POWDER METALLURGY AND ITS APPLICATION TO NON-FERROUS METALS

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Abstract

The paper introduces the subject of powder metallurgy based on the studies of bond which exists between two atomically smooth surfaces when brought close together. After dealing with the theoretical principles and practical results of sintering homogeneous as well as heterogeneous powders, the applications of powder metallurgical technique to non-ferrous metals and alloys are discussed at length. Recent notable developments in powder metallurgy, in the field of heat-resistant metallic compositions, essentially of non-ferrous compositions, are dealt along with other developments such as the modern liquid disintegrator method for making metals and alloys into powder and infiltration technique. The paper deals with cermets and latest carbide compositions. The paper concludes with a reference to the possibilities of applying powder metallurgical techniques to Indian non-ferrous industries.

Introduction

SINCE there are between adjacent free atoms repulsive and attractive forces which give a resultant force pattern along the middle curve, namely line K, L_1 and M_1 of Fig. 1[1], two atoms moving closer together attract each other with increasing force until at a particular spacing between them a characteristic peak attractive force is reached. On the spacing being further reduced the attractive force declines in value and becomes null at a characteristic lattice spacing at which the two engaging atoms form a stable link. Fig. 1 suggests that there are considerable attractive forces between atoms separated by several times the normal lattice spacing. This is also borne out as in the case of steel gauge surfaces, finished to the flatness of half a wavelength of visible light, which surfaces may be ' rung ' together and will form a joint possible to be broken by perpendicular stress of at least one ton per square inch.

The approach of two metal surfaces must be closely equivalent to the two-atom link example treated in Fig. 1, with the exceptions that each atom will present only part of its total force field and the total force of attraction will depend on the number of effective links between atoms over the contacting area of the two surfaces. If the two surfaces are not of simple cubic lattice atoms, atoms below the surface planes will also contribute to the

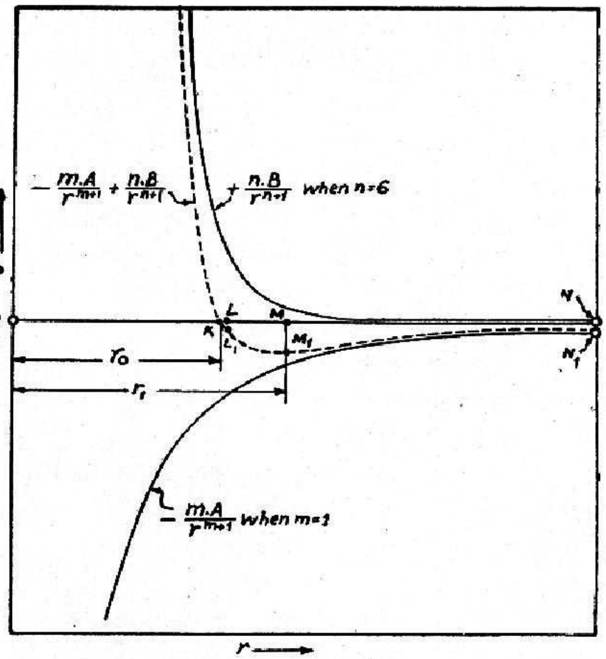

FIG. 1 — IN THIS PLOT OF THE FORCE FIELD OF AN ATOM, P REPRESENTS FORCE AND r THE DISTANCE FROM THE CENTRE OF THE ATOM. THE ATTRACTIVE FORCE IS GIVEN BY $-\frac{m.A}{r^{m+1}}$ AND THE REPULSIVE FORCE BY $+\frac{n.B}{r^{n+1}}$ WHERE A, B, m AND n ARE CONSTANTS. THE RESULTING CURVE FOR INTERATOMIC FORCE LIES IN THE MIDDLE

total force. Even if the surfaces are not of the same orientation and kind of atoms, the reasoning ought to apply still since the only condition which would seem necessary for atomic bonding is that the constituent atoms should come close enough so that the original surface boundary vanishes and becomes just another crystal plane. For the generalized case of two surfaces holding together the magnitude of the force is dependent on the geometrical fit, crystallographic orientation and the strength of the force fields of the engaging atoms. Thus powder metallurgy is a process wherein metal powder particles, whether admixed or not with non-metallic constituents, are formed into useful solid shapes. The metal powders may be of any kind, namely individual, mixed or alloy. In this instance the importance of the process is in the context of the utilizability of the above-mentioned force fields of engaging atoms.

Sintering

The elementary technique of powder metallurgy is to press the powders into compacts of necessary shape and to heat the compacts for requisite time at a temperature which is always much lower than the melting point of the material. Compacts can be distinguished according as they are composed of a homogeneous metal powder or heterogeneous mixtures of metal powders. On pressing the particles come into close mutual contact. Thus by substituting single interfaces for opposite surfaces which subsequently on recrystallization are eliminated, pressure itself accomplishes at the concerned places the stage of sintering called 'adhesion'[2]. During the main process of sintering as brought about by the thermal treatment, the driving force, in the case of homogeneous metal powders where neither melting nor inter-diffusion takes place, is the progress by changes in surface area whereby lower and lower surface energy tends to be attained. This results for these compacts in 'adhesion' finishing partly or completely its course and the setting in of 'densification'. During 'densification'[3] a great deal of atomic rearrangements occur because of which necks between interstices close off and the voids from their original interconnected form become isolated and spheroidized. In fact, densification can proceed to the limit when all the voids disappear entirely. For reasons of economy and shape distortion the sintering is not done with a view to density. Thus sintered compacts of even homogeneous powders contain an inherent porosity. In passing it may be mentioned that the technique of preparing porous compacts by adding to the metal powders a powdered substance that decomposes during sintering facilitates a number of channels to remain open irrespective of the outcome of densification, so that it is possible to sinter compacts with interconnected porosity even in cases which would otherwise result in being with isolated pores. This process is adopted where permeability is an advantage and is practised in connection with both homogeneous and heterogeneous metal powder compacts[4].

Sintering of Heterogeneous Powders

The thermal treatment of heterogeneous powder compacts might be done at a temperature at which the lower melting point constituent melts. In the circumstance sintering can be classified according as the constituent powders alloy or not and whether the non-melting constituent is soluble in the melted one. The following considers the several cases in respect of sintering and its results.

(a) In the case of heterogeneous powders which alloy together the sintering process is quick facilitated by osmotic pressure. They densify faster than homogeneous powder compacts. Side by side with densification they homogenize in composition under the functioning of diffusion. These sintered alloy materials also, as pointed out before, can be secured with the interconnected porous structure.

(b) In the case of heterogeneous compacts which do not alloy as in Cu-Pb the low melting constituent present to a sufficient extent forms a continuous matrix which on solidifying holds the components together. The strength in this instance, therefore, must be at least the strength of this matrix or the adhesibility of this matrix to the non-melting phase, whichever factor is less.

(c) In compacts where the non-melting phase is soluble in the melted one, small particles of the former dissolve in the latter and on cooling most of the dissolved phase is thrown out of solution and precipitates on the unmelted larger particles. This phenomenon is known as bonding by bridge formation where the low melting constituent forming the grain boundary phase is bonded via the bridge of these precipitates on to the main body of the larger particles of the unmelted phase. A very good bond between the particles takes place along with high density of the compact.

Practical Results of the Technique of Powder Metallurgy

The foregoing considerations show that the practical results of the technique of powder metallurgy are:

(a) Solid metallic preformed shapes with controlled porosity are obtained at temperatures much lower than the melting point of the material concerned in the case of homogeneous metal powder compacts.

(b) By using heterogeneous mixtures alloys are formed at temperatures of sintering much lower than the melting temperature with the additional advantage that by controlling sintering interconnected porosity as well as alloys exhibiting peculiarly determined non-equilibrium states can be secured. The latter facility makes powder metallurgy a technique of non-equilibria making possible a set of properties which might be superior to those of the completely homogenized alloy.

(c) The theoretical basis that any two atoms can combine to form a stable link implies the possibility that, unlike in the case of melting and casting where phase rule considerations limit the number of phases which can be contiguous, the number of phases in a powder metal compact can be unlimited. Further, since the nature of the boundary phase can be controlled in a powder metal compact, this fact and the foregoing reason are the main bases of powder metallurgy synthesis.

(d) From the manufacturing standpoint powder metallurgy employing moulding and sintering is a mass production technique complete in itself in respect of making the articles which after sintering retain their shape and, except where close dimensions are called for, are almost complete requiring no further operations except mostly a cold-pressing operation called ' coining '.

The Bearing of Powder Metallurgy on Non-ferrous Metals

In discussing the importance of powder metallurgy for non-ferrous metals, the chief items of interest are:

(1) powder metallurgy is the only available manufacturing method for certain non-ferrous metals and alloys;

(2) the possibilites and otherwise unattainable advantages which the technique offers because of its synthetic and fabricational aspects; and

(3) the simplicity and advantages of the technique being a mass production method for manufacturing porous as well as dense materials.

High melting point metals, which are all of them non-ferrous, are advantageously processed for temperature reasons by the technique of powder metallurgy. The other advantage which sintering offers is in respect of grain size which in a powder metal compact can be secured to extremely fine limits depending on the dimensions of the constituent particles used to form the compact. The possibility of usefully producing fine-grained metal by casting with even subsequent working is very limited. Since strength and workability are related to grain size, the importance of the above statement is critical for metals such as W, Mo, Ta, etc. In another instance, namely Pt, which incidentally could originally be processed for temperature reasons by powder methods only, the metal as sintered is superior to the cast product. The explanation in these cases is that the boundary substance of sintered bodies is within means of control as to quantity and composition, the means of control being by selection of suitable sintering temperatures, times and atmosphere of sintering and by the accurate control of chemical composition and elimination of impurities from the metal powder particles.

The above observation leads to the next feature of non-ferrous powder metallurgy wherein the composition as well as constitution of the boundary phase is predetermined by utilizing the phenomenon already referred to as 'bridge formation' so as to overcome grain boundary weakness. For instance, in Cu-W-Ni alloys the Cu-Ni phase is the melting one in which W dissolves. On solidification dissolved W is thrown out at appropriate places between neighbouring grains of W and between grains of W and the boundary phase. The bridges of fine W particles so formed help to bond the alloy in a particularly strong fashion. Such a phenomenon is also the basic principle underlying the synthesis of hard metals.

Hard metals are sintered compositions of refractory carbide particles, particularly WC, TiC and TaC, with generally Co as binder. The extraordinary strength of these bonded carbides, facilitated so by the bridge-head bonding which in this case is by the concerned precipitated refractory carbide particles, highlights the alloys and the powder metallurgy synthesis against the contrast of comparatively poor results obtainable with the same compositions as melted and cast. Regarding carbide compositions, synthesis has been further carried forward by combining in solid solution, using again powder metallurgy means, WC and TaC, WC and TiC, WC-TiC and TaC, WC-TaC and CbC, and WC-TiC-TaC and CbC, and cementing these multicarbides generally with Co and in some few cases with Ni as binder[6]. Each composition has its advantage of performance characteristics regarding the several grades and kinds of machining as well as machinability of the work. In this respect it must be remarked that by increasing tool life and by permitting greater speeds and accuracy of machining hard metals have brought about considerable production increases which extend in some of the cases to phenomenal limits.

The other branches of non-ferrous powder metallurgy alloys are refractory metal alloys and alloys of immiscible elements. Examples[7] of the former are: W-Mo used as supporting elements in incandescent lamps and electronic tubes, W-Ta indicated as a superior resistor heating element, W-Th and Mo-Th used as wires in thermionic emission cathodes. As regards alloys of immiscible elements, incidentally most of them contain refractory metal constituents. Examples[8] of this group of alloys are: W-Ag, Mo-Ag and W-Cu which find application as heavy-duty contact materials, and W-Ni-Cu and Mo-Ni-Cu, known as heavy metals because of their high density, which find applications as radium containers, screen material for α-rays and X-rays and particularly in heavy-duty electric contact service. Thus these alloys combine the low contact resistance, high current-carrying capacity and thermal conductivity of a metal such as Ag or Cu with high mechanical and arc-resisting properties of W and are examples of powder metallurgy composite compositions. In this connection it may be pointed out that the nature of a composite composition is a combination of the respective but independent provenances of the constituents composed together rather than an average of the properties of the constituents going to form the unit. By its very nature, since powder metallurgy is fitted to make composite compositions, it can outdo in the line melting and casting because of basic superiority as a means and because it can transcend not only miscibility, operating temperature and alloyability restrictions as we have seen in the above contact alloy compositions, but, as hard metals, refractory metals and other examples to follow would show, the other besetting restrictions connected with physico-chemical equilibrium and phase rule. Since graphite, Ni and Co have also good arc-resisting properties, composite alloys of Cu-graphite, Ag-Ni, Ag-CdO, Cu-Cd-B, Cu-Ag and Cd, Cu-Cr are made, all of which add proof to the diverse ability of powder metallurgy to make composite compositions.

The most evident fabricational advantage of powder metallurgy is the unique structure of interconnected porosity possible in sintered metal parts. The porosity can be predetermined to a high degree as in porous self-lubricating bearings[9]. These bearings, called Oilite or self-lubricating bearings, are made chiefly of bronze composition as well as in Al, Cu and Zn alloys. Similar to porous bearings are metallic filters, which are available in nickel and bronze compositions with standard pore sizes.

Whereas porosity is a characteristic property of powder metallurgical materials, the reduction of porosity to a minimum is desirable for certain applications. For the purpose, methods such as hot-pressing, repressing, cold and hot-working of sintered parts are adopted. By choosing a suitable method or a combination of methods even the full theoretical density values are attainable. However, where close tolerances are called for and higher densities are enough for the manufactured part, hot-pressing[10] seems to be the most direct method. In this procedure the powder is heated in suitable moulds to sintering temperature while under pressure. The pressures vary according to the metal powder and according as there is a liquid phase or not. Because of the intense mechanical deformation, sintering takes place in minutes and not in hours as in the ordinary procedure of sintering after cold-compacting. However, hot-pressing is a complicated technique as regards equipment, and since most metal powder parts do not have to be more than 75-80 per cent dense, hot-pressing is not widely practised except in the field of carbide tools and thus is still in the initial stages of exploitation.

Powder metallurgy as a mass production technique is necessary to be stressed. Besides saving in time and reduced scrap metal losses, the use of pressing does away with machine tools, costly tooling and machining. Unheard-of economy results. To cite an example[11], on one job 68 men with powder metallurgy technique produced as many parts as it was estimated 2500 men could have accomplished by the orthodox method in similar time over a period of a year. In fact, because of this advantage powder metallurgy has usurped in its individual right as a mass production technique the orthodox method in respect of making small machine parts. The non-ferrous compositions used in this instance are mostly based on copper and brass powders. Mouldings of machine parts such as cams, levers, sprockets and gears are in common practice.

Finally, powder metallurgy technique in general is most attractive for rather small and simple parts only, where again mass production scale only is economical from the standpoint of manufacturing costs.

Modern Developments

Examples of recent development are: (1) the modern liquid disintegrator method[12] for making metals and alloys into powder, (2) infiltration technique[13] to eliminate pore system and to synthesize certain super alloys, and (3) metal-ceramics and some advanced carbide compositions[14].

The liquid disintegrator method, which is a modified atomization process, makes any metal into powder faster than the older methods of milling, machining, electrolytic deposition, etc., and is suitable, unlike the older methods, for all metals and alloys practically without restriction. Complex alloys such as Cu-Ni-Zn and Cu-Pb series in some of their composition ranges rendered into powder by this method are reported to have structures approaching those of metallic emulsions and for that reason possess characteristic bearing properties. In respect of the broader field of manufacture of machine and other parts by powder metallurgy process, the advent of the liquid disintegrator method is advantageous because it produces the powders in quantities of output unequalled by other processes and the alloy powders made by it are particularly suitable for sintering.

Infiltration, referred to above, is the technique by which the naturally existent pore system of a sintered metal body is charged with a penetrating melt which may be either metallic or non-metallic. Pore-free densities are attained. Examples are steel-backed high-duty bearings of Cu-Ni porous layer infiltrated with a babbit metal or Pb-Sn-Sb anti-friction alloy. In this case also it may be seen as to how the composite nature of the composition helps. Thus this bearing which in the skeleton is composed of Cu-Ni composition adheres to the steel-backing because of sufficient Cu atoms undiffused into Ni being available at the backing interface, is mechanically strong because of the Cu-Ni complex skeleton and serves in the bearing use because of the infiltrant. Other examples of infiltration include those of carbides of W and Ti with Co-WC, Ni-Cr, Co-Cr and also W and W-Cr with Ni and Co base alloys. The aim in both cases is to produce a super alloy resistant to high temperatures, corrosion, creep and fatigue. This brings us to the considerations of hard metals in respect of their refractory characteristics.

The range of hard metals has been widened to include many high melting hard substances having metallic characteristics, as represented by the refractory carbides, borides and to some extent silicides of the transition metals of the fourth to sixth groups of periodic system. In the case of W, Mo and Ta, these compounds are not sufficiently oxidation resistant for service at the highest temperatures. For serivce temperatures below 800°C. TiC is very promising. In this connection the best high-temperature performance is reported for TiC bonded with corrosion-resistant Co-Cr, Ni-Cr and Co-Ni-Cr alloys. The highest oxidation resistance was recorded for a composite of TiC and a solution of carbides rich in TiC (60 per cent TiC composite with 15 per cent solid solution of NbC-TaC-TiC) bonded with 20 per cent Co. This composition, commercially named Kentanium K-138-A[15], has stress to rupture strength at 980°C. of 100,000 p.s.i., an endurance limit at 820°C. of over 45,000 p.s.i., while its specific gravity is only 5·8. On a strength at high temperature per unit weight basis the stated properties of this powder metallurgy composition are pronouncedly superior to any available alloys made by melting. Redmond[15] concludes that Kentanium K-138-A and similar compositions may be suitable for applications requiring high strength, resistance to oxidation and thermal shock up to an operating temperature of 1090°C. TiC bonded with Co-Cr, Ni-Cr and Co-Ni-Cr (trade designation WZ) has a short-time transverse rupture strength of 125,000 to 150,000 p.s.i. at 1000°C. When the TiC phase is replaced by TiC-base solid solutions of carbides, results comparable to those obtained with TiC-TaC-NbC solid solutions are secured (trade designation WZ-3). A related material to WZ, namely Elmet-H, developed in England has an oxidation resistance only slightly inferior to the Nimonic alloys while having heat shock resistance superior to Nimonic alloys.

Some pure refractory oxides such as BeO, Al_2O_3 and ZrO_2 and also combinations such as silicates and aluminates combine good resistance to oxidation with high strength at elevated temperatures. For oxidation resistance these ceramic compositions are unsurpassable, but they are brittle and susceptible to thermal shock. Ceramic frits can be produced with metal powders like Cr which over carbides would protect the latter from oxidation. This powder metallurgy synthesis is termed metal ceramics and the resulting composites are the cermets or Ceramels[16]. Thus a coating containing 80 per cent by weight of Cr and 20 per cent by weight of alkali-free frit (glass) formed over 20-80 Co-TiC reduces the oxidation resistance in air at 980°C. and exhibits the same thermal shock resistance as the base material. In this way hard metal materials can be secured which promise applicability at service temperatures markedly higher than possible with the best alloy made by conventional metallurgy. However, at temperatures higher than 1100°C. the oxidation resistance of even TiC lags behind that of the ceramic materials. But there are hard metals particularly in the class of borides of transition elements[17] which at temperature in excess of even 1100°C. exhibit stability and oxidation resistance equal to those of ceramics while being at the same time, unlike ceramics, highly thermal shock resistant. Thus the field of high-duty service at and above 1100°C. definitely belongs only to a powder metallurgy synthesized composition based on nonferrous metals.

Position of India regarding Interest in Powder Metallurgy

We have seen that powder metallurgy is a technique at once liberating and conceived on a basis which results in gigantic outcome. The process produces on the mass scale and does so in respect of unique materials which themselves would contribute colossally as tools of further production or as members under severe and extraordinary service. Thus refractory metals and alloys, hard metals and compositions, electrical materials and products, porous bearings and filters, about all of which mention has been made during the course of this paper, are outstandingly important to improve the economy in the present-day industrial world. As regards the technique itself it has the basic advantages of approach based on synthetic, fabricational and experimental aspects. Further, unlike melting, the technique is not restricted, as a pointed reference has been made in this paper, by the factors of phase rule, physico-chemical equilibrium, alloyability and solubility, with the result that the basic ability for making composite compositions inherent in the technique has really amounted to possibilities for material compositions, physical properties and process control unknown as possible to conventional metallurgy and inventive in nature. India, which has more and more of industrialization and high production to accomplish, cannot afford to neglect such a versatile and boon-like resource as powder metallurgy, as regards the benefits that are already known and those that would accrue upon active enterprise with this essentially experimental metallurgy.

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