P/M (Powder Metallurgy) and Potential Applications in Jewelry Manufacturing

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ABSTRACT

P/M (Powder Metallurgy) involves the use of metal powders in industrial applications with the primary utilization being the net shape manufacture of parts. P/M represents the fastest growing sector in manufacturing as several techniques are competitive with investment casting, discrete machining, and can produce materials not possible via traditional manufacturing methods. However, P/M methods are not fully realized in the jewelry manufacturing industry.

This paper will present an overview of the science of P/M and many of the P/M technologies that are well developed in industry including press and sinter (P&S), metal injection molding (MIM), hot pressing, hot and cold isostatic pressing, roll compaction, extrusion, and fusion processes (braze and solder pastes, thermal spray and spray forming). A review of the current status of P&S and MIM in jewelry manufacturing will be presented as well.

This presentation of alternative manufacturing methods using P/M may seed some ideas for potential P/M applications in jewelry manufacturing.

KEY WORDS

Powder, Powder Metallurgy (P/M), sintering, Metal Injection Molding (MIM), Press and Sinter (P/S), Hot Isostatic Pressing (HIP), Cold Isostatic Pressing (CIP), powder extrusion, powder rolling, thermal spraying.

I INTRODUCTION

Powder Metallurgy (P/M) entails the use of metal powders in industrial and manufacturing applications. P/M is well established in the processing of iron-based parts including stainless steels. Aluminum, copper, and refractory alloys are also commonly processed via P/M methods. The full scale use and industrialization of P/M has occurred primarily in the past 50 years in production of iron-based components. The P/M industry in North America is currently \$1.8 billion per year, 60% being automotive (1).

P/M is most commonly utilized as a net or near net shape manufacturing method, that is, the as-formed part is used without secondary manufacturing steps. In its most fundamental form P/M involves the consolidation of powder into a defined shape followed by a thermal treatment (sintering) to develop bonds between the particles which impart strength and metallurgical integrity. P/M competes with investment casting and discrete machining on a cost basis. Although metal powder costs more than their cast or wrought counterparts economic advantages are realized by reductions in machining operations, the overall number of processing steps, and in scrap generation. The final P/M part becomes a direct replacement for cast or wrought parts as it has the same utility and form. P/M processing has a well established set of design criteria and in many cases P/M is the preferred method of part manufacture.

There are also applications where P/M is the preferred manufacturing method because it produces a superior material or allows the processing of a material that cannot be processed by traditional methods (cast/wrought/machining). For example, many complex alloys of the super alloy family and the tool steel family are difficult to cast because of chemical/component segregation upon cooling (2). This segregation yields poor properties. P/M processing starts with powder where each particle is the target composition, thus, the degree of segregation is orders of magnitude less than a casting and improved properties are achieved.

WC/Co tool materials, otherwise known as cemented carbides, can only be processed via P/M. WC (tungsten carbide) powder and cobalt powder are milled together, pressed to shape, and sintered to full density. There is no cast counterpart to these alloys. Other examples include sintered filters and bearings. For these cases maximum density is not achieved in the sintering operation. The particle size and the degree of compaction and sintering allow various configurations of the residual pore network in order to yield a permeable body to act as a filter or to be impregnated with a lubricant.

P/M encompasses other powder uses including solder and brazing pastes, powders for cladding operations via welding, laser, and thermal spray methods, and for loose sintering operations to make filters and in the use for bio-implants to enhance grafting through surface modification.

II OVERVIEW OF THE SCIENCE OF P/M

P/M processing entails three primary entities: powder production, powder consolidation (to impart shape to the powder), and sintering (a thermal treatment to promote particle bonding and part densification). This section will review each of these topics.

A. Powder Production

There are several commercial-scale processes for producing metal and metal alloy powders. Each technique produces a powder with unique characteristics and properties that effect subsequent powder processing steps. There are four primary powder production methods; 1) Chemical reaction, 2) Electrolytic, 3) Mechanical, and 4) Atomization.

1) Chemical Reaction: The most common powder production methods via a chemical reaction is the reduction of a metal oxide. For example, iron oxide that has been mined, concentrated, and milled is subjected to a reducing gas at elevated temperatures which reduces the iron oxide to elemental iron. The resultant powder is highly irregular in shape and porous. Figure 1a. is a photomicrograph of reduced iron powder.

Iron and nickel can also be produced by the thermal decomposition of an organometallic compound, i.e. iron carbonyl (Fe (CO)₅) or nickel carbonyl (Ni(CO)₄). The organometallic decomposes in the presence of heat and a catalyst. The resultant powder is usually very fine (sub-micron to 20 microns) and highly agglomerated.



Figure 1. Representative metal powders: (a) chemical: sponge ironreduced ore; (b) Electrolytic: copper; (c) Mechanical: milled aluminum powder; (d) Water Atomization: iron; (e) Gas atomization: nickel-base alloy (3). Metal powder can also be produced my precipitation from a liquid. A salt of the metal is dissolved in an aqueous solution and reduced with another compound. The metal compounds may undergo this reaction from molten salts or salts dissolved in an aqueous solution. Many precious metals, including gold, silver, and platinum are made using the latter variant of this method. The size of the powder particles is generally on the fine size, usually less than 15 microns, and the morphology ranges from spherical to irregular to spiky. This technique is primarily used to produce pure metals, however, composite materials can be produced by using one metal particle to act as the nucleant for the precipitation of a second metal.

Another method of powder production is precipitation from a gas. The most common variant is the evaporation of a metal halide and subsequent reduction with hydrogen. Recent developments in the formation of nano-scale powders use this method to produce powders in the 10 to 1000 nanometer size range (1 micron equals 1000 nanometers). These powders are highly agglomerated and very reactive because of their high specific surface area. Most nano-scale metals will spontaneously combust (oxidize) if exposed to air.

2) Electrolytic Powder Production: Electrolytic deposition is common in plating and the build up of bulk cathode material. Electrodeposition entails the reduction of ionic metal species from an electrolyte by an externally imposed current. The metal ions in solution are dissolved from an anode and re-deposited on a cathode. To manufacture powder rather than a coating or bulk build up electrolyte concentrations are reduced while the current density is increased. In addition, the cathode is continually wiped to remove the particles that are being deposited. The result is a fine dendritic powder. Figure 1b. is a photomicrograph of dendritic copper. Post processing, such as milling, modifies the shape to that of a sponge material.

3) Mechanical Methods: Mechanical methods are used to either break down bulk materials into powder or further reduce existing powder particles to finer sizes. Mechanical methods involve impacting, shearing, attrition, even machining and grinding. One common method is milling where the bulk material and a milling media, such as balls or rods, are processed in a rotating milling jar. The rotation provides a continual cascading of the milling media onto the bulk material where it eventually fractures into smaller particles. Mechanical methods for producing powders are more effectively used on materials with limited ductility and toughness such as ceramics, intermetallics,





refractory metals, etc. The morphology of brittle material that has been milled is irregular and blocky with sharp, angular edges. Materials with high degrees of ductility, such as copper, aluminum, and most precious metals, would smear and flake if processed in this manner and may even cold weld and agglomerate to larger particles if milled. Milling ductile material produces flakes such as the powder used in leafing applications.

Milling is also used to "mechanically alloy" mixtures of powder to form a homogenous mixture for subsequent P/M processing. ODS (oxide dispersed strengthened) alloys are made by co-milling an oxide powder with a relatively tough and ductile matrix alloy. The final powder is a stable mixture of the oxide dispersed in the parent alloy. This dispersion is retained throughout the P/M processing to provide strengthening in the final dense P/M processed material. Figure 1c. is a photomicrograph of milled aluminum powder.

4) Atomization: Atomization is generally defined as the breakup of a liquid into droplets. In the case where the liquid is a molten metal the droplets subsequently solidify into the particles which make up the powder. The majority of powder is produced by atomization. Atomization offers the greatest economy of scale and is able to produce powders with the greatest diversity of particles sizes, morphologies, compositions, and microstructures.

The most common methods to breakup molten metals are 1) impinging the molten metal with another fluid (gas or liquid), 2) mechanically disintegrating the melt by impact or centrifugal action.

Two-fluid atomization is the atomization of one fluid (molten metal) by the action of an impinging second fluid (gas, water, oil). A stream of molten metal is poured into a chamber where it is disintegrated by jets of high pressure fluid. The second fluid also promotes cooling and solidification and the powder is collected in the chamber or cyclone.

Gas atomizers are configured either as "free-fall" or "close-coupled". Figure 2. shows the configuration of these two configurations. In the free-fall design the liquid metal is poured into the interaction zone where the independent gas jets disintegrate the liquid stream. The liquid stream may have to fall several inches (up to 12 or so) before impingement from the gas jets. Gas velocity (and thus energy) falls off rapidly with distance and thus "free-fall" atomizers are not particularly efficient and produce fairly coarse powder. "Close-coupled" atomizers confine the molten metal to a zone where the gas jets act in much closer proximity on the order of fractions of an inch. In this configuration far less gas velocity is lost and greater coupling of the two fluids increases the atomization efficiency and finer powder can be produced. In addition, the draw of the liquid metal through the atomization nozzle is dependent of the gas pressure and flow rate thus allowing greater control on the process.

Powder particles produced by gas atomization are generally spherical as the cooling rate is low enough for the surface tension to act and allow the molten droplet to spheroidize prior to solidification. Free-fall atomizers produce powders with mean particle sizes of 50 to 150 microns. Close-coupled atomizers produce powders with mean particle sizes from 10 to 75 microns. Figure 1e. is a photomicrograph of a gas atomized nickel-based alloy.

Water and oil atomization systems are typically of the free fall configuration. High pressure/velocity jets of water do not lose their velocity with distance as rapidly as gas jets thus the standoff distance between the water jet and the stream of liquid metal is not as critical. Most commercial water atomization systems operate at pressures between 500 and 3000 psi and produce powder with mean particle sizes between 50 and 150 microns. Higher pressures can be used to produce mean particle diameters approaching that of close coupled gas atomization. The cooling rate is approximately an order of magnitude higher with respect to gas atomization and the droplets do not achieve their spherical shape prior to solidification thus the water atomized particles are irregular in shape. Figure 1d. is a photomicrograph of a water atomized iron alloy.

Atomization with water may be detrimental to some metals as it may cause excessive oxidation. Plain carbon steel alloys are commonly water atomized. The powder is subjected to a hydrogen anneal to reduce the surface oxides and yield a usable P/M grade powder. Some alloys contain additions whose oxides cannot be easily reduced and oil atomization may be used in these cases. The particle size and shape produced by oil atomization are similar to those produced by water atomization.

Molten metal can be disintegrated into droplets by mechanical means rather than by impingement by gas or water. One common method is to pour a stream of molten metal onto a rapidly spinning disk as shown in Figure. 3. The melt spreads over the disk and this thin film is broken up by the centrifugal forces at the edge of the disk. In a similar fashion the end of a rapidly spinning ingot of material can be arc, laser, or electron beam melted and the forming



Figure 3. Schematic of rotating disk atomization (3).

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liquid is disintegrated in a similar fashion. These methods eliminate contamination from the atomization gases or fluids. Typically these methods are performed in vacuum or low pressure gas chambers where the cooling rate is very low and the resulting particles are very spherical. The particle sizes are relatively coarse with typical mean diameters between 150 and 200 microns.

All atomization processes produce a wide range of particles sizes, some of which may be inappropriate for P/M processing, thus, most atomized powders are classified (sieved to remove particles outside of the required size range) prior to use.

B. Sintering

Sintering is an essential processing step that is an integral component to the myriad of powder compaction, consolidation, and shaping methods that make up the P/M technologies. In short, sintering is a high temperature heat treatment that increases atomic motion and mobility which results in particleto-particle bonding and densification of the powder compact. Achieving useful engineering properties such as strength, ductility, toughness, and conductivity depends on particle bonding and densification. Sintering is not as commonly understood for those primarily involved in casting (melting and solidification) as most sintering phenomena occur as a result of solid state diffusion and may not involve melting. A synopsis on sintering, including its driving forces and mechanisms, will give the reader a more tenable feeling for this phenomenon.

For a given mass of material, the more it is physically divided into parts, the greater the amount of surface area the mass has. There is a surface energy associated with the surface area. For an assembly of particles, such as in a mass of powder, there is an excess amount of surface area and its associated surface energy with respect to the same mass of solid material. The excess surface is that surface between particles and the interfacial area between a particle and a pore. A physical system will always tend to evolve to its lowest thermodynamic energy state. A redistribution of material in such a way as to eliminate the excess surfaces and excess surface energy would be energetically favorable for the overall system. Thus the driving force for this redistribution of material is the reduction of excess energy.

Mass transport on the atomic scale is the mechanism by which this redistribution occurs. Atoms diffuse to the points of contact between particles

and effectively weld the particles together forming a cohesive metallurgically integral bond and lowering the energy of the system. As atoms from the interior of the particles diffuse to the contact site the particle centers approach each other. In addition, the pores are also eliminated in a similar fashion. These mechanisms are manifested macroscopically as shrinkage of the overall compact. Figure 4. is a schematic of the four basic stages of sintering.

The diffusion of atoms is a thermally activated process; increased temperature provides the energy for diffusion. At room temperature the amount of atomic motion is negligible. At temperatures above one half the melting point of the metal the atomic mobility is increased to a point where appreciable diffusion exists and sintering can occur.

Smaller particles have a greater amount of surface area and energy per mass and thus the driving force for sintering is greater and therefore may require lower temperatures to activate the sintering mechanisms. Coarse powders act more sluggish and will require higher temperatures for sintering.

Thus an assembly of particles, when subjected to elevated temperatures, will rid itself of excess surface area and energy by atomic diffusion. This diffusion of material eliminates free surfaces by welding the particles together and eliminating pores, both which result in shrinkage of the compact.

Sintering is performed under controlled atmospheres, usually reducing, to prevent oxidation and to reduce oxides that would inhibit sintering. Some variants of sintering involve some liquid phase. The presence of a liquid phase greatly speeds up the sintering process as atomic diffusion is more rapid in the liquid and the liquid is mobile to fill in pores. For pre-alloyed powder a predetermined amount of liquid can be produced by heating above the solidus temperature, hence the name supersolidus sintering. For a mixture of powders liquid phase sintering will occur if the melting temperature of one of the components is exceeded. If the liquid is absorbed and alloyed with the other components it may disappear at the without having to reduce the temperature. This is called transient liquid phase sintering and an example is the silvermercury amalgam used in dental work. When the two components are first mixed the mercury is liquid. With time the mercury absorbs silver and becomes solid. If the liquid exists until the temperature is reduced it is called persistent liquid phase sintering. Cemented carbides are sintered in this manner. The initial powder is a mixture of tungsten carbide and cobalt. The mixture is



Intermediate Stage

Final Stage

Figure 4. Schematic of loose powder sintering (5).

sintered at a temperature that exceeds the melting point of the cobalt phase and the molten cobalt wets the carbide particles, fills the pores, and "cements" the tungsten carbide particles together. Only when the temperature is reduced does the cobalt phase solidify.

Liquid phase sintering is a commercially used sintering technique, however, a disadvantage is that the powder compact may slump or loose dimensional tolerance due to the mobile liquid phase. In addition, the grain growth rate is also increase in the presence of a liquid phase. To minimize slumping and grain growth the amount of liquid phase should be kept to a minimum.

III P/M MANUFACTURING TECHNIQUES

One of the primary advantages of P/M is the ability to impart shape to the powder in a relatively easy and uncomplicated manner, at least with respect to machining, forging, and casting. The consolidated body of powder is sintered and is often used directly in this form without subsequent machining operations. This is called net shape processing. Other variants of P/M are classified as near net shape processing where P/M methods are used to make bulk forms, such as sheet or billets, where the final shape is derived by machining, stamping, forging, etc.

Net shape P/M processing include die compaction, MIM (Metal Injection Molding), and some variants of hot pressing and CIP (Cold Isostatic Pressing). HIP (Hot Isostatic Pressing) and powder rolling and extruding are near net shape P/M processes.

Die Compaction:

P/M processing is most commonly identified by die compaction. In die compaction consolidation of the powder is achieved by compaction in a rigid die between punches. The die and punches generate the shape of the compact. Figure 5 is a schematic of a typical die pressing routine. Powder is fed into a die cavity with the bottom punch in the lowest position. The upper punch is inserted into the die cavity and the powder is compacted. The upper punch is then withdrawn and the lower punch ejects the part from the die. The presses are highly automated and cycle times can



Figure 5. Schematic of die compaction sequence (5).





approach 1 part per second (6). Pressures range from 10 tons per square inch (tsi) to 50 tsi. Die compaction and sintering can produce fairly complex parts such as ID or OD gears with tolerances below 0.003 in/in and in some cases less than 0.001 in/in. Die compaction is limited to aspect ratios of less than 5 (height to diameter), the geometry is generally axisymmetric, and undercuts are not possible (7). These constraints are based on the necessity to achieve as little density gradient in the part as possible. The sintered density is dependent on the pressed density. Density gradients in the as-pressed part will translate to distortions in the sintered part. Figure 6 shows several examples of parts that can be produced by die compaction.

The compacted powder part is called a "green part". One of the requirements of the green part is to possess sufficient strength so that it may be handled without breaking. The compressibility of the powder and the green strength of the compact are a result of the characteristics of the powder. For most die-pressing operations the powder must be fairly coarse (50 to 150 microns) and its morphology must be irregular, preferably with asperities to enhance mechanical interlocking during pressing. Powder with an irregular shape is generally produced by water atomization. Lubricants are typically added to the powder to reduce die wall friction and to act as a binder in a secondary fashion. The lubricant is added at a level of 0.5% to 2% by weight and must be burned off prior to sintering.

Conventional press and sinter powder metallurgy processing has been practiced on a commercial scale for over 50 years. It competes with casting and machined parts where it 1) has an economic advantage or 2) is the only way in which a part or material may be processed.

Economic advantages arise from the elimination of machining steps by being able to produce complex designs in the pressed part, also known as "net shape" processing. P/M offers greater material utilization than machining since it eliminates the scrap and chips associated with machining processing. This becomes more important as the cost of material increases. The economic advantages are only realized for large production quantities since the tooling, set-up, presses, and sintering furnaces are very capital intensive. The press and sinter technology lends itself readily to automation and continuous processing. Minimum quantities for common iron-based press and sinter parts to be competitive with castings or machined parts can be between 10,000 and 50,000 parts (8).

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There are technological aspects that make P/M processing the only method for producing certain materials. For example, cemented carbides (tungsten carbide/cobalt alloys) can only be produced by P/M as they cannot be cast or forged.

Most conventional P/M methods produce materials with some residual porosity. Adequate tensile strength and ductility to compete with cast material can be achieved in many cases with up to 10% porosity. The main detriment to the residual porosity is the decrease in dynamic properties such as fatigue strength and fracture toughness. To achieve dynamic properties competitive with wrought materials in critical applications the porosity level has to be reduced to less than 1% (9). This is difficult to achieve with conventional P/M processing and subsequent forging or coining may be used to achieve these high densities and improved dynamic properties. Automotive connecting rods are made by the sinter-forge method. A compact is pressed to a connecting rod blank and sintered to 80% to 90% density. While still at the sintering temperature it is then close-die (flashless) forged to over 99% density. GM, Ford, Chrysler, Toyota, and Porsche are currently using this technique to manufacture many of their connecting rods.

Hot Pressing:

Hot pressing combines die compaction and sintering in one step. Metal powder is loaded in a uniaxial rigid die much like conventional die compaction, however, the die is heated and the compaction takes place at much lower strain rates for longer periods of time. The pressing may take several minutes to the better part of an hour and the pressures are much less than used with conventional die compaction (less than 10 tsi rather than 10 to 50 tsi). The dies are typically made of graphite or other materials that will suscept in an induction field. Other refractory materials such as silicon carbide or alumina may be used and flame or radiant heat may also be used. The elevated temperature and applied pressure cause the powder particles to undergo deformation which enhances densification. Full densities are typically achieved.

Hot pressing is versatile in that it can be used with just about any powder type and morphology. Ideally, spherical powders with a wide size distribution (as produced by gas atomization or rotating processes) will achieve the highest packing density prior to compaction. However, the plastic flow induced by hot pressing will help densify powder with poorer packing factors. Hot pressing is most often applied to refractory or high temperature materials or composites. Beryllium is typically processed by hot pressing. In this case the product is usually small billets to be machined to final shape. Industrial diamond tools, such as metal bonded diamond wheels, are hot pressed to tolerances that only require truing and dressing as a final step. These parts are a composite of metal powders which make up the matrix material and diamond powder or grit to provide abrasive properties. Hot pressing allows full density of the metal matrix at lower temperatures and shorter times than would be required for conventional separate press and sinter operations. This is important as the diamond degrades at elevated temperatures.

In general hot pressing is a low production rate process with respect to conventional press and sinter operations and lower tolerances are produced.

Cold Isostatic Pressing (CIP):

CIP is a compaction technique that subjects the powder body to uniform (isostatic) pressure. This is achieved by using a flexible die (such as rubber) immersed in a fluid which is then pumped to high pressures (also known as wet bag CIP). Figure 7 is a schematic of the CIP system. CIP eliminates the die wall/powder friction which limits the achievable pressures and aspect ratios practiced in conventional die compaction. The compacted part has a much greater degree of uniformity in density and lubricants or binders are generally not used. Since the green part relies on mechanical deformation and interlocking of the powder particles water atomized powder (with its irregular morphology) is most commonly used. Spherical powders are generally not used as without any shear (CIP only imposes isostatic compaction) the particles cannot interlock. In some cases a binder may be used to enhance the green strength.

CIP also allows the compaction of larger parts and allows re-entrant angles and undercuts. However, CIP yields lower production rates and geometric tolerances and the surface finish is much poorer.

One variant of CIP which allows for higher production rates is dry bag CIP. In this case a flexible mold with many cavities is hydrostatically pressurized from one side and supported by a rigid wall on the other. Loading the powder and unloading the pressed parts does not entail exposing the fluid reservoir. Ceramic spark plug insulators are made in this manner.



Figure 7. Schematic of Cold Isostatic Press (CIP) (5).

Hot Isostatic Pressing (HIP):

HIP is to CIP as hot pressing is to cold die compaction. HIP combines heat and isostatic pressure simultaneously for deformation enhanced sintering and densification. HIP equipment is typically a cold wall autoclave, that is, a furnace within a pressure vessel. The powder "mold" is usually a metal or glass can whose shape is roughly that of the desired piece. The mold is filled with powder, a vacuum is applied to remove gases, and then the can is sealed to make it gas tight. The HIP vessel uses high pressure gas to provide isostatic pressure. Pressures up to 30,000 psi and temperatures in excess of 3600°F are possible. The mold material must be chosen so that it deforms at the elevated temperature of the HIP cycle and transfers the heat and pressure to the powder. After the HIP cycle the can is stripped off by machining or acid etching and the piece is finished with conventional machining methods. HIP is a near net forming process.

HIP is used to process powder materials that are may be difficult or impossible to process via other P/M methods. Nickel-based super alloys and tool steels, both high-strength alloys with elevated temperature properties, can be processed via HIP. These powders are available as gas atomized spherical powders and do not respond well to die compaction. HIP requires the maximum packing factor when filling the can thus spherical powders are most commonly used. If the powder has a low packing density the can may buckle during the HIP cycle.

HIP processing is quite slow and the fabrication of the cans can be challenging. If the can leaks then high pressure gas is essentially sintered into the part. Subsequent heat treating of the part can cause thermally induced porosity (TIP) which degrades the properties of the material or can even fail the part.

HIP is capable of making very large pieces such as the rotors for jet aircraft motors which may be up to 30 inches in diameter.

HIP can also be used without a cans if the part is greater than 92% density. Above 92% density the porous network is not interconnected and the piece can be acted upon directly by the environment in the HIP. Pores that connect to the surface will not sinter shut. HIP can be used on non-P/M pieces to heal internal porosity such as the type of porosity found in castings. Healing of these internal pores greatly increases the dynamic properties of these castings.

Metal Injection Molding (MIM):

MIM, in simplest terms, is an integration of P/M processing and plastic injection molding. The goal is to produce parts of the same level of complexity, ease, and with economy of scale as plastic parts but with the strength and functionality of metallic materials. Figure 8 is a schematic of examples of geometries that are possible with MIM: undercuts, spheres, fins, studs, tapers, off-axis and perpendicular features. Edge radii down to 0.005" and corner radii down to 0.010" are possible. Surface finishes are generally better than 32 rms (10).

MIM is comprised of many technological disciplines including metallurgy, plastics processing (polymer engineering and rheology), organic chemistry, fine particle processing, and also tool and die design and process control and automation technologies. Proper choreography of all those involved will produce a part with the shape, properties, and economics required to compete with existing technologies. A schematic of the MIM process is shown in Figure 9. The process starts with adding fine metal powder to a polymer binder, generally a mix of thermoplastics, to form a homogeneous mixture. The polymer imparts fluid properties (viscous flow) to the metal powder so that the mixture may be injection molded; filling a permanent die cavity by simultaneous heating and pressurizing the mixture. The injection molding methods used are very similar to conventional plastic injection molding with the die design and process parameters modified to accommodate the different thermal and rheological properties of the powder/binder mixture. The injection molded material cools and solidifies in the die cavity. It is then removed and trimmed of its gating system. This "green" part has a crayon-like consistency. The next step, debinding, is the removal of the polymer binder. This usually involves a thermal treatment where the binder liquefies, evaporates, or decomposes in a controlled manner as not to distort or crack the part. Binder removal may also be accomplished by solvent extraction, wicking, or by a vacuum process. The debound part is fragile and has the consistency of soft chalk. The debound part is then sintered to achieve metallurgical bonding of the powder particles and to allow densification of the part. This occurs with an attendant shrinkage which has been accounted for in the design of the die cavity.

The metal powders used in MIM processing should satisfy two general criteria: 1) they should have a high specific surface area (energy) to enhance



Figure 8. Examples of potential MIM geometries (5).



Figure 9. Schematic of MIM process (5).

sintering and 2) they should have a minimum amount of surface area to assist mixing with the binder, minimize the amount of binder needed, and promote viscous flow during molding. These apparently contradicting requirements can be fulfilled by utilizing fine, smooth, spherical powders. For most MIM operations the average particle size is less than 20 microns (-635 mesh). The particle-size distribution should be truncated sharply on the coarse end and the material should have a minimum of sub-micron particles.

The use of fine powders allow for part designs with more intricate geometries, sharper edges, thinner walls, and superior surface finishes. Fine powder readily sinters and the smooth spherical shape will pack most efficiently and allow the binder/powder mixture to maximize the solids loading. This in turn lessens distortion during debinding and reduces the overall shrinkage during sintering.

Powders that possess these characteristics can be produced by gas atomization and, in some cases, depending on the material or alloy, chemical precipitation or carbonyl decomposition.

Alloys that are not available in a pre-alloyed form may be created by mixing elemental powders in proportions of the desired alloy. If an alloying addition is a minor component of a few percent, the addition may have to be of a much finer powder to achieve a homogeneous mixture during blending. Alloys made from elemental additions may require higher sintering temperatures, longer sintering times, or both to achieve chemical homogeneity in the sintered part.

Many of the advantages of MIM are intrinsic to all P/M technologies, in particular the ability to produce fine-grained microstructures with a high degree of chemical homogeneity. Material utilization is also high for P/M. MIM rates among the highest for this quality as scrap is easily recycled into the input feedstock loop and also due to the elimination of secondary machining operations and the "chips" associated with them. MIM is a high production, relatively high productivity manufacturing method and lends itself well to automation.

MIM has demonstrated the ability to produce complex parts with high tolerances, however, it shares these attributes with investment casting and discrete machining. The best tolerances reported for MIM are +/- 0.1% (+/- 0.001 in/in) (11) with +/- 0.5% (+/- 0.005 in/in) being more typical. The 0.1% represents the current limit for MIM and would most likely not be

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economically attainable for all but a few critical dimensions per part. MIM operations are very efficient when tolerances are relaxed to 0.8% to 1.0%. However, tighter tolerances can be achieved by machining and investment casting methods. Machining is also more competitive for small production runs as MIM requires approximately 5000 parts for initial production. MIM tooling is permanent thus future runs can be appreciably smaller and still be economical, a valuable attribute shared with investment casting.

MIM does not usually compete with press and sinter P/M. If a part is being produced at an economically acceptable level with P/M the high cost of the MIM feedstock and processing will not be justified in the part design. MIM generally does not compete with stampings or with materials that can be die cast.

Powder Rolling and Extrusion:

Forms such as sheet and rods can be made by bulk processing of powder. Two techniques used are powder rolling and powder extrusion.

Powder rolling may be thought of as a continuous die compaction operation. Figure 10 is a schematic of the powder rolling process. Powder is fed into the gap between two rolls and the powder is subjected to maximum compaction as it exits the rolls. Powder must be gravity fed into the rolls as it cannot be pulled into the rolls as is the practice with conventional strip rolling. The green strip must be sintered and it is done so in a continuous operation. In order to achieve full density the sintered strip is subjected to subsequent cold or hot rolling passes.

As the green strip relies on particle interlocking for its strength irregular shaped powder, such as that produced by water atomization, is used in this application. Spherical powder cannot be used.

Powders can also be processed using extrusion techniques. One technique is a variant of HIP and the other is a variant of MIM. Hot extrusion of powders can be achieved by first filling a can with powder, much like that used in the HIP process. The powder-filled can is heated in a conventional furnace and then hot extruded in a conventional extrusion press. The can confines and protects the powder as the can and powder are subjected to the extrusion. The can deforms and collapses around the powder and the final product is a rod of full dense material still encapsulated by the can material. The can is removed by machining or etching. Similar to HIP it is desired to



Figure 10. Schematic of powder rolling process (5).

maximize the packing density in the can prior to extrusion so ideally spherical powder with a wide particle size distribution is used.

Another powder extrusion technique is similar to the MIM operation. In this case the powder is mixed with a binder to the consistency of a paste or modeling clay. This is then directly extruded into a continuous rod. The rod is cut to length, debound, and sintered to density. This technique is used to form rods of WC/Co materials which are subsequently used for drills and milling tools. The powder characteristics required for this method of extrusion are similar to MIM powder requirements.

Fusion P/M:

"Fusion" implies melting and this is one application of metal powders which is well established in jewelry manufacturing in the form of solder and braze pastes. These pastes are a mixture of fine alloy metal powder, a carrier vehicle, and additives for fluxing. The carrier vehicle provides a medium to contain the solder alloy powder and additives so that they remain homogeneously suspended to be conveniently dispensed through a syringe. Fluxing agents may be included to enhance solder wetting. These ingredients combined in the paste provide the necessary properties for precise placement and quantity of solder material for an optimum joint.

The primary attributes important to the metal powders used in pastes include particle size, size distribution, morphology (shape), and alloy composition. The rheology (flow properties) of the paste is greatly influenced by the metal powder. Spherical particles allow better flow than irregular particles and large particles flow better than small. There is a limit to the particle size imposed by 1) syringe nozzle diameter, 2) joint configuration, and 3) required homogeneity of the paste mixture. Solder powder is sieved to limit the upper size of the particles. Torch pastes can be as coarse as -200 mesh (75 micron upper limit) while some special furnace applications may use powder that has been sieved to -400 mesh (38 micron upper limit). The powder used in solder pastes is usually produced by inert gas atomization.

The alloy composition is engineered to provide satisfactory mechanical and corrosion properties of the solder joint, flow characteristics and flow temperature range, and color at the required karatage. Since the powder particles are melted in the soldering operation there are no artifacts remaining from the initial powder in the final joint.

Thermal Spray:

Thermal spraying with powder is analogous to spray painting with molten metal. A plume of molten metal drops is directed to a surface where they impinge and solidify. Thermal spraying has been around for many decades in the form of "metalizing guns" and flame sprayers, however, recent technological developments have increased the type of materials that can be sprayed and the adherence and quality of the coatings.

Thermal spraying is used to restore a substrate to proper dimensions by adding material or it can be adding a new material to the surface with enhanced properties for hardfacing, corrosion resistance, or cosmetic applications. Thermally sprayed material has a minimum of metallurgical interaction (dilution) with the base material and the primary bonding is mechanical, thus, the substrate should be roughened prior to spraying. Thermally sprayed coatings are best used in compression (journal bearings) rather than cyclic loadings (such as ball or roller bearing race surfaces or poppet valve seats) due to the fairly weak interface strength.

Thermal spraying techniques vary primarily with the source of the liquid metal drops and the methods of propulsion. Early flame spraying guns simply fed powder into an oxygen/fuel torch where the powder would be entrained in the torch plume. The powder would melt and be deposited onto a surface. Wire feed methods use metal wire or wires as electrodes where they are disintegrated by an electric arc into a jet of gas. The gas jet carries the molten metal particles to the part surface. Other early techniques, such as zinc metalizing guns, continuously melted a zinc rod into a gas stream. The gas would atomize the zinc and deposit it on a substrate.

Contemporary thermal spray techniques include plasma spraying and HVOF (high velocity oxygen fuel) deposition. Both of these techniques use pre-existing powder that is fed into a plasma torch or an oxy-fuel torch. Figure 11 is a schematic of a plasma torch for spray deposition. The powder is drawn into the plasma or flame where it is melted and accelerated towards the substrate to be coated. Both of these more modern techniques are capable of very high temperatures (in excess of 3000°C) and velocities (Mach 3) which enables the processing of even most refractory materials and the increased

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velocity enhances the bonding strength. Most thermal spray applications are for relatively thin coatings; several thousandths to less than 0.1".

The powder used for thermal spraying techniques vary with the specific technique. However, in general, the powder must be free-flowing and must be able to be carried in a gas stream from the powder reservoir to the hot zone of the torch or gun. Powder that is too coarse settles out of the gas stream or may be too large to reach its melting temperature while in the hot zone of the torch. Powder particles that are too small may evaporate in the hot zone and never reach the substrate as a liquid.

The type of materials that can be thermal sprayed include plastics, metals, and ceramics and mixtures as well. Mixtures are used to form composite or alloyed coatings.

As one might expect, the amount of "over-spray" is similar to that of painting with as little as 10% material usage efficiency (but rarely over 50%) (12). Some of the over-spray may be able to be reclaimed, however, general practice is to discard or recycle the over-spray rather than to attempt to re-use it directly.

Direct Spray Forming:

Spray forming or spray deposition is a technique that possesses aspects of thermal spraying and gas atomization. The formation of powder is actually bypassed as this technique atomizes the material from the melt and directly deposits it on a substrate without intermediate solidification and subsequent remelting. Figure 12 shows a schematic of a spray forming process. Whereas thermal spraying is used to build up coatings spray deposition builds up bulk material such as tubes, billets, and other general forms. The deposited material may reach many inches in thickness. In many cases the material may be used in the as-deposited form. Residual porosity can be eliminated by rolling, extruding, or forging.

The operational parameters are set so that the material reaches the substrate in a semi-solid form. This allows the material to splat/deform to maximize the density of the buildup. Since the material is being applied in individual droplets the degree of chemical segregation is minimized making this process advantageous to difficult to process materials such as super alloys. The final material has a fine-grained fully dense microstructure. As with thermal



Figure 12. Schematic of spray forming (4).

spraying the material usage efficiency is not 100%, however, above 80% is achievable for larger parts (13).

Welding Applications:

Metal and metal alloy powders have been used in welding for many decades. The coating on coated electrodes, the core of flux-cored wire, and the flux of submerged arc welding all contain metal powders which add alloying additions as well as bulk to the filler metal. Recent developments in welding technologies have found new uses for metal powders. One that is used in production is direct laser cladding. This technology entails covering the substrate or work piece with a powder and using a high-powered laser to melt the powder and weld it to the substrate. This differs from thermal spraying and direct spray forming in that the powder and thermal energy are applied separately and, in the case of direct laser cladding vs. thermal spraying, the substrate is intentionally melted to ensure the development of a true metallurgical bond.

The primary advantage of this technology with respect to conventional weld overlay techniques is that the overlay material does not have to be available in a rod or strip form. Many materials useful for cladding are not able to be produced in these bulk forms, however, they are readily available as powders. Furthermore, powders can be mixed to form numerous additional compositions and metal and ceramic powders can be mixed to yield composite claddings.

The powders used in direct laser cladding are usually spherical and classified to remove the fines and very coarse oversize; most of the powders are produced by either gas atomization or centrifugal atomization.

Rapid Prototyping (Stereolithography):

Rapid prototyping (RP) is currently one of the most active areas in manufacturing R&D. The basis of RP is the manufacture of a part by additive processes as opposed to traditional subtractive processes, i.e., the building of a part by adding material only where it is needed in the part rather than subtracting (removing) material from a bulk piece by machining and producing scrap.

RP starts with a CAD (computer aided design) model of the part and sections it into layers. The part is then created by building these layers

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successively. There are many variants of RP including epoxy curing of a liquid epoxy by laser scanning, layering of laser cut sheet material, inkjet application of plastics and waxes, and sintering of powders by laser. Each RP method yields unique properties and they compete on accuracy (tolerance), size, speed, and economics. However, none is currently able to make a direct substitute part, that is, a part made from the material that will eventually be used in the production part.

The ability to use RP to make a fully functional part from a metal is an active area of current RP R&D. The most common approach to this is direct laser sintering of powder. A bed of powder is doctored onto a platen to a controlled thickness. A laser then scans the powder and the thermal energy of the laser partially sinters the powder to a solid. Successive layers of powder are built up and laser scanned/sintered. The excess powder is removed at the end of the process and the partially sintered part is subjected to a sintering cycle in a furnace to yield full density.

The ability to reliably doctor a controlled thickness of powder and get repeatable sinter shrinkage requires a free-flowing powder. This is best achieved with a powder with a narrow size distribution of spherical particles. Gas or centrifugally atomized powder that has been precision classified to size is the current powder of choice.

The ability to RP a part in metal has incredible potential, however, it is far from a reality at this time. It has been found that direct sintering is difficult as the coupling of the laser energy to material in powder form is inefficient and erratic and the in-situ shrinkage makes it difficult to maintain part tolerance. A second approach uses a binder mixed with the powder which is melted by the laser and acts to bond the metal particles. The metal/binder composite is then subjected to a debinding and sintering treatment to yield the part. This area of P/M is very challenging. There is sufficient potential for overcoming the current technical obstacles, however, it is presently far from being able to be used as a manufacturing tool.

A similar technology, Directed Light Fabrication (DLF), also uses metal powder and a laser to produce near net shapes. In this RP method the powder is melted and deposited rather than sintered. The result is a fully dense part, however, the technology currently suffers from the downfalls of other RP processes, namely, tolerance, surface finish, speed, and overall economics (14).

IV CURRENT APPLICATIONS OF P/M PROCESSES TO JEWELRY AND PRECIOUS METAL

P/M processes have been shown to be used in manufacturing for net and near net shape processing, bulk material processing, joining, and for surface applications. P/M processing is a relatively new technology with respect to casting, forging, and machining, however, it has become the manufacturing process of choice in areas where it competes favorably on cost, where it provides superior quality, or when conventional manufacturing methods are not able to process the materials.

P/M is used in many precious metal applications such as in the dental field as amalgams and ceramic bond coatings, electronic applications such as contacts and solder pastes, and in jewelry manufacturing as solder pastes. P/M, for net shape manufacturing, generally requires many thousands of parts to make it economically feasible. In this respect P/M has not been commercially applied towards those jewelry items currently cast and stamped in quantity as P/M has only been recently been introduced to this field for high volume processing. Jewelry items such as watch cases and watch band parts are currently in production but in stainless steel or WC/Co (watch cases). However, there a few applications of P/M that currently exist in other areas of jewelry and art.

Press and Sinter: Beynon, et. al. (15) have been practicing P/M with precious metals for over 15 years. Their application involves the press and sinter technology alone and in combination with rolling to achieve special visual effects and material bonds not able to be brought about otherwise. A mix of precious metal powder is die compacted to a form and sintered. However, rather than producing a homogenous mixture, the different metal and alloy powders are loaded into a die individually to achieve a layered or random pattern. The sintered compact can be sliced and polished at this stage. The cross section has a very unique pattern. This is similar to work done by Taylor et. al. (16) more recently. In another variation Beynon rolls

the sintered compact which further densifies it and changes the patterning by melding some of the interfaces and adding some directionality. Each piece of jewelry has unique patterns, texturing, and colors as many of the processing steps such as powder mixtures, die loading, slicing, and rolling are varied for each batch.

Thermal Spray: Thermal spray technology has been applied to artwork in the form of coating large scale sculptures to achieve colors and designs not able to be produced by casting. This primarily cosmetic use of thermal spraying began as a government project developed at Los Alamos National Laboratories (LANL) for nuclear containment. The recent push to commercialize these government sponsored internal technologies has lead to a spin-off company involving LANL scientists and artists working in the local art community (17). The metal spray technology can apply practically any metal as a coating but copper alloys, stainless steels, and monels and nickel alloys are the primary focus. Silver and silver alloys have been thermally sprayed at LANL and also for naval research applications such as coatings for sea water valves (18), however, it also has potential for large scale sculpture. Although it was mentioned earlier that the material usage efficiency is low, applications to large expanses of surface area will increase this efficiency. Castings which are too large to be plated can have precious metal coatings applied via thermal spraying.

Precious Metal Clay: Currently available commercially is a clay made of a water soluble binder and precious metal powder (19). This material works much like modeling clay and its advantage over MIM type materials is that it can be worked at room temperatures and at low pressures (by hand). The material is available in silver, gold, and platinum alloys. Debinding and sintering are done in air in fairly standard kilns. The binder content of these clays is much higher than typical MIM feedstocks and thus the amount of shrinkage is greater as well. These clays are difficult to sinter to full density; 85% is about the limit achieved in simple ovens. This finished part has a interconnected porous network and a matt surface finish. If a reflective surface is required the surface must be burnished. The low density will yield lower strength and ductility with respect to cast or high-density P/M material. In addition, the interconnected porous network is detrimental as the material will act as a sponge to the ambient environment.

The precious metal clays are not meant as a mass production tool, rather, they add another dimension to the art of jewelry as the finished piece retains its hand-crafted features and artifacts.

V P/M APPLICATIONS WITH POTENTIAL FOR MASS PRODUCTION OF JEWELRY

P/M technologies have competed with and successfully replaced investment cast and machined parts in numerous non-precious metal systems. In the case of conventional materials the primary benefits of P/M are in the reduction of the manufacturing costs by elimination of secondary operations and labor overhead. In most cases the cost of the powder is greater than that of wrought or cast material but the increased material usage efficiency of P/M yields net savings in material cost as well. This increased efficiency in material usage should be especially attractive to mass production of precious metal components.

The two P/M manufacturing methods most suited for mass production are 1) press (die compaction) and sinter (P/S) and 2) MIM.

Press and sinter has not been applied to mass producing jewelry items. For the most part conventionally cast jewelry products made from karat gold and silver alloys do not exhibit the geometrical attributes that would give P/S processing an advantage. However, ring and coin blanks, being axially and radially symmetric, are prime candidates for P/S processing. The residual porosity in these P/S parts will be reduced to insignificant levels by the subsequent coining and rolling of the blanks as they would be subjected to in their conventional processing. Coin blanks are typically made by stamping sheet. Ring blanks can be made from casting, stamping, or slicing tubing made either by sheet processing or continuous casting. In all of these cases the production of scrap affects the economics of the process. It has been shown previously (20) that the yield for conventional coin blanking via the cast/roll/stamp process is approximately 35% and the yield for ring blanks produced via the cast/roll/tube/slice process is approximately 50% (21) whereas press and

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sinter processing yields approximately 90% product from each melt. The majority of the savings is due to the efficiency of the pressing operation as only the material needed for each blank is used rather than putting added value into material that will ultimately be scrap. The savings are amplified for materials which require significant work to melt and process such as platinum alloys. The growing market for platinum wedding bands should stimulate investigation into the powder processing of platinum.

The current status of P/S in jewelry applications is in R&D investigation only.

MIM has been very successful in competing with investment casting for manufacturing small highly detailed parts from stainless steel (22). Figures 13 and 14 summarize the process steps for MIM and investment casting, respectively. A visual comparison of the two figures shows that MIM entails fewer steps and is less complex than investment casting. The plastic injection of the core is similar to injection of the MIM feedstock, however, substantial cost savings are a result of the complete elimination of the investment process, casting, and the associated labor. Most of the MIM process steps require lower levels of labor skills with respect to investment casting.

One early obstacle to the acceptance of MIM was the need for rigid tooling and plastic injection molding technology to manufacture the green part. Only recently has the use of plastic injection molding to produce plastic cores become widely accepted and implemented in the jewelry industry (23). Prior to this cores were produced by wax injection into rubber molds and many interested in investigating MIM wanted to retain this technology for making MIM green parts. Unfortunately the pressures and temperatures required to process a typical MIM feedstock are much higher than can be tolerated by the rubber mold system. Plastic injection using rigid tooling is becoming more commonplace for investment cast core production in the jewelry industry and familiarity with it will open more opportunities for MIM to be considered.

Numerous prototype precious metal jewelry items have been produced by MIM and a selection are shown in Figure 15. One concern of the investigators was the surface finish of the as-sintered part. Most potential users of MIM technology would like to retain as much as possible of their current manufacturing methods for reasons of economics

MIM



Figure 13. MIM process flow chart.

INVESTMENT CASTING PROCESS



Figure 14. Investment casting process flow chart.



Figure 15. Prototype MIM jewelry pieces.

and familiarity and have rejected MIM parts because they may require different finishing techniques than currently in-house. The finishing technology is progressing and new methods are emerging, such as magnetically stirred steel shot and needles. The philosophy to retain older finishing technologies may not be justified. In actual practice on prototype precious metal parts it has been found that MIM parts can be easily finished to the same high standards as investment cast parts (24).

Investigations of prototype jewelry parts made by MIM show advantages when applied to small parts such as findings or small charms. Many of these parts can be processed by MIM more reliably than investment casting, especially those that are difficult to tree or those with small cross sections that are difficult to fill (25). In addition, satisfactory surface finish and properties have been achieved at the 97% to 98% density level (26). This represents a material savings which can be very economically beneficial for parts sold on a per piece basis.

VI CURRENT ISSUES PERTINENT TO THE DEVELOPMENT AND IMPLEMENTATION OF P/M TECHNOLOGIES IN JEWELRY MANUFACTURING

P/M processing has replaced several manufacturing practices in applications with conventional materials. The advantages of P/M in these cases can be directly conveyed to precious metals and sometimes amplified due to the inherently higher material usage efficiency of P/M. Yet progress investigating and implementing P/M as a primary process in jewelry manufacturing is slow.

P/M is now the fastest growing method of parts manufacturing yet it has been a commercial entity for over 50 years. P/M technologies were once thought of as too unconventional and risky for traditional manufacturers to invest time and money. It took many years for the infrastructure to develop and evolve to a degree where P/M no longer appeared to be an academic curiosity or a highly specialized technology that was difficult comprehend and master. However, with respect to precious metals, P/M is still relatively new and the infrastructure is not yet in place to provide materials (precious metal alloy powder), properly scaled equipment, and a knowledge base to the extent that these technologies are available "off the shelf". Much of the P/M processing technology, such as compaction die design, MIM injection processing parameters and part and mold design is available from other manufacturing sectors but a communication link has not been established between the conventional material P/M industry and jewelry manufacturing. Of more importance is a need for a knowledge base for sintering precious metal alloys and sources of precious metal alloy powder. Precious metal alloy powders are available and may be obtained from those concerns currently producing powder for solder pastes. Equipment for producing powders specifically tailored to these P/M applications are commercially available as standard items (27,28). Alloy development is needed to optimize the precious metal alloys compositions for P/M applications. The characterization of these powders and their sintering response to the various combinations of time, temperature, and atmosphere type is the basis of the R&D that has to be undertaken by those interested in investigating precious metal P/M.

The development of this infrastructure may occur within the individual jewelry manufacturer which would keep the information proprietary. Another possibility is for precious metal powder manufacturers to develop the P/M technologies and offer this information as a package with sale of materials.

VII CONCLUSIONS

P/M processes are varied and comprise technologies capable of producing fundamental shapes, net shapes, coatings, brazes and solders, among many other functions. Many P/M processes are well-developed in the manufacturing of conventional (non-precious metal) materials and are the primary method of choice in many parts manufacturing applications.

This paper has presented a overview of P/M technologies including those that are well developed and commercialized and those that are in the R&D stage. This paper has pointed out many direct applications of P/M in jewelry manufacturing, however it is left to the reader's creativity to envision other applications that may have potential.

Prototype jewelry items have been produced by P/M technologies, specifically MIM, and have been found to be competitive with investment cast parts on a quality basis.

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