

Aug. 17, 1971

F. A. BADIA ET AL
PROCESS FOR PRODUCING AT LEAST ONE
CONSTITUENT DISPERSED IN A METAL

3,600,163

Filed March 25, 1968

2 Sheets-Sheet 1

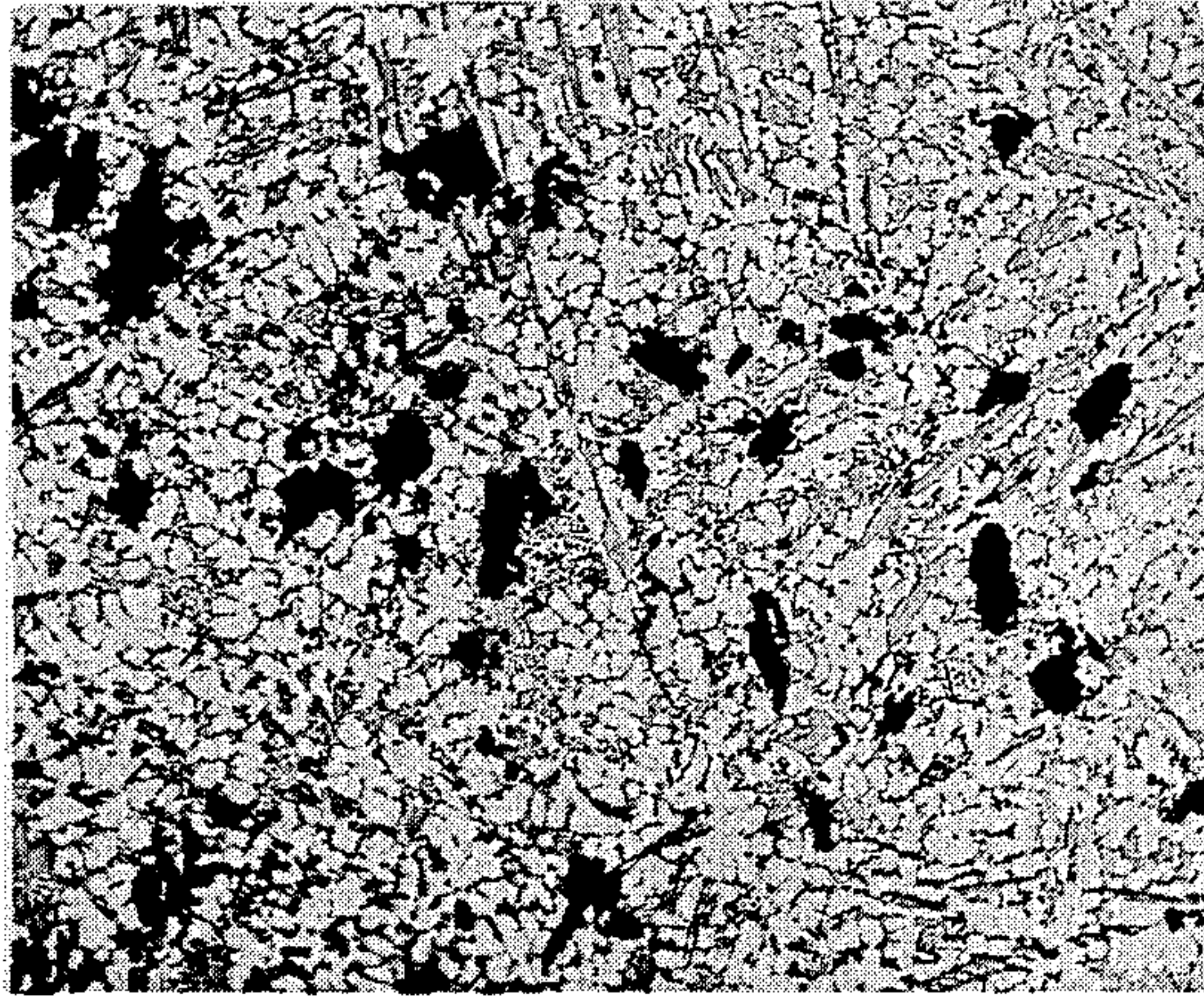


FIG. 1

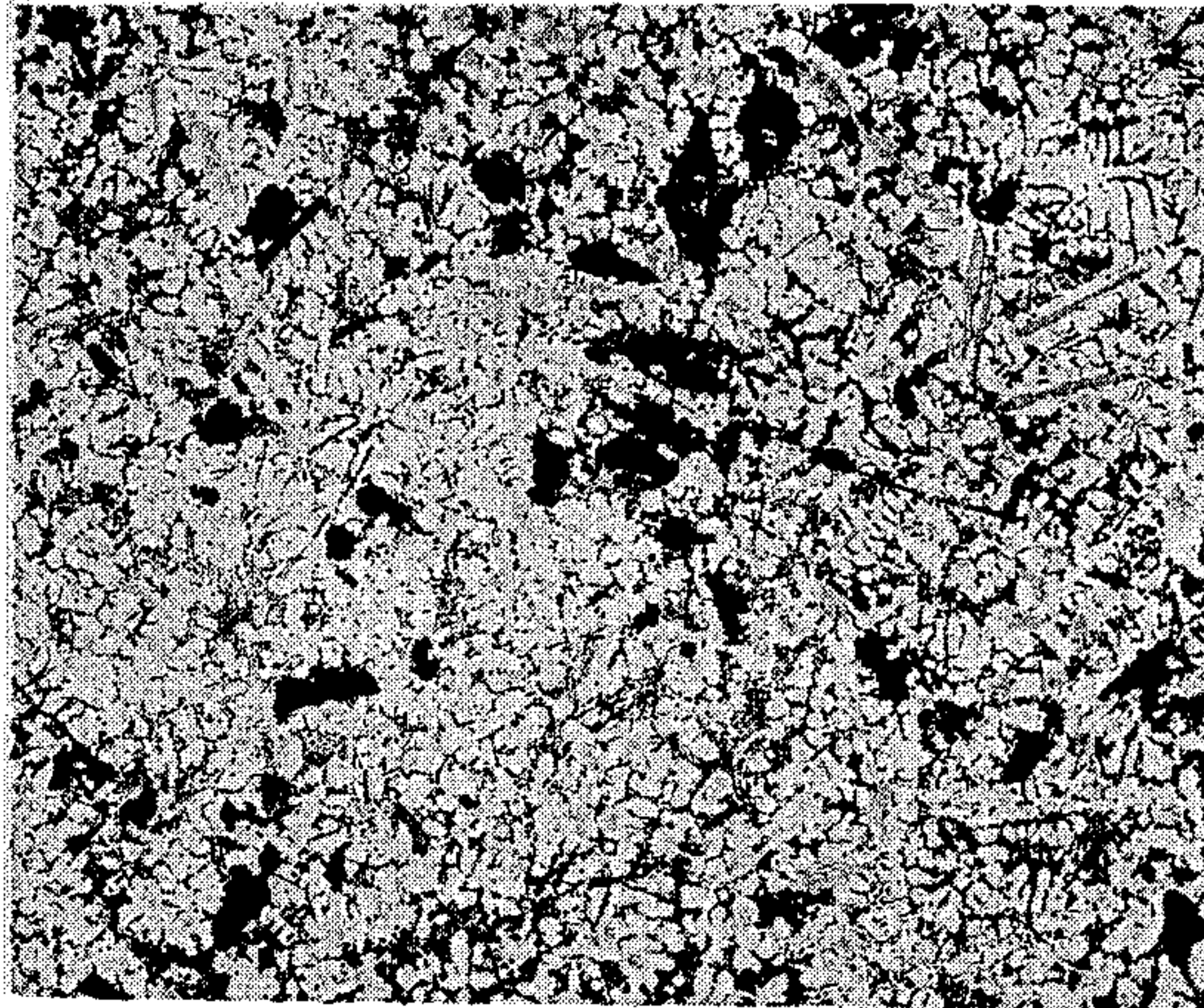


FIG. 2

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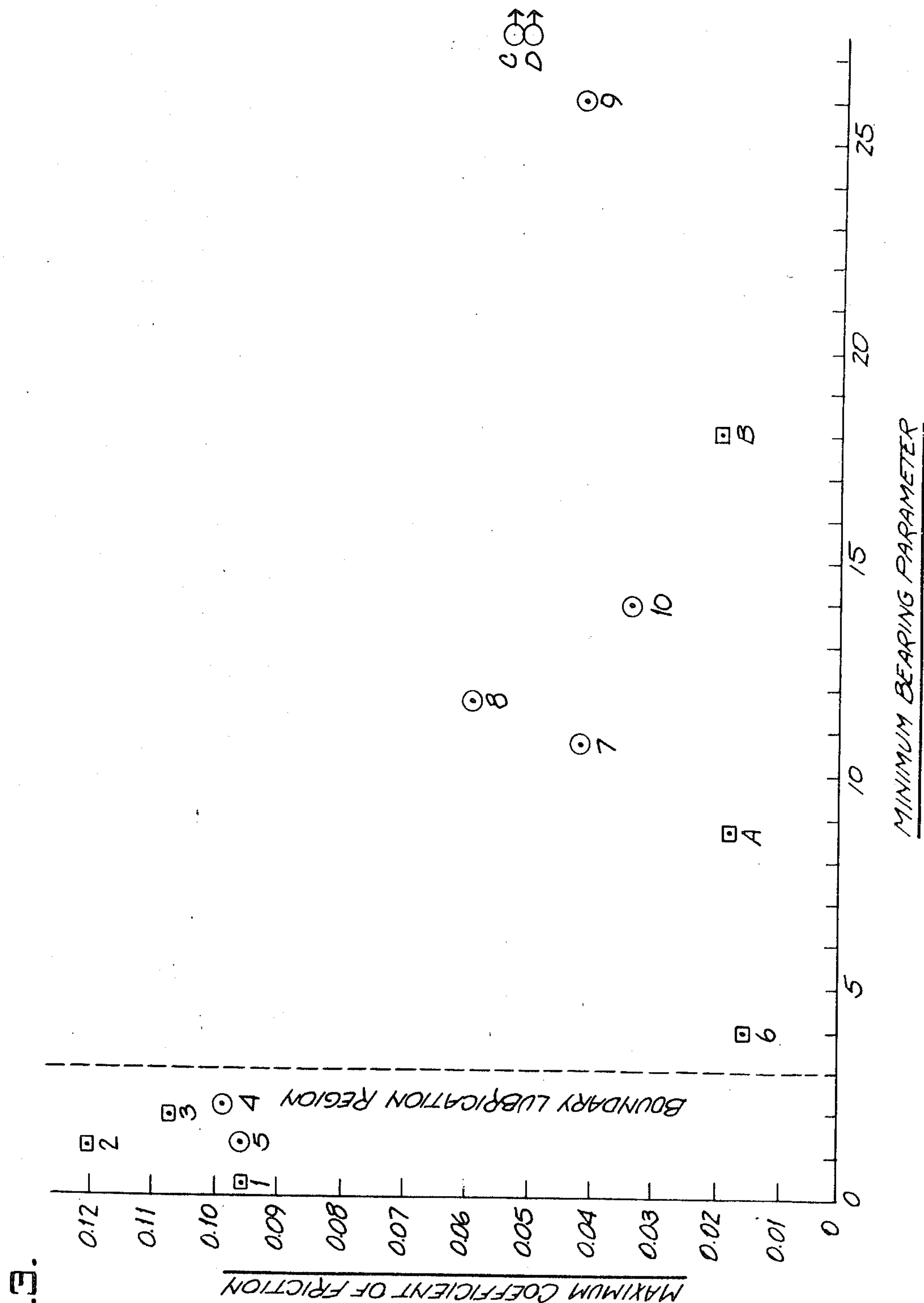
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PROCESS FOR PRODUCING AT LEAST ONE CONSTITUENT DISPERSED IN A METAL

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Continuation-in-part of application Ser. No. 644,429, May 25, 1967, which is a continuation-in-part of application Ser. No. 585,097, Oct. 7, 1966. This application Mar. 25, 1968, Ser. No. 715,937

Int. Cl. C22c 1/10

U.S. Cl. 75—135

33 Claims

ABSTRACT OF THE DISCLOSURE

Alloys containing at least one constituent dispersed in metal in which the constituent is normally insoluble or incompatible when the metal is in the molten state (e.g., graphite in aluminum), are produced utilizing melt processing in which the constituent in particulate form and having a coating, particularly metal, is injected into a molten bath of incompatible metal and the melt is thereafter solidified.

This application is a continuation-in-part of application Ser. No. 644,429, filed May 25, 1967, now abandoned which is a continuation-in-part of application Ser. No. 585,097, filed Oct. 7, 1966, now abandoned.

It is well recognized in the metallurgical art that various metals manifest any number of beneficial properties, properties often enhanced by alloying with other constituents. For example and by way of illustration only, aluminum has many desirable characteristics, e.g., light weight, resistance to the corrosive effects of many media and relatively high strength in relation to weight. However, experience in the prior art has shown that aluminum surfaces are quite susceptible to surface damage such as galling and scoring when subjected to sliding contact with other aluminum surfaces.

The frictional characteristics of aluminum and known aluminum alloys are such that aluminum articles cannot be used in self-mated sliding contact without maintaining therebetween a fluid film lubrication condition, a condition often impossible to maintain, particularly where contact pressures are high or sliding speeds are low. Therefore, where two articles are to be used in sliding contact with each other it has been necessary for most practical purposes to make one of the articles of a metal other than aluminum or to provide an interposing metal therebetween. For example, the skirts of aluminum pistons used in aluminum cylinder blocks have been plated with iron, chromium or tin or an iron liner has been provided in the cylinder. It perhaps should also be mentioned that a type of surface damage known as "cold scuffing" has been a major drawback to the use of aluminum pistons in aluminum cylinders without interposition of coatings or liners therebetween.

Now, graphite has been long known to be a good lubricant but the solubility thereof in molten or solid aluminum is practically nil, e.g., less than 0.05%. In view of this extreme lack of mutual solubility, these constituents are generally considered metallurgically incompatible in the sense that when graphitic carbon is mixed with molten aluminum it is rejected from the melt. This degree of incompatibility is strikingly emphasized by the fact that it is even difficult to contaminate aluminum with graphite, a point reflected by the commercial practice of using graphite boats in the zone refining of aluminum and of employing clay-graphite crucibles

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in melting aluminum alloys. At any rate, although a period of at least 50 years has been spanned since some of the earlier efforts were made to produce an alloy of aluminum and graphite using melt processing, no such alloy, insofar as we are aware, has ever been commercially produced which contained an appreciable amount of graphite, say, 0.5%, 0.6%, or more, and which significantly affected the frictional characteristics of the aluminum.

More recent attempts to provide aluminum materials having good frictional characteristics have been directed to powder metallurgical techniques in which sintered compacts are produced comprising mixtures of aluminum and carbon. Although a modest degree of success for limited purposes is sometimes achieved, such methods are not satisfactory in many instances in view of the high cost thereof, the metallurgical properties, e.g., strength or ductility, are not wholly satisfactory for wide application and many useful parts cannot be made due to complexity in design or to size and weight limitations. Thus, there has been a particular need for a cast aluminum alloy (with or without subsequent working) having improved frictional characteristics in combination with additional characteristics required for pistons in internal combustion engines, including toughness, ductility, and also high hardness, strength and abrasion resistance at room temperature and at elevated temperatures.

While the foregoing discussion is directed to the aluminum-graphite metallurgical system, other systems, in which one constituent is insoluble or cannot be dispersed as a practical matter, in a molten bath of a second are clearly contemplated in accordance herewith. For example, zinc and magnesium are also characterized by metallurgical incompatibility with graphitic carbon and it is desired to obtain lubricity and machinability benefits of graphite as a dispersoid in these metals. Illustrative of other incompatible environments contemplated are silicon carbide in nonferrous metals, e.g., aluminum, zinc or copper; diamond in metals such as aluminum and zinc; mica in such incompatible low melting point metals as zinc, lead, aluminum and magnesium; heavy oxides in lead; silica, magnesia, alumina and other oxides in metals such as copper and nickel; silica, magnesia and others in aluminum; etc.

Accordingly, it is an object of the invention to provide alloys having improved characteristics, the alloys having dispersed substantially throughout a constituent (dispersoid) normally incompatible with the base metal when the latter is in the molten condition.

A particular object is to provide aluminum alloy products characterized by improved resistance to scoring, galling and/or seizure when used in sliding contact against aluminum alloys under conditions of poor lubrication.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing in which:

FIGS. 1 and 2 are reproductions of photomicrographs (magnification 100 diameters), of etched sections of an aluminum alloy casting in accordance with the invention; and

FIG. 3 is a chart illustrating frictional characteristics of alloys both within and outside of the invention.

Generally speaking, the present invention contemplates production of compatible compositions of matter by a process comprising injecting particles of at least one constituent, e.g., graphite, in loose powder form into a molten bath predominantly of metal in which the constituent is, as a practical matter, insoluble, e.g., metal from the group consisting of aluminum, magnesium and zinc in the case of graphite, the constituent particles being characterized by coatings effective to impart com-

positional stability to the molten bath, and thereafter solidifying the resulting alloy with the constituent particles (dispersoids) distributed therein. The coating should act much in the manner of a barrier layer for a period sufficient to accomplish suitable introduction and dispersibility of the constituent particles throughout the bath. It is deemed that the coating coats to confer or, in effect, it contributes to imparting sufficient wettability between the otherwise incompatible materials such that dispersion one in the other is retained until solidification can be achieved. Thus the integrity of the coating should be substantially maintained while dispersing the particles within the melt.

In carrying the invention into practice, it is advantageous to propel or otherwise force the coated particles into the molten bath by gas pressure. Especially rapid and efficient injection and dispersion is achieved by propelling the particles in a non-reactive gas stream flowing through a conduit and exiting into the lower extremity of the melt, advantageously at the maximum depth of the melt. For example, the particles can be injected with an inert gas stream in a tube at a positive pressure of about 2 pounds per square inch (p.s.i.) to about 5 p.s.i.

It is believed that the nonreactive gas functions in the manner, inter alia, as a protective medium for the coatings up through at least the point of introducing the coated particles into the melt and for a period thereafter to enable the metal to be cast, since upon coming into contact with the melt the gas forms bubbles which in turn contain or envelop the coated particles. Inert gases, including nitrogen, argon, helium and other gases that are nonreactive with the particle coating and which are not detrimental to the bath metal at the injection temperature, can be used for the gas pressurized injection. Accordingly, particularly in respect of metal coatings, gases which would be oxidizing or chlorinating to the coating or bath metal during injection should generally be avoided. Gas pressure may also be provided by heating and volatilizing a gas-forming material. For instance, the coated particles may be introduced below the surface of the bath using a capsule containing a loose powder mixture of the coated particles and a nonreactive gas-forming agent which is rendered volatile by the heat of the bath to propel and disperse the particles in the bath metal.

In order to obtain and retain satisfactory uniform dispersion of the constituent particles, at least in the case of graphite, it is beneficial to control the temperature of the bath from about 200° F. to about 300° F. above the liquidus temperature thereof during and after injection. With graphite, for example, dispersion of coated particles throughout the bath is not consistently satisfactory if the injection temperature is excessively low, e.g., less than 100° F. above the bath metal liquidus. Detrimental segregation of the graphite particles often occurs with unfavorable rapidity if the bath temperature becomes excessively high, e.g., more than 450° F. above the liquidus.

Most advantageously the constituent particles are metal coated. And in this connection, such coatings have exterior surfaces which are essentially metal, i.e., are in the metallic condition characterized by being essentially uncombined metal and essentially devoid of oxides or other compounds, and are effective to provide sufficient compositional stability to the molten metal or alloy containing the constituent particles to enable producing a casting of satisfactory particle or dispersoid distribution. The coated particles must be injected below the surface of the bath with sufficient positive pressure, i.e., pressure above atmospheric pressure, to penetrate the bath metal and any surface film thereon and to overcome the static pressure of the molten metal at the depth of the injection. As mentioned above, the integrity of the coatings must be maintained to successfully introduce and disperse the normally incompatible constituent. After injection, the coatings become partially or even wholly dissolved or otherwise incorporated in the molten bath and in certain

advantageous embodiments ultimately impart enhanced, useful characteristics. Beneficially, the alloy is chill cast, e.g., permanent mold cast or die cast, or is similarly rapidly solidified such as in the continuous casting of ingot stock that is continuously solidified and withdrawn from the mold.

For best results, i.e., in striving for the maximum percentage of retained particles in the melt and final product based upon the amount of particles added, the coatings on the particles should be completely continuous over the entire surface of each particle. While, for practical purposes, the coatings need not be entirely perfect, it is to be emphasized that in this connection the particles must be substantially surrounded by the coatings, e.g., coatings over at least 90%, advantageously 95%, of the surface of the particle. Experience has shown that agglomerations or combinations of metal and graphite, for example, which do not have substantially continuous metal coatings over the particles are not effective for successful practice of the invention, inasmuch as retention of the particle in the melt is not satisfactory if the coating does not cover at least about 80% of the surface area of the particle, i.e., though the invention might be carried out the percentage of graphite retained in the melt becomes unnecessarily and undesirably lower than when the coating covers a greater amount of surface area.

Coatings, particularly metal, about 0.2 to about 50 microns thick applied by known methods, including vapor or chemical deposition, e.g., nickel deposition from the decomposition of nickel carbonyl, deposition of copper by galvanic or other chemical methods, etc., are particularly satisfactory. Coating thickness should be at least about 2 microns to insure the particle is essentially covered. To avoid introducing excessive amounts of coatings the thickness is preferably not greater than about 5 microns; however, thickness is not as important as the requirement that the coating cover essentially the entire particle and satisfactory results may be obtained with thicknesses of as little as 0.05 micron. Particularly good results have been obtained with nickel-coated graphite powder such as nickel-coated graphite comprising about 75% nickel and 25% carbon with average particle size about 80 microns. Metal coatings may also comprise, or consist essentially of, in addition to nickel, copper, cobalt, iron aluminum or zinc and alloys thereof.

Particles injected in accordance herewith are preferably at least about 40 microns in average cross-section size, particularly in the case of graphite. With respect to graphite, excellent results, however, have been and can be attained with smaller particle sizes, say, a mean particle size of about 20 microns, but it is deemed easier to coat larger particle sizes and this should contribute to some extent to the ease of achieving a substantially continuous coating about the graphite particles. Moreover, ease of mechanically handling the particles is facilitated through larger particle size, and there is also the built-in virtue of minimizing flowability difficulties that might otherwise possibly ensue should extremely fine particle sizes (e.g., sub-micron) be used.

Particle size advantageously should not exceed about 200 microns, inasmuch as larger particles may tend to segregate too rapidly. With respect to graphite particularly, especially good recovery and uniform dispersion obtains with an average particle size of about 40 or 60 to 120 microns. In some exceptional instances, if solidification can be brought about very quickly after injection, e.g., in about 3 to about 30 seconds, satisfactory results can be obtained with particles as large as 2000 microns.

Accordingly, and while mean particle sizes down to 10 or 5 microns or even much finer can be used and though on occasion particle sizes up to 2000 microns can be employed, for the production of dispersoid-containing metal castings, such as those containing graphitic carbon, the particles should be of sizes which average about 40 to about 200 microns. It should also be mentioned that

fluidity for producing castings is benefited by having, at least in the case of graphite, particles of generally equiaxed configurations, e.g., relatively spheroidal or lump-like and thus not acicular or flake-like.

For obtaining particularly good results, the graphitic aluminum should contain at least 0.6% graphite, advantageously at least about 1.2% graphite, in order to have satisfactory frictional characteristics under conditions of poor lubrication, such as the mixed film condition where the fluid film partially breaks, and to be slidably operable to a substantial extent in the boundary lubrication region. For toughness and good fluidity, the graphite content should be controlled to be not greater than 5% and advantageously not higher than 2.5%.

For the purpose of giving those skilled in the art a better understanding of the invention the following illustrative examples are given:

EXAMPLE I

A molten bath was established of an aluminum-base alloy which contained 9.26% silicon, 2.94% copper, 1.11% magnesium, 0.24% iron, 0.01% manganese, 0.02% zinc, 0.12% titanium, 0.01% nickel, less than 0.005% carbon and balance aluminum. Nickel-coated graphite particles were introduced into the bath in a stream of nitrogen gas while the bath was maintained at a temperature of about 1400° F., which was about 300° F. above the liquidus temperature. The average particle size (including coating, which was about 2 microns thick) was about 80 microns with essentially all of the particles fine enough to pass through a number U.S. Series 100 screen. (Screen size mesh numbers hereinafter are U.S. Series Equivalent numbers.) Actually, a considerable amount of the coated powder passed through a 325 mesh screen and the average particle size 80 is a numeral representing the approximate average of the largest (about 149 microns) and smallest (on the order of, say, one micron to a few microns) particles.

The particles were introduced into the melt from a batch feeder assembly comprising a gas pressurized hopper with a valve at the bottom of the hopper for regulating flow from the hopper, a steel tube connected to the valve exit and leading downward from the hopper, and a graphite nozzle attached at the lower end of the tube. Nitrogen was provided from a pressurized cylinder connected to the feeder assembly by two conduits, with one of the conduits leading from the cylinder into the hopper, thereby pressurizing the hopper, and with the second conduit leading into the steel tube below the hopper. The graphite nozzle extended below the surface of the bath into the lower extremity of the melt and directed the flow of nitrogen and nickel-coated particles toward the bottom of the bath. Injection was successfully accomplished with a positive pressure of about 2 p.s.i. The weight of particles introduced into the bath was about 10% of the initial weight of the bath. Dispersion and retention of the particles in the bath metal were very satisfactory and at least about 90% of the graphite particles were retained in the melt. After introduction of the nickel coated graphite particles, the bath metal was cast (Alloy 1) at a pouring temperature of about 1400° F. into iron chill molds for cast rods and other castings. Metallographic examination confirmed that the castings contained a great number of graphite particles dispersed uniformly throughout the matrix.

The chemical composition of Alloy 1 is set forth in Table I along with the chemical compositions of Alloys 2-12, which were also prepared in the manner of Alloy 1. In preparing Alloys 2 through 6, 9, 11 and 12, the nickel coatings were about 2 microns average thickness, whereas for 7, 8 and 10 the coatings were about 15, 50 and 30 microns, respectively, in average thickness. Chill mold castings containing graphite dispersed with satisfactory uniformity were thus produced, although the recovery of graphite in Alloy 10 (made with, for graphite, undesir-

ably large particles of 400 microns size) was only marginally acceptable. The extent, if any, to which the nickel coatings remained on the particles of Alloys 1 to 12 could not be determined. Optical and electron micrographic examination did not disclose any nickel coating around the graphite particles in the solidified alloys.

TABLE I

Alloy No.	Percent							Graphite size ²
	C ¹	Ni	Cu	Si	Mg	Fe	Al	
1-----	1.80	6.3	2.4	8.1	1	0.23	Bal. ³	80
2-----	1.88	5.4	2.7	12.4	1	0.28	Bal---	80
3-----	1.42	4.9	2.4	9.8	1	0.88	Bal---	80
4-----	0.66	4.24	0.47	9.9	0.3	0.61	Bal---	60
5-----	0.72	5.14	0.43	10.0	0.3	0.66	Bal---	120
6-----	0.26	4.6	2.6	7.8	1	0.26	Bal---	80
7-----	0.55	4.19	0.47	10.6	0.3	0.65	Bal---	200
8-----	0.26	5.14	0.43	9.2	0.3	0.63	Bal---	200
9-----	0.11	4.25	0.48	9.9	0.3	0.60	Bal---	<40
10-----	0.08	4.72	0.46	9.9	0.3	0.66	Bal---	400
11 ⁴ -----	0.9	6.0	0.5	11.5	0.4	0.6	Bal---	<40
12 ⁴ -----	1.12	2.0	0.5	11.5	0.4	0.6	Bal---	<40

¹ C=percent graphitic carbon.

² Graphite size=The numeral 60 refers to particles which passed through a 200 mesh screen (opening about 74 microns) but retained by a 325 mesh screen (opening about 44 microns), and is thus a representative approximate average of the largest and smallest of such particles. Determined in the same manner, the numeral 120 denotes particles passing through a 100 mesh (opening about 149 microns) but retained by a 200 mesh (opening about 74 microns); the numeral 200 depicts particles passing through a 60 mesh (opening about 250 microns) and retained by an 80 mesh (opening about 177 microns); and the numeral 400 refers to particles passing through a 40 mesh (opening about 420 microns) but retained by a 45 mesh (opening about 350 microns). The numeral 80 sets forth a particle size as previously described in connection with Example I. And the symbol <40 indicates that the particles all passed through a 325 mesh screen (opening about 44 microns) and the approximate average particle size as determined in accordance with the above would be approximately 20 microns.

³ Bal.=Balance essentially.

⁴ Nominal composition except for graphitic carbon content.

Uniform dispersions of graphite particles in accordance with the invention are illustrated in FIGS. 1 and 2 by microstructures from a 7-inch long, 2-inch diameter chill cast bar of Alloy 3 cast in the vertical position. FIG. 1 was taken from a section of the bar which was near the top during casting and solidification, FIG. 2 being taken from near the bottom. Accordingly, microstructures from the same casting at cross sections separated by a vertical distance of about 6 inches show that the graphite particles remained uniformly dispersed and did not detrimentally segregate by floating, sinking, agglomeration or otherwise. FIGS. 1 and 2 also reflect the effectiveness of the nickel coatings in providing sufficient compositional stability to the molten alloy to enable casting and statically solidifying the alloy to thereby produce castings of a uniform graphitic alloy composition.

Nickel-coated graphite particles were also successfully injected with nitrogen into a molten bath containing about 6.5% tin, the balance being essentially aluminum. Metallographic examination showed a high recovery of uniformly distributed graphite.

The success of preparing graphitic aluminum using copper-coated particles was demonstrated with particles containing about 75% copper and about 25% graphite. Thus, using the batch feeder assembly and with the melt temperature at about 1300° F. to 1350° F., graphite particles having 2-micron thick copper coatings were injected in a nitrogen gas stream into a melt containing about 11.5% silicon, less than 0.005% carbon and balance essentially aluminum along with the nominal amounts of about 0.6% iron, about 0.5% copper and about 0.3% magnesium that are generally present in this type of alloy. Graphite particle size ranged from about 75 to 150 microns (passed through a 100 mesh screen but retained on a 200 mesh screen). Rate of injection was about 0.03 pound per minute and the weight of the injected powder was about 10% of the initial weight of the melt. The alloy was cast at about 1250° F. into chill molds. Graphite particles were dispersed satisfactorily and the alloy contained 4.7% copper and 0.69% graphitic carbon.

In an earlier and similarly conducted run, copper-coated particles from a different batch of powder resulted

in the retention of about 0.06% graphitic carbon. Upon examination of other copper-coated particles from this batch of powder it was determined that a goodly percentage of the graphite particles did not have proper copper coatings, i.e., the surface areas of the graphite were not substantially enveloped by the copper as required herein. It is deemed that the greater quantity of graphite particles having acceptable copper coatings was largely responsible for the greater percentage (0.69% vs. 0.06%) of retained graphite.

Nickel-coated graphite particles (as described in Example I) and comprising about 75% nickel were also injected in a nitrogen gas stream into a melt containing about 4% aluminum and balance essentially zinc at about 1100° F. Microexamination of vertical cross sections of the castings showed a high recovery and uniform distribution of graphite. No sign of any nickel coating was observed around the graphite particles. Chemical analysis revealed that the alloy contained 1.15% graphitic carbon, 3.25% nickel and 4.16% aluminum. Similarly, metal-coated graphite particles can be injected in the same manner into other known zinc alloys, including alloys containing up to about 30% aluminum, up to about 4% copper, up to about 0.4% lead, up to about 0.3% cadmium, up to about 0.5% magnesium and balance essentially zinc.

Graphitic magnesium alloys containing 0.05% or more graphite can also be produced in accordance with the invention by gas injection of metal-coated graphite into molten magnesium baths containing up to 10% aluminum, up to 6% zinc, up to 4% rare earth metals, up to 3.3% thorium and up to 0.75% zirconium.

With regard to gases other than nitrogen, argon was used in injecting nickel-coated graphite particles (of the type used in Example I) through a tube into an aluminum-11.5% silicon alloy bath at about 1350° F. Chemical analysis indicated that the alloy contained 1.4% graphite and 4.65% nickel. Graphite recovery was about 70%, which was of the order of good recoveries, e.g., 70% to 90%, frequently obtained using nitrogen in otherwise similar injection processes.

Use of highly chlorinating or oxidizing gases are generally avoided in order to avoid less satisfactory recoveries of graphite. For example, when a mixture of about 80% nitrogen and 20% chlorine was used for injecting nickel-coated graphite particles into aluminum, the graphite recovery was only about half the recovery that should have been obtained if essentially pure nitrogen were used.

Using prior art teachings, even in combination with "some" of the concepts of the subject invention, the phenomenon concerning graphite incompatible metallurgical environments has again been confirmed. To explain, when graphite particles averaging approximately 80 microns but which did not have coatings were injected into an aluminum-11.5% silicon alloy by using the batch feeder assembly and the techniques described hereinbefore the uncoated graphite particles were rejected by the bath metal in a mist emanating from the bath. Chemical analysis showed the alloy contained less than 0.01% carbon.

Even increasing the proportion of uncoated graphite injected to as high as 300% to 400% of that utilized in producing Alloys 1 to 12 did not provide a panacea. Thus, attempts to incorporate uncoated graphite particles, using particles of four different sizes (approximate average), namely, 10, 35, 200 and 300 microns, into a molten aluminum-11.5% silicon alloy (which alloy also contained incidental amounts of magnesium, copper, etc.) by injection techniques that were successful for injecting metal-coated particles resulted, comparatively speaking, in practically total rejection of the uncoated graphite. In each test, natural flake graphite was injected at a temperature of about 1350° F. in a nitrogen stream, the amount of graphite injected being about 8% (as compared with about 2% in Example I). Mere visual inspection quickly indicated that the graphite was rejected and

upon analysis the percentages of retained graphite were found to be 0.03%, 0.01%, 0.02% and 0.02%, respectively.

In other approaches the use of a much higher bath temperature failed to afford satisfactory results. Thus, injection of uncoated graphite particles about 80 microns in average size into molten commercially pure aluminum, the temperature being maintained at about 2000° F., resulted in a rejection (loss) of 99.9% of the graphite. The percentage of graphite was still further increased to 10%; nonetheless, only 0.01% was retained.

Retention of graphite was also unsatisfactorily low or negligible even when graphite particles were nickel-coated, i.e., the same type injected to make Alloys 1, 2 and 3, and then mixed by mechanically stirring (a practice advanced in the prior art) the particles into induction melts of aluminum-silicon alloys under atmospheres of air, nitrogen or argon. Failure was again experienced when nickel-coated graphite particles were wrapped in aluminum foil (with air entrapped within) and plunged into an aluminum-silicon alloy melt. In this regard, the air did not function as a nonreactive gas-forming agent which would volatilize under the heat of the melt to propel and disperse the particles within the bath. Very poor results with high rejection of the particles were obtained when another portion of the 80-micron graphite particles described in connection with Example I but having oxidized nickel coatings were injected with nitrogen into an induction melt of a molten aluminum alloy containing about 9.5% silicon, 3% copper, 1% magnesium and the balance substantially aluminum.

Good compositional stability of graphitic aluminum prepared by injection of nickel-coated graphite in accordance herewith was exemplified by chill casting fourteen automotive pistons from a melt of molten graphitic aluminum. After injection, molten metal for each piston was tapped and hand ladled to the mold as a separate operation, with stirring or skimming before each tap, so that the period while the metal was held in the furnace, tapped, ladled and cast covered about 40 minutes. (As indicated above herein, and in accordance with the invention, graphite dispersion in a melt is very good; however, particularly in dealing with large size melts, stirring is deemed beneficial in maintaining such graphite distribution.) The alloy was a commercial type nominally containing 9.5% silicon, 3.5% copper, 1% magnesium, the balance being aluminum. Chemical analysis of the pistons reflected that each contained at least 1.25% graphite. Using a conventional permanent mold, an aluminum piston containing 3.89% graphite has been successfully cast and thereafter readily machined without difficulty.

Graphitic aluminum castings made by the process of the invention have also been induction melted, stirred and recast without excessive loss of graphite, thereby demonstrating that for commercial purposes, master alloys or scrap castings, gates, risers, etc., can be used as melting stock for making graphitic aluminum cast articles and other products. Good compositional and microstructural stability at room temperature and elevated temperatures is another favorable attribute of the alloy.

To further illustrate the invention, Alloys 1-10 were chill cast and wear tested using a Hohman tester. In this test circular discs were rotated in contact with shoe specimens having concave surfaces which mated with the peripheral surfaces of the disc specimens. During test, the specimens were submerged in lubricating mineral oil (Aturbrio). The testing cycle, except when specimens galled so greatly that binding caused rotation to cease and necessitated discontinuance of the test, was to rotate the specimens at 830 revolutions per minute (r.p.m.) and to increase the bearing pressure in steps until the pressure forcing the mating surfaces together reached a maximum level of 2480 p.s.i. When the maximum bearing pressure was reached, the rotational speed was decreased (without decreasing the load) in steps until rotation ceased due to

binding or else, if galling did not occur, until the heat and friction increased to about the limiting capacity of the test apparatus.

A bearing parameter,

$$B = \frac{ZN}{P}$$

where Z is the oil viscosity in centipoises, N is the rotation speed in r.p.m. and P is the pressure in p.s.i. at the mating surface, was used as an index of lubrication conditions at the mating surfaces of the specimens. Inasmuch as the bearing parameter is inversely proportional to the pressure, which increases during test, and is directly proportional to the viscosity and the speed, which decrease during test, the specimens were subjected to progressively deteriorating lubricating conditions during test.

One characteristic evaluated was resistance to seizure (due to galling) under conditions of poor lubrication, e.g., mixed lubrication or boundary lubrication, conditions where some breakdown of the lubricating oil film occurs. Alloys which did not seize at relatively low bearing parameters are characterized by good galling resistance superior to that of alloys which seized at relatively high bearing parameters.

As a further part of the overall wear test, the maximum coefficient of friction at which sliding contact operation was successfully maintained during test, i.e., the maximum coefficient of friction prior to seizure (if seizure occurred) was determined. High maximum friction coefficients (Max. Mu) show good frictional characteristics and vice versa. In general, where high Max. Mu coefficients of 0.07 or greater were obtained, the alloys were satisfactory under boundary lubrication. If less than 0.07, the alloy failed to reach a boundary lubrication condition characterized by a bearing parameter not greater than 3.0 and could be operated only in mixed or full film lubrication.

Results of the Hohman tests are set forth in Table II. Except for Alloys 2 and 3, the bearing shoes were made from chill castings of an alloy which is commercially used in cast cylinder blocks for internal combustion engines and nominally contains about 12% silicon, less than 0.005% carbon with the balance being aluminum. As to Alloys 2 and 3, the shoes were made of the same alloy as the rotating disc. The lubricating oil for the aluminum-silicon alloy shoes was a No. 50 oil having a viscosity of 29 centipoises at 100° F. and the oil for the selfmated tests was a No. 60 oil having a viscosity of 60 centipoises at 100° F. The numbers in the columns "Average Max. Mu." and "Average Min. B" in Table II show the average values of the highest friction coefficients and the lowest values of the bearing parameter, respectively, that were reached at the finish of each test.

TABLE II

Disc alloy	Number of tests	Average max. mu	Average min. B
1.-----	3	0.096	¹ 0.27
2.-----	4	0.121	¹ 1.10
3.-----	5	0.107	1.82
4.-----	3	0.098	2.03
5.-----	3	0.096	1.3
6.-----	2	0.016	4.00
7.-----	3	0.042	10.6
8.-----	3	0.060	11.9
9.-----	3	0.044	26.0
10.-----	3	0.034	14.0

¹ No galling.

Table II, shows that Alloys 1 through 5, which contained at least 0.6% graphite, were operable up to and into boundary lubrication conditions characterized by a combination of a high coefficient of friction of at least 0.07 and a low bearing parameter not greater than 3.0. Alloys 1 and 2, containing at least 1.8% graphite were slidably operable and resisted galling and seizure under severe boundary lubrication conditions characterized by very high friction coefficients of at least about 0.09 in combination with very low bearing parameters not ex-

ceeding about 1.5. In contrast, alloys which did not contain as much as 0.6% graphite all failed to resist galling and seizure when subjected to lubrication conditions which were not as severe as the boundary lubrication conditions endured by Alloys 1 through 5.

The test results in Table II are plotted, for convenience, in FIG. 3. It is evident that Alloys 1 through 5 are all in the area where the friction coefficient is at least 0.07 and the bearing parameter is up to 3.0, whereas the plots for the alloys with lesser amounts of graphite fall at points very remote therefrom.

Hohman tests of greater severity, wherein the bearing load was increased to a maximum of about 3000 p.s.i., were performed with specimens of Alloys 11 and 12 mated against aluminum-silicon alloy shoes and using Aturbrio 50 oil. Both alloys operated successfully into the boundary lubrication region and resisted galling until very low bearing parameters of 0.75 with Alloy 11 and 0.47 with Alloy 12 were reached, the maximum coefficients of friction obtained at galling being 0.110 and 0.099, respectively.

As indicated herein, incompatible systems include those in which a constituent is insoluble in alloys as well as the base metals which might form the alloys. Thus, by way of illustration, in respect of the graphite-aluminum system, aluminum bath metals include not only pure aluminum (both commercially pure and high purity) but also aluminum alloys containing, in addition to a major proportion of aluminum, up to about 25% silicon, up to about 25% tin, up to about 15% copper, up to about 15% magnesium, up to about 20% zinc, up to about 10% nickel, up to about 8% cobalt, up to about 5% manganese, up to about 1% chromium and up to about 1.5% iron. Such alloys preferably contain at least 5%, e.g. at least 8%, silicon to promote uniform distribution of graphite in the melt and to avoid detrimental segregation of graphite during solidification. For good toughness and wear resistant characteristics, from 5% to 16%, say, 8% to 13%, silicon is beneficial. However, the silicon should be controlled in relation to any nickel so that the total percentage thereof does not exceed about 20% in order to avoid alloy embrittlement. Small amounts of optional elements, e.g., titanium, boron, zirconium, vanadium, antimony and cadmium, may be included for purposes such as grain refinement, strengthening, raising the recrystallization temperature, improving weldability, etc. (The amount by weight of aluminum in an aluminum-base alloy herein is greater than that of any other element. This applies to other alloy base metals as well.)

Of course, in formulating alloy compositions within the invention, the amount and nature of coating metal is taken into account. Up to 10% nickel, e.g., 0.05% to 10% nickel, can be added and is particularly advantageous for producing graphitic aluminum alloys since it melts, dissolves or is otherwise incorporated into the alloy, e.g., as a nickel aluminide, and provides, especially in amounts of at least 4%, e.g., 4% to 7%, hardness, strength and wear resistance at room temperature and at elevated temperatures, and high retention and uniform distribution of the graphite particles.

With specific reference to graphitic alloys, beneficial improvements in frictional and/or machinability characteristics of metals such as aluminum, zinc or magnesium are obtainable through utilizing the process of the invention to incorporate graphite in amounts of at least 0.2%, and upwards to 5%, 10% or even 15% or more in these metals. While improvement is obtainable with as little as 0.05% graphite, the characteristics of such alloys are greatly less desirable. Accordingly, it is of considerable benefit to have substantially greater amounts of graphite, e.g., at least 0.2%, or, more advantageously, at least 0.6% or 1.8% dispersed throughout the matrix metal. An especially advantageous alloy contains about 1.2% to about 2.5% graphitic carbon, about 4% to about 7% nickel, about 8% to about 13% silicon, up

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to 4% copper, e.g., 0.5% to 4% copper, up to 1.2% magnesium, e.g., 0.3% to 1.2% magnesium, up to 0.6% iron, the balance essentially aluminum and possesses, when in the chill cast condition, gall and heat resistant characteristics particularly well suited for sliding contact elements in internal combustion engines, e.g., pistons.

As will be appreciated by those skilled in the art, in the selection of the two or more incompatible materials, the constituent to be injected into the molten bath of the dispersion medium, should not be one which decomposes at the bath temperature. In addition to the incompatible systems enumerated hereinbefore, i.e., graphite in aluminum, zinc and magnesium; mica in zinc, lead aluminum and magnesium; diamond in aluminum and zinc, etc., it is contemplated that the constituent to be dispersed can be selected from the group consisting of oxides, carbides, nitrides and borides. Molybdenum disulfide would be another such constituent, particularly for lubricity qualities. Various intermetallic compounds are also contemplated. Too, among other coatings that might be used, in addition to those previously given herein, and this depends, of course, upon what might be desired in the final product, are silicon, tin, cadmium, antimony, chromium and tungsten.

As to graphite specifically, while the foregoing discussion has centered about producing graphitic alloys of aluminum, zinc or magnesium, particularly aluminum, the invention contemplates injecting coated graphite into other molten bath metals in which graphite is virtually insoluble or otherwise metallurgically incompatible, including copper and copper-base alloys, advantageously brass and bronze, lead alloys and tin alloys.

As a practical matter, in dealing with various incompatible systems the densities of the respective incompatible constituents should be such that one does not exceed the other by a factor of about three; otherwise, there is the possibility of encountering immediate or rapid segregation as by sinking or floating. Advantageously, the difference in respective densities should not exceed a factor of two. Incompatible systems include those in which the mutual insolubility obtains and there is nonreactivity at temperatures up to several hundred degrees above the melting point of the dispersion medium.

The subject invention is particularly applicable in the production of graphitic alloys for sliding contact elements including pistons, bearings, cylinder liners and blocks, sliding valves, internal combustion engine rotors, electrical pick-up shoes, etc. The invention is also applicable to the production of wrought articles including rods, bars, tubes, plates, etc., made by working cast, including continuously cast, graphitic alloys provided herein. For example, a graphitic aluminum alloys containing 0.51% carbon and 4.1% nickel was hot forged, hot rolled, cold rolled into rod and thereafter cold drawn to produce wire. Furthermore, the new graphitic alloy, particularly of aluminum, is useful for providing wear and/or gall resistant surface claddings or overlays, e.g., welded overlays, on composite articles.

Graphitic alloys of the present invention are not to be confused with carbide alloys which contain carbon in combined form, e.g., carbides such as molybdenum carbide or tungsten carbide, rather than in uncombined graphitic form.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for producing a graphitic alloy, the alloy being characterized by a retained graphite content of at least about 0.2%, which comprises providing a molten

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bath predominantly of metal selected from the group consisting of aluminum, magnesium and zinc, injecting under positive pressure into the bath graphite particles of average particle sizes of about 40 microns to about 2000 microns and having surrounding metal coatings effective to impart compositional stability to the molten alloy containing the particles and thereby provide retention of the particles in the bath, pouring molten metal from said bath having retained graphite particles into a mold and thereafter solidifying said metal to provide a graphitic alloy casting.

2. A process as set forth in claim 1 wherein the amount of retained graphite is at least 0.6%.

3. A process as set forth in claim 1 wherein the molten bath is predominantly aluminum.

4. A process as set forth in claim 1 wherein the molten bath is predominantly zinc.

5. A process as set forth in claim 1 wherein the molten bath is an aluminum-base alloy containing about 5% to 25% silicon.

6. A process as set forth in claim 1 wherein the particle coatings are of metal selected from the group consisting of nickel, copper, cobalt, iron, aluminum, zinc and alloys thereof.

7. A process as set forth in claim 1 wherein the particles have coatings consisting essentially of nickel.

8. A process as set forth in claim 1 wherein the particles have coatings consisting essentially of copper.

9. A process as set forth in claim 1 wherein the graphite particles are about 40 microns to about 200 microns in average cross section size.

10. A process as set forth in claim 1 wherein the metal coatings on the particles are 0.2 micron to about 50 microns in thickness.

11. A process as set forth in claim 1 wherein the particles are injected in a nonreactive gas stream.

12. A process as set forth in claim 11 wherein the gas is nitrogen.

13. A process as set forth in claim 11 wherein the gas is argon.

14. A process as set forth in claim 1 wherein the alloy is continuously cast and at least partially solidified in a chill mold and is continuously withdrawn from the mold.

15. A process for producing a solidified graphitic alloy comprising providing a molten metal bath predominantly of a metal selected from the group consisting of aluminum, magnesium and zinc at a temperature about 100° F. to about 450° F. above the liquidus temperature of the bath metal, injecting into said bath nickel-coated graphite particles of average particle sizes from about 40 microns to about 200 microns having surrounding metal coatings about 0.2 micron to about 50 microns in thickness and having exterior surfaces in the essentially metallic condition by flowing said particles in a nonreactive gas stream through a tubular conduit exiting below the surface of the bath while maintaining said exterior surfaces in the metallic condition at least until the coated particles are in the bath metal, pouring from said bath molten metal having said injected particles retained therein into a mold and thereafter solidifying the metal to provide a graphitic alloy casting.

16. A process for producing a graphitic alloy comprising providing a molten bath predominantly of metal characterized by metallurgical incompatibility with graphite, injecting under positive pressure into the bath graphite particles of average particle sizes of about 40 microns to about 2000 microns and having surrounding metal coatings effective to impart compositional stability to the molten alloy containing the particles and thereby provide retention of the particles in the bath, pouring molten metal from said bath having retained graphite particles into a mold and thereafter solidifying said metal to provide a graphitic alloy casting.

17. A process for producing an alloy containing graphitic carbon and at least one metal normally charac-

terized in the molten condition by metallurgical incompatibility therewith which comprises, establishing a molten bath predominantly of graphitic incompatible metal, injecting below the surface of the molten bath graphite particles the surface areas of which are substantially enveloped by coatings of essentially uncombined metal devoid of detrimental oxides, said coated particles being injected under positive pressure while substantially maintaining the metallic condition of the metal coating until introduced into the molten bath, and thereafter solidifying the molten metal whereby a graphitic alloy characterized by a significant percentage of retained graphite is produced.

18. A process utilizing melt processing techniques to greatly overcome the drawbacks in respect of the insolubility of graphite in metal by reason of the metal being in the molten condition and from which graphite is normally rejected whereby (a) an alloy system of metallurgical stability and compatibility is achieved rather than one of mutual incompatibility and (b) an alloy of comparatively high graphitic carbon content and enhanced frictional properties is attained as opposed to a relatively graphiteless alloy of inferior frictional characteristics, which comprises, establishing a molten bath containing at least one metal in which graphitic carbon is ordinarily virtually insoluble, achieving a graphitic alloy condition of substantial compositional stability by injecting metal coated graphite particles below the surface of the molten bath under positive pressure and in a gaseous stream substantially innocuous in respect to both the metal coatings and molten metal, said metal coatings enveloping at least 80% of the surface areas of the graphitic particles and being of essentially uncombined metal devoid of detrimental oxides, the overall particle size (graphite plus coating) being not greater than about 400 microns, and thereafter solidifying the molten metal.

19. A process for producing a composition of matter containing at least one constituent dispersed in metal normally characterized in the molten condition by metallurgical incompatibility therewith which comprises, establishing a molten bath predominantly of such metal, introducing into and dispersing within the molten bath said constituent in particulate form by injecting such particles under positive pressure below the surface of the molten bath, said particles being characterized in that the outer surface areas thereof are substantially enveloped by a coating effective to impart substantial compositional stability between the molten metal and particles, the integrity of the coating being maintained during injection for a period sufficient to achieve dispersibility and retention of the particles throughout the melt, and thereafter solidifying the molten bath.

20. A process for producing a dispersoid composition of matter having a matrix of dispersant metal and containing dispersoid particles normally characterized by metallurgical incompatibility therewith when the metal is in the molten state which comprises, establishing a molten bath predominantly of such metal, introducing into and dispersing within the molten bath particles of an incompatible material selected from the group consisting of graphite, oxides, carbides, nitrides, and borides by injecting the particles under positive pressure below the surface of the molten bath, said particles being characterized in that the exterior surface areas thereof are substantially enveloped by coatings of essentially uncom-

bined metal effective to impart substantial compositional stability between the molten metal and particles, the integrity of the coating being maintained during injection for a period sufficient to achieve dispersibility and retention of the particles throughout the melt and thereafter solidifying the molten bath.

21. A process for producing a composition of matter containing at least one constituent dispersed in a metal normally characterized in the molten condition by metallurgical incompatibility therewith which comprises introducing under positive pressure and dispersing particles of the constituent material within a molten bath containing said metal, the particles being characterized in that the outer surfaces thereof are substantially enveloped by a coating sufficient to impart compositional stability between the molten metal and the constituent particles, said coated particles being introduced while maintaining the integrity of the coatings for a period sufficient such that the ability of the coating to confer compositional stability is not detrimentally impaired and thereafter solidifying the molten bath.

22. A process in accordance with claim 21 in which the coating is metal.

23. A process in accordance with claim 22 in which the incompatible materials are graphite and aluminum.

24. A process in accordance with claim 23 in which the metal coating is from the group consisting of nickel, copper, cobalt, iron, aluminum and zinc and alloys thereof.

25. A process in accordance with claim 24 in which the metal coating is from the group consisting of nickel and copper.

26. A process in accordance with claim 22 in which the constituent material is from the group consisting of silica, alumina and silicon carbide.

27. A process in accordance with claim 26 in which metal incompatible with silica, alumina and silicon carbide is from the group consisting of aluminum, aluminum alloys, zinc and zinc alloys.

28. A process in accordance with claim 26 in which the constituent material is silicon carbide.

29. A process in accordance with claim 27 in which the constituent material is silicon carbide.

30. A process in accordance with claim 26 in which the constituent material is silica.

31. A process in accordance with claim 27 in which the constituent material is silica.

32. A process in accordance with claim 26 in which the constituent material is alumina.

33. A process in accordance with claim 27 in which the constituent material is alumina.

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RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

75—134, 138, 153, 166, 168, 170, 178; 29—191.2; 148—32; 164—97

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,600,163 Dated August 17, 1971

Inventor(s) FRANK ARTHUR BADIA and PRADEEP KUMAR ROHATGI

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 62, for "0.05%" read --0.005%--.
Column 2, line 36, for "graphte" read --graphite--.
Column 7, line 41, for "chloriating" read --chlorinating--.

Signed and sealed this 22nd day of February 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents