that 97% will pass through a 325 mesh screen and the Asbury graphite is even finer being all minus 325 mesh in size.

In the powdered iron compositions of our invention the copper serves to densify the iron by liquid phase sintering and aid in the bond between iron particles and to thus impart strength. About 4% of this ingredient is optimum but we can use up to about 6% and as little as 1½% to 2% with good results. As previously stated, the copper may be entirely omitted but as in the case of omitting graphite, such has undesirable features. When the copper is omitted, it is essential to sinter at temperatures higher than 2050° F. or for longer periods than one-half hour to attain equivalent densification. Moreover, in such cases substantial amounts of undesired primary carbides may form.

Examples of finely divided powdered copper we can use, are electrolytic type powdered copper such as electrolytic type "C" copper and electrolytic type "ML" copper made by American Metal Climax, Inc., New York, New York. The copper will preferably be between 100 to 325 mesh size. Copper "C" is 95% minus 325 mesh, and "ML" copper is all minus 100 mesh and 70% minus 325 mesh. The size of the copper particles is not of great importance as it melts in sintering. However, the finer sizes are preferred because it aids in briquetting.

A portion or all of the copper may, when desired, be replaced by a metal such as tin or lead or combinations thereof having a melting point below the sintering temperature used and which substituents are not strong deoxidizers (i.e., like aluminum) and will have boiling points above the sintering temperature. Moreover, alloys of copper, tin, and lead may be employed.

The ferrous particle content of the composition may be in the form of pure iron, iron oxide (FeO), millscale (Fe_3O_4) a partially reduced iron for example a 30% reduced iron (30% Fe_3O_4), or mixture of any of these. If 100% millscale (Fe_3O_4) (86% iron) is used, there is considerable loss of this magnetite because of the reducing action during sintering. The millscale can also be

used in partially reduced condition. Examples of commercially available iron powders that may be used are "Hysqvarna" iron, an electrolytic iron made by Huskavarna of Sweden, Hoeganses "Anchor 80" iron, a reduced magnetite iron made by Hoeganses Sponge Iron Corporation, of Riverton, New Jersey, and "Pyron" iron, a reduced millscale type iron made by Puron Iron Corporation, Niagara Falls, New York.

We can also use ferrous particles which are iron alloys. The extent of alloying ingredients in the iron will preferably not exceed about 40% by weight of the particle. For example nickel-iron and manganese-iron alloy particles may be used and will preferably contain in greatest amount about 10% by weight of nickel and/or manganese. When silicon or chromium are the alloying ingredients these will preferably not exceed 15% by weight of the particle. The latter two alloying constituents are especially desirable where corrosion resistance is to be obtained.

The iron powders should preferably be in major amount of a size between 200 to 325 mesh. "Anchor 80" iron is about 75% of this size and the balance is between 80 to 150 mesh.

In carrying out the process of the present invention, according to a preferred procedure, the mixture of the selected finely comminuted or powdered ingredients is thoroughly blended in a conventional manner to produce a mass in which the ingredients are substantially uniformly distributed, using a wetting agent such as kerosene when graphite is present. The blended mass is then placed in a mold and pressed to the desired form of the article or product by suitable dies using a briquetting pressure above 20,000 p.s.i., preferably at least 40,000 p.s.i., and up to about 60,000 p.s.i. Under such pressures the particles of the composition, if properly selected, are compacted closely together forming briquettes of sharply defined shapes that are self-sustaining. It is found that the density of the briquettes falls off rapidly when the pressing pressure is below about 40,000 p.s.i. During pressing there is a cold welding of the iron particles at points of contact.

The green briquettes are then sintered in a suitable furnace at a suitable temperature between 1900–2300° F. (above the melting point of the copper when present) preferably 2000° F. to 2050° F. where pure iron powders are employed in a reducing atmosphere for a period between about 30 to 60 minutes at temperature. During sintering, diffusion occurs across the previously cold welded interfaces causing the particles to grow together and bond into a cohesive mass. It also effects flow of any copper present to aid in bonding and more importantly densification of the mass.

To provide for a reducing atmosphere, the chamber of the furnace may be provided with suitable inlets through which dry hydrogen, cracked gas, or other reducing gases may be supplied and which inlets may be later be used for feeding an oxidizing atmosphere such as air, steam, or oxygen. Moreover, the furnace may be electrically heated or gas fired externally in any desirable manner so as to maintain the required sintering temperature.

When the briquettes have ben sufficiently sintered, the briquettes while still in a reducing atmosphere are permitted to cool to the temperature described above in the range 1050°–2150° F. where change from a reducing to an oxidizing atmosphere is to take place, for instance, about 1500° F. where the composition is primarily composed of substantially pure iron powders.

The furnace chamber is now cleared of the reducing atmosphere, and then air, steam, oxygen, or other oxidizing atmosphere is admitted thereto and passed therethrough. While subjected to the oxidizing effects of such oxidizing atmosphere, the briquettes are substantially uniformly cooled down to a temperature below which nonuniform cooling outside the furnace will not promote warpage from thermally induced stresses, usually a temperature between 300° F. to 500° F. and preferably ambient temperature, before being removed from the furnace. By preference the parts will be thus cooled at a rate between 50° to 500° F. per hour, preferably between 100° F. to 250° F. per hour in the case of pure iron powders, for best oxidizing results.

During treatment, the austenite and/or subsequently formed pearlite or cementite formed by sintering will be partially decarburized. This prevents the formation of excessive amounts of pearlite and promotes internal oxidation forming one or more of the iron oxides, magnetite (Fe_3O_4), wüstite (FeO) and hematite (Fe_2O_3) to produce a product dimensionally stable when subsequently exposed to high temperature application. It has been found advantageous in using some oxidizing agents to modify the cooling procedure described above to initially cool the sintered product in the protective atmosphere down below the upper oxidizing temperature, for instance, to 300° F. or ambient temperature, then to reheat the product in either a protective or oxidizing atmosphere to the aforesaid oxidizing temperature and then to cool again in an oxidizing atmosphere in the manner previously described.

If the composition initially contains magnetite as its essential iron ingredient, the sintering is preferably carried out in dry hydrogen for best reduction results, during which a 50% to 70% reduction occurs. The sintered product is then preferably cooled down to about 1500° F. in hydrogen and then cooled to room temperature in an oxidizing atmosphere as described above. Use of magnetite as the major iron constituent is preferably limited to applications where shrinkage is not an important design factor.

The tensile strength of the resultant sintered products of our invention will be between 12,000 to 17,500 p.s.i. at ambient temperature depending upon the briquetting pressure (35,000 to 60,000 p.s.i.) used and will be somewhat lower where the products have received the oxidizing treatment in cooling. Their strength at 1200° F. in the as-sintered and preoxidized condition will be about 6500 p.s.i.

The various effects made possible by application of one or more of the features of our invention may to some extent be appreciated from consideration of a composition containing by weight 86% iron, 4% copper, and 10% graphite.

Thus cooling down the sintered briquette of such a composition in the conventional manner in dry hydrogen to ambient temperature results in a particle structure principally of large particle areas of pearlite and ferrite, and small areas of copper, which pearlite and ferrite, as previously described, will in service be oxidized at high temperature, and effect a growth of the structure to cause dimensional changes of a magnitude apt to cause distortion and other undesired effects.

On the other hand, with sufficient graphite present, such graphite will form a considerable part of any wearing surface of the structure to provide initial dry lubrication and control the wear rate of the wearing surface.

When, as previously described, the article is cooled in a protective atmosphere down to the transfer temperature or cooled to ambient temperature in a protective atmosphere and subsequently reheated to the transfer temperature and then in either case cooled in air or oxygen, there are substantial areas of iron oxides from the group magnetite, wüstite and hematite formed, or areas of such oxides associated with graphite. Moreover, any partially decarburized and spheroidized pearlite will be surrounded by such iron oxides and/or iron oxides and graphite.

After a thousand hours of service at 1200° F., the portion of the composition adjacent the wear surface is principally composed of the iron oxides, of magnetite, wüstite and hematite, substantially no pearlite, and some ferrite, and there is a change to magnetite of the partially decar-

burized and spheroidized pearlite areas produced during cooling. Such additional oxidation improves the wearing qualities without causing the dimensional instability which is inherent in oxidation of a structure where there has been no pre-oxidation treatment of the structure as in the present invention. The graphite present during service maintains the character of the previously formed iron oxides and imparts resistance to galling wear by dry film lubricant section.

The following examples illustrate a number of preferred embodiments within the scope of our invention:

Example I

A green composition was prepared as described above containing by weight 86 parts of Anchor 80 iron powder, 4 parts of "C" copper and 10 parts of Asbury F.G. graphite. The composition was pressed in a die to the shape of a flat seal for the regenerator of a gas turbine engine, the approximate size being 20" in outside diameter by 18" in inside diameter by 3/32" in thickness. The briquette thus formed was then sintered at a temperature of 2050° F. for thirty minutes in a reducing atmosphere employing dry hydrogen gas. After sintering, the part was cooled down to ambient temperature in the presence of dry hydrogen. A strong, readily handled seal having a tensile strength above 12,000 p.s.i. was obtained. During sintering there was a slight shrinkage in the part which offset the spring-out in size due to release of elastic strain upon ejection of the part from the die. These changes in dimension generally balanced each other so that the die cavity could be made size for size to the finished dimension of the part. The seal exhibited considerable wear resistance in service on a turbine engine at 1200° F. Its wear resistance was comparable, however, to a solid graphite member but possessed great strength as compared to graphite, and 20 to 50 times the oxidation resistance of graphite. The seal was, however, subject to dimensional change due to substantial growth during service, this latter condition also causing interference with other parts of the engine and producing buckling. Hence a part as here made has a limited application to service conditions below 900° F. or at higher temperature where brief use is intended as in the case of missile parts, for example, seals or bearings.

Example II

A seal was prepared in accordance with Example I and subsequently steam treated for fifteen minutes in superheated steam at about 900° F. After treatment, during which some growth took place, the part was machined to print dimension and subjected to service at 1200° F. The part exhibited good wear resistance, but the treatment while producing a better product than the part prepared in accordance with Example I was not found to possess adequate dimensional stability for long time service at high temperature, and therefore has similar restricted application.

Example III

A green compact was prepared in accordance with Example I in the form of a seal and sintered at 2050° F. for thirty minutes in a reducing atmosphere employing dry hydrogen. The sintered compact was then cooled in a reducing atmosphere employing dry hydrogen down to a temperature of approximately 1500° F. Air was then admitted to the furnace after the hydrogen was purged therefrom and the part cooled in air at the rate of 100 to 200° F. per hour down to a temperature below which non-uniform cooling outside the furnace did not promote warpage from thermally induced stresses. In the present example, the part was cooled down to 300° F. During this treatment certain seal dimensions grew about 0.003" per linear inch. The part was then machined or ground to exact size. The disturbed metal area caused by grinding or machining was etched from the wearing surface and graphite was then restored to its wearing surface by mechanical impregnation (rubbing) to minimize break-in-wear. The part was then placed in service at 1200° F. The part exhibited comparable wear resistance to the seals of Examples I and II and was substantially dimensionally stable, that is to say, that during service in the order of 100 hours at 1200° F. the seal readily conformed itself to changes in the mating regenerator parts caused by uneven heating and no buckling was observed, such as would occur due to excess growth. The part had a tensile strength of about 15,700 p.s.i. at room temperature and 6220 p.s.i. at 1200° F. It will be understood that by a few tests, it is possible to accurately estimate the extent of growth in the briquette upon oxidation treatment and such growth anticipated in the die design so as to avoid subsequent trimming or machining of the part to finished dimensions and subsequent impregnation with graphite.

Example IV

A green composition as called for in Example I was pressed in a mold using a die to form a regenerator center bearing of approximately 2¾" O.D., ⅞" I.D., and 2" length. The bearing was sintered at 2050° F. in a reducing atmosphere employing dry hydrogen for thirty minutes and then cooled completely in dry hydrogen. This part was suitable for use where close tolerances in the bearing dimensions was not required in service.

Example V

A bearing was prepared as in Example IV, but following sintering the part was cooled in dry hydrogen to approximately 1500° F. and then air cooled at the rate of about 100 to 200° F. per hour down to a temperature of about 300° F. During sintering, there was a slight shrinkage which offset the spring of the compact in the die and there was a growth of about 3% upon oxidizing the part. Since no allowance had been made for this growth, the bearing following cooling was machined to accurate dimensions and was thereafter capable of use in service at 1200° without dimensional change and was possessive of excellent wear characteristics.

Example VI

A green compact was prepared in accordance with Example I in the form of a seal and sintered at 2050° F. for thirty minutes in a reducing atmosphere employing dry hydrogen. The sintered product was then cooled to ambient temperature in dry hydrogen after which it was again reheated to about 1500° F. in air and then cooled down again in air at the rate of about 100 to 200° F. per hour to ambient temperature. The seal was thereafter placed in service and exhibited after 1000 hours similar wear characteristics and oxidation resistance to the product of Example III.

Although several preferred embodiments of the invention are disclosed, it will be understood that numerous changes may be made in the time, temperature and rate of cooling relationship and in the proportions and character of ingredients without departing from the spirit and scope of our invention as set forth above and in the appended claims. For example, the following table will provide suggested cooling rates and ranges for a composition such as described in Examples No. III and VI for different starting temperatures of oxidation treatment. We do not, however, desire to be limited thereto.

Peak Oxidizing Temperature	Minimum Cooling Rate in Degrees F./hr.	Maximum Cooling Rate in Degrees F./hr.
1,050° F		50
1,200° F	50	100
1,300° F	50	500
1,400° F	100	150
1,500° F	100	200
1,600° F	200	300
1,700° F	300	400
1,800° F	350	450
1,900° F and higher	400	500

We claim:

1. In a process of producing sintered powdered ferrous products having substantial dimensional stability under service conditions at temperatures up to about 1200° F. the steps comprising briquetting a composition containing at least about 79% by weight of ferrous powder particles into a predetermined shape capable of being handled, sintering the briquettes in a reducing atmosphere at a temperature sufficiently high to cause the ferrous particles to bond together and produce a relatively dense iron particle structure, cooling the sintered product in a reducing atmosphere and during processing substantially uniformly cooling the sintered product in an oxidizing atmophere from a temperature between 1050° F. to 2150° F. at a rate not exceeding about 500° F. per hour.

2. In a process of producing sintered powdered ferrous products having substantial dimensional stability under service conditions at temperatures up to 1200° F., the steps comprising briquetting a composition containing at least about 79% by weight of powder particles selected from the group consisting of iron and iron alloys and mixtures thereof into a predetermined shape capable of being handled, sintering the briquette in a reducing atmosphere at a temperature sufficiently high to cause the ferrous particles to bond together and produce a relatively dense iron particle structure, cooling the sintered product in a reducing atmosphere to a temperature at which the product will not be subject to catastrophic oxidation, and during processing substantially uniformly cooling the product in an oxidizing atmosphere at the rate of about 50° F. to 500° F. per hour from said last mentioned temperature to a temperature at which the product will not be subject to warpage upon exposure to cooling of a non-uniform character.

3. In a process of producing sintered powdered ferrous products having substantial dimensional stability under service conditions at temperatures up to 1200° F., the steps comprising briquetting a composition essentially containing at least about 79% by weight of ferrous powder particles into a predetermined shape capable of being handled, sintering the briquette in a reducing atmosphere at a temperature between 1900° F. and 2300° F. sufficiently high to cause the ferrous particles to bond together and produce a relatively dense iron particle structure, cooling the sintered product in a reducing atmosphere to a temperature below about 2150° F. at which the product will not be subject to catastrophic oxidation and during processing cooling the sintered product substantially uniformly in an oxidizing atmosphere from a temperature corresponding substantially to said last mentioned temperature to a temperature in the order of 500° F. below which the product will not be subject to warpage upon exposure to cooling of a non-uniform character and at a rate between about 50 to 500° F. per hour.

4. In a process of producing sintered powdered ferrous products having substantial dimensional stability under service conditions at temperatures up to 1200° F., the steps comprising briquetting a composition containing by weight at least 79% ferrous powder particles and up to about 15% graphite powder particles into a predetermined shape capable of being handled, sintering the briquette in a reducing atmosphere at a temperature between 1900° F. to 2300° F. sufficiently high to cause the ferrous particles to bond together and produce a relatively dense iron particle structure, cooling the sintered product in a reducing atmosphere to a temperature between 1050° F. to 2150° F. and during processing substantially uniformly cooling the sintered product in an oxidizing atmosphere at the rate of between about 50° F. to about 500° F. per hour from a temperature of about 1050° F. to a temperature below about 500° F.

5. In the process of producing sintered powdered metal products having good wearing qualities the steps comprising briquetting a particle composition comprising 6% to 15% by weight of graphite and a remainder comprising at least 79% of ferrous metal into a predetermined shape capable of being handled, sintering the briquette in a reducing atmosphere at a temperature between 1900° F. and 2300° F., sufficiently high to cause the ferrous particles to bond together and produce a relatively dense ferrous particle structure, cooling the sintered product in a reducing atmosphere to a temperature at which the product will not be subject to catastrophic oxidation and during processing cooling the sintered product in an oxidizing atmosphere from a temperature below said last mentioned temperature.

6. In a process of producing sintered powdered ferrous products having substantial dimensional stability and good wearing properties under service conditions at temperatures up to about 1200° F., the steps comprising briquetting a particle composition comprising 6% to 15% of graphite, 1½% to 6% copper, and at least 79% iron into a predetermined shape capable of being handled, sintering the briquette in a reducing atmosphere at a temperature between 1900° F. to 2300° F. sufficiently high to reduce the copper to a liquid phase and to cause the iron particles to bond together and produce a relatively dense iron particle structure, cooling the sintered product in a reducing atmosphere and during processing cooling the sintered product in an oxidizing atmosphere from a temperature between 1050° F. to 2150° F. to a temperature below about 500° F.

7. In the process of producing sintered powdered ferrous products having substantial dimensional stability under service conditions at temperatures up to 1200° F., the steps comprising briquetting a composition comprising ferrous particles into a predetermined shape capable of being handled, said composition containing at least about 79% by weight of ferrous particles, sintering the briquette in a reducing atmosphere at a temperature between 1900° F. to 2300° F. and sufficiently high to cause the ferrous particles to bond together and produce a relatively dense iron particle structure, cooling the sintered product in a reducing atmosphere down to a temperature between 1050° F. to 2150° F. and then further cooling the thus cooled product in an oxidizing atmosphere to a temperature below about 500° F. and at a rate not exceeding about 500° F. per hour.

8. In the process of producing sintered powdered ferrous products having good wear properties under service conditions at temperatures up to 1200° F., the steps comprising briquetting a composition comprising iron powder particles in amount by weight at least 79% of the composition, copper between 1½% to 6% and graphite between 6% to 15% under suitable pressure into a predetermined shape capable of being handled, sintering the briquette in a reducing atmosphere at a temperature between 1900° F. to 2300° F. and sufficiently high to convert the copper to a liquid phase and to cause the ferrous particles to bond together and produce a relatively dense iron particle structure, cooling the sintered product in a reducing atmosphere down to a temperature below 2150° F. at which the product will not be subject to catastrophic oxidation upon further cooling and then further cooling the thus cooled sintered product in an oxidizing atmosphere at the rate of 50° to 500° F. per hour to a temperature at which the product will not be subject to warpage upon exposure to cooling of a non-uniform character.

9. In a process of producing sintered powdered ferrous products having substantial dimensional stability under service conditions at temperatures up to 1200° F., the steps comprising briquetting a composition comprising by weight 79% to 92½% ferrous powder particles, 1½% to 6% copper powder and 6% to 15% graphite powder into a predetermined shape capable of being handled, sintering the briquette in a reducing atmosphere

at a temperature between 1900° F. and 2300° F. sufficiently high to reduce the copper to the liquid phase and to cause the ferrous particles to bond together and produce a relatively dense iron particle structure having dispersed graphite, cooling the sintered product in a reducing atmosphere to a temperature below which the product will not be subject to catastrophic oxidation, reheating the product to a temperature which is between 1050° F. and 2150° F. and then substantially uniformly cooling the sintered product in an oxidizing atmosphere to a temperature below about 500° F. at which the product will not be subject to warpage upon further cooling of a non-uniform character.

10. A process as claimed in claim 5 wherein graphite is present in about 10% by weight of the composition.

11. In the process of producing sintered ferrous products having good wearing quality, the steps comprising briquetting a composition comprising essentially iron powder and between about 10% to 15% graphite under suitable pressure between 20,000 to 60,000 p.s.i. into a predetermined shape capable of being handled, sintering the briquette for 30 to 60 minutes in a reducing atmosphere at a temperature between about 1900° F. to 2300° F. sufficiently high to cause the briquetted iron powder to bond together and form a relatively dense iron particle structure and cooling the sintered product in a reducing atmosphere down to a temperature which is at least below about 2150° F., and at which the product will not be subject to catastrophic oxidation upon further cooling and subjecting said product thereafter to cooling in an oxidizing atmosphere from a temperature between 1050° F. to 2150° F. to a temperature below about 500° F.

12. As an article of manufacture, a sintered powdered metal product for a seal or bearing operable at elevated temperatures up to 1200° F. and having substantial dimensional stability when exposed to said elevated temperatures, comprising a compacted and sintered matrix of bonded ferrous particles having an oxidized grain structure which is characterized by the appearance of substantial amounts of iron oxide from the group consisting of magnetite, wüstite and hematite and mixtures thereof between and around particles of ferrite and pearlite from the group consisting of partially decarburized pearlite and spheroidized pearlite and mixtures thereof.

13. As an article of manufacture a sintered powdered metal product for a seal or bearing operable at elevated temperatures up to 1200° F. and having substantial dimensional stability when exposed to said elevated temperatures comprising a compacted and sintered matrix of bonded ferrous particles having an oxidized grain structure which is characterized by the appearance of substantial amounts of iron oxide from the group consisting of magnetite, wüstite, and hematite, and mixtures thereof between and around particles of ferrite and pearlite from the group consisting of partially decarburized pearlite and spheroidized pearlite and mixtures thereof, said iron oxide being present in amount at least 10% to 20% by weight of the oxidized structure.

14. As an article of manufacture a sintered powdered metal product for a seal or bearing operable at elevated temperatures up to 1200° F. and having substantial dimensional stability when exposed to said elevated temperatures comprising a compacted and sintered matrix of bonded ferrous and graphite particles having an oxidized grain structure containing dispersed graphite particles and characterized by the appearance of substantial amounts of iron oxide from the group consisting of magnetite, wüstite, and hematite and mixtures thereof between and around particles of ferrite and pearlite from the group consisting of partially decarburized pearlite and spheroidized pearlite and mixtures thereof.

15. As an article of manufacture a sintered powdered metal product for a seal or bearing operable at elevated temperatures up to 1200° F. and having substantial dimensional stability when exposed to said elevated temperatures and having good wear properties comprising a compacted and sintered matrix of bonded ferrous, copper and graphite particles having an oxidized grain structure containing dispersed graphite particles and copper and characterized by the appearance of substantial amounts of iron oxide from the group consisting of magnetite, wüstite, and hematite and mixtures thereof between and around particles of ferrite and pearlite from the group consisting of partially decarburized pearlite and spheroidized pearlite and mixture thereof.

16. As an article of manufacture a sintered powdered metal product for a seal or bearing operable at elevated temperatures up to 1200° F. and having substantial dimensional stability when exposed to said elevated temperatures comprising a compacted and sintered matrix of bonded particles comprising by weight 79% to 92½% ferrous powder, 1½% to 6% copper powder, and 6% to 15% graphite powder, said matrix having a grain structure containing dispersed graphite particles and copper and characterized by the appearance of substantial amounts of iron oxide from the group consisting of magnetite, wüstite and hematite and mixtures thereof between and around particles of ferrite and pearlite from the group consisting of partially decarburized pearlite and spheroidized pearlite and mixtures thereof.

17. As an article of manufacture for a seal or bearing operable at elevated temperatures up to 1200° F., a sintered powdered metal product having substantial wear qualities and dimensional stability when exposed to said elevated temperatures comprising an oxidized compacted and sintered matrix of bonded particles comprising by weight about 85% to 94% ferrous powder and 6% to 15% graphite powder.

18. As an article of manufacture for a seal or bearing operable at elevated temperatures up to 1200° F., a sintered powdered metal product having substantial dimensional stability and wear qualities when exposed to said elevated temperatures comprising an oxidized compacted and sintered matrix of bonded particles comprising by weight about 86 parts of iron powder, about 4 parts of copper powder and about 10 parts of graphite powder.

19. As an article of manufacture for a seal or bearing operable at elevated temperatures up to 1200° F., a sintered powdered metal product having substantial dimensional stability and wear qualities when exposed to said elevated temperatures comprising an oxidized compacted and sintered matrix of bonded particles comprising by weight 79% to 92½% ferrous particles selected from the group consisting of iron and iron alloys containing up to 40% by weight of alloying ingredients, and mixtures of said iron and iron alloys and 6% to 15% graphite particles, said oxidized matrix having a grain structure characterized by dispersed graphite and by the appearance of substantial amounts, at least 5% to 20% by volume of the internally oxidized areas, of iron oxide from the group consisting of magnetite, wüstite and hematite and mixtures thereof between and around particles of ferrite and of pearlite from the group consisting of partially decarburized pearlite and spheroidized pearlite and mixtures thereof.

20. In a process of making a seal between a pair of parallel surfaces of parts having relative motion with respect to each other and at least one of which is subject to a temperature up to about 1200° F., the steps comprising briquetting a composition comprising ferrous powder particles and graphite into a shape to produce said seal and capable of being handled, sintering the seal

forming briquette in a reducing atmosphere at a temperature sufficiently high to cause the ferrous particles to bond together and produce a relatively dense iron particle structure, cooling the sintered seal in an oxidizing atmosphere from a temperature between 1050° F. to 2150° F. to a temperature below about 500° F. and thereafter assembling said seal between said parallel surfaces.

References Cited in the file of this patent

UNITED STATES PATENTS

2,187,589	Lenel	Jan. 16, 1940
2,855,659	Thomson	Oct. 14, 1958
2,945,759	Shaw et al.	July 19, 1960
3,070,439	Grant et al.	Dec. 25, 1962