FABRICATION OF A 3D STRUCTURE FROM GRANULES VIA SINTERING

Dr. Joseph Tunick Strauss

The use of granules to decorate a surface is well known and has been practiced for centuries. This work investigates the construction of a 3D piece entirely from granules. The granules will be arranged in a mold to impart a three-dimensional form. Diffusion bonding of the granules to each other will be achieved by sintering or hot pressing: the application of heating and deformation. The goal is to produce a robust form with a unique aesthetic appeal.

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INTRODUCTION

The work for this study was inspired by David Huycke's paper on granulation.[1] Here he introduces "structural granulation", which is the construction of an entire piece from granules alone rather than just adding granules to a surface for decoration. Granulation, in any application, is a very labor-intense operation as each granule must be individually bonded in place and a piece can contain thousands of granules. One of the goals of this paper is to see if this can be streamlined using powder metallurgy processing.

Another goal of this project is to expand on structural granulation to make an object that may be more than a single layer of granules in thickness, using multiple sizes of granules, and to deform them at their points of contact to get an unusual artistic effect.

GRANULATION AND POWDER METALLURGY

There are some similarities between structural granulation and powder metallurgy as both are used to make objects from spheres. Obviously, there is difference in scale: granulation uses spheres that are generally between 1 mm and 4 mm in diameter whereas powder metallurgy uses powder particles that are typically two orders of magnitude smaller in size.

In the method of granulation described by Huycke, reaction soldering is used to bond the granules to each other. In short, this entails coating the granule with a metal salt that decomposes to the metal, which then alloys with the granule to form a phase that has a lower melting temperature than the granule. Under controlled heating, this results in a formation of a liquid layer on the surface of the granule and the substrate. A "neck" is formed between the granules and/or the granule and the substrate. This is shown in Figure 1. Similarly, powder metallurgy relies on neck formation between particles for bonding. However, this is usually achieved without the addition of a liquid. The formation of the neck is achieved by solid state diffusion of the atoms from the individual particles to the contact point between the particles. This process, carried out at elevated temperatures, is called “sintering.”

Figure 1: The formation of a neck between the granule and a substrate.[1] *The granules are 2 mm in diameter.*

Sintering: In most powder metallurgy processes, a technique (pressing, molding) is used to impart a shape to a mass of powder. However, this shape has little or no useful mechanical properties as the individual metal particles are not metallurgically bonded to each other. Sintering is the high temperature heat treatment that increases atomic motion and mobility so that particle-to-particle bonding and densification of the powder compact can occur. At elevated temperatures the atoms within the powder particle can diffuse across particle contacts and bond the particles together.

The driving force for sintering is the reduction of surface area and its associated surface energy. For a given mass of material, the more it is physically divided into parts (powder particles, for example), the greater the amount of surface area the mass has. The specific surface area of powder is very high compared to granules or larger objects. There is a surface energy associated with the surface area of all entities. With respect to a mass of solid material, a collection of powder particles contains an excess amount of surface area and its associated surface energy. The excess surface is that surface between particles and the interfacial area between a particle and a space or 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. Contact points are replaced by grain boundaries, which can further reduce the surface area with subsequent grain growth.

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

The diffusion of atoms is a thermally activated process; increased temperature provides the energy for diffusion. 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 specific surface area (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 sluggishly 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 bonding the particles together and eliminating pores, both which result in shrinkage of the assembly of powder particles. This is shown schematically in Figure 2. The progression of sintering, as defined by the extent of neck formation, is shown from a through d. Figure 2a shows the beginning of sintering: bonding and initial neck formation. Figure 2b shows further neck development. Figure 2c Shows pore rounding and closure and Figure 2d indicates densification and pore shrinkage.

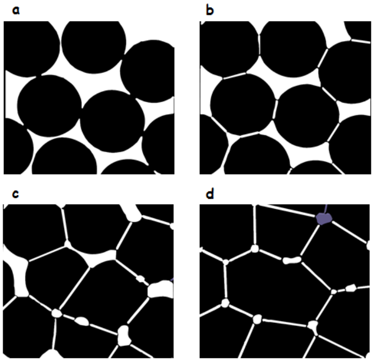


Figure 2: Schematic of sintering development:
a. Initial bonding, neck formation, b. Neck growth, c. Pore channel closure and Pore rounding, d. Densification/pore shrinkage.

Powder particles vs. granules: Figure 3 shows an assembly of powder particles, approximately 10 microns in diameter, that have started to sinter. The development of the necks between the particles is very similar to that of the necks shown in Figure 1. However, as mentioned above, the size (diameter) of a powder particle is about 1/100th the diameter of a granule used in surface decoration.

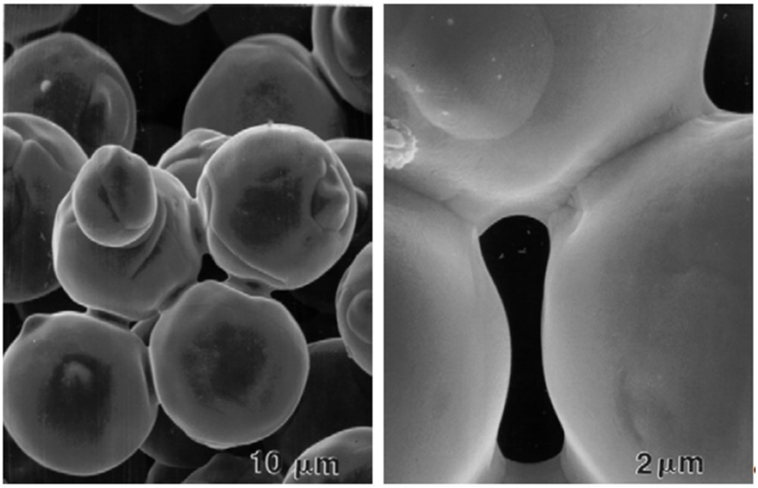


Figure 3: Particles 10 microns in diameter showing necks developed in sintering.

SINTERING THEORY

For this study, it is not necessary to cover the thermodynamics behind sintering theory. Of greater importance and application is to examine the geometric factors, specifically particle size, and see how they relate to the time necessary for sintering.

Consider a simple model of two particles sintering together as shown in Figure 4. The geometric development of neck formation is referred to as X/D where x is the diameter of the forming neck and D is the diameter of the particle.

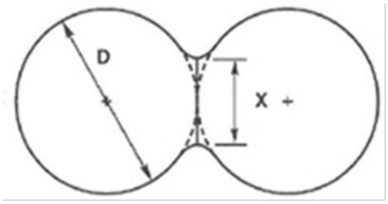


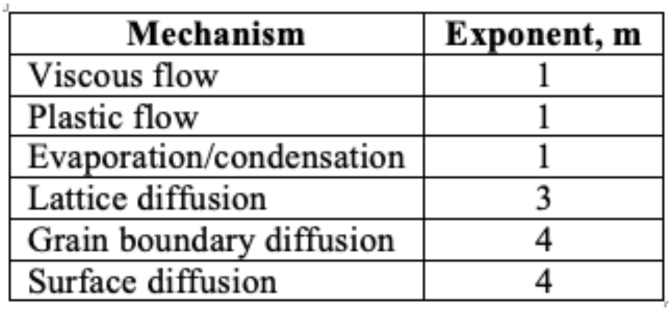
Figure 4: Schematic of model for describing the particle diameter (D) and the developing neck (X) (from Kuczynski[3]).

Herring[4] further developed on this model to scale the time to develop a neck with the diameter of the particle.

$$(t_1/t_2) = (D_1/D_2)^m$$

Here, t_1 is the time to sinter particles of diameter D_1 to a specific X/D ratio, t_2 is the time to sinter particles of diameter D_2 to the same X/D ratio, and m is the atomic transport mechanism exponent. Table 1 summarizes the mechanism and the associated exponent.

Table 1: Atomic transport mechanisms and their associated exponents for the Herring model.



Mechanism	Exponent, m
Viscous flow	1
Plastic flow	1
Evaporation/condensation	1
Lattice diffusion	3
Grain boundary diffusion	4
Surface diffusion	4

The physical implication of the Herring model is that if the time to sinter to a certain (X/D) and diameter of those particles are known, then the time to sinter to the same extent for larger particles can be estimated as a function of the atomic transport mechanism. Again, if one is deforming the particles to develop a neck (plastic flow) the time to achieve a certain level of sintering is simply the ratio of the particle diameters. However, if other mechanisms are controlling the atomic transport, then the time to sinter may be greatly increased. For example, in Figure 3 the time to develop necks to that extent via surface diffusion between these 10 micron particles was probably in the vicinity of 30 minutes. In the case of sinter-bonding granules of 2 mm (200 times larger than 10 microns), the time to develop necks to the same extent would require a factor of 1.6 x 10^9 greater if the atomic transport mechanism is controlled by surface diffusion. This translates to approximately 91,000 years. Even if the temperature was increased to allow lattice diffusion to dominate, the time for solid state sintering of 2 mm granules is on the order of 450 years.

Clearly, relying on solid state diffusion alone for sintering of granules is not tenable. However, we can examine sintering to a lesser extent on this size scale. Also, one of the goals is to deform the particles for aesthetic reasons. This will significantly reduce the time for neck development.

OBJECTIVES

The primary goal of this study is to fabricate a structure made from granules of mono-sized or mixed sizes and partially deforming them. Figure 5 is a CAD rendition of this goal. The second goal is to do this in a manner that does not require the labor-intensive manual operation as detailed in.[1]

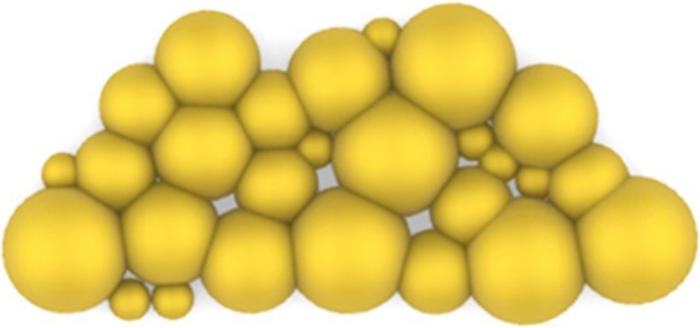


Figure 5: CAD rendition of the goal of this project (from Poirier).

METHODS

Copper spheres were used for the study as they were readily available in various sizes. The techniques used for copper should be applicable to most other ductile metals providing that their oxides can be reduced in the nitrogen/hydrogen atmosphere at or below the sintering temperatures.

Sintering was performed in an atmosphere-controlled retort furnace. A mixture of nitrogen and hydrogen was used as the process atmosphere.

In order to eliminate the individual placement and bonding of the granules, graphite tooling was made to contain the granules in a plane or other geometry such as a cylinder, band, or ring.

INITIAL SINTERING TRIALS OF SPHERES

To test the feasibility of solid-state sintering of these large spheres, a small graphite mold was filled with 3 mm Cu spheres and sintered at 1025°C/1877°F for 24 hours. Figure 6 is a picture of the sintered product. Although the spheres sintered together into a coherent mass, the bonding strength was low, and the piece shed some of the outer spheres when handled roughly. Further experiments at higher temperature (up to 1040°C/1900°F) and for longer times (48 hours) produced stronger pieces.

Figure 6: Cylinder made from 3 mm spheres loose sintered in a graphite mold.

TEST PIECES: SINTERED MONO-SIZED SPHERES

Based on the initial success, graphite molds were made in several configurations: plane (approximately 12.7 cm, 5” square), strip (approximately 1 cm x 6.4 cm, 3/8” x 2.5”), a ring (2.54 cm OD x 1.9 cm ID, 1” OD x 3/4” ID), and various sizes of cylinders. In all cases spheres could be easily loaded into place. Figure 7 shows the planar array prior to sintering. These molds were filled with 3 mm copper spheres and sintered for 48 hours at 1040°C/1900°F.

Figure 7: Planar array of 3 mm copper spheres. Size is approximately 12.7 cm (5”) per side.

Figure 8 is a closeup of the contact area between two spheres after sintering. The neck can clearly be seen to show that the sintering process is operational even at this large scale. The neck is about ¼ mm (0.010”).

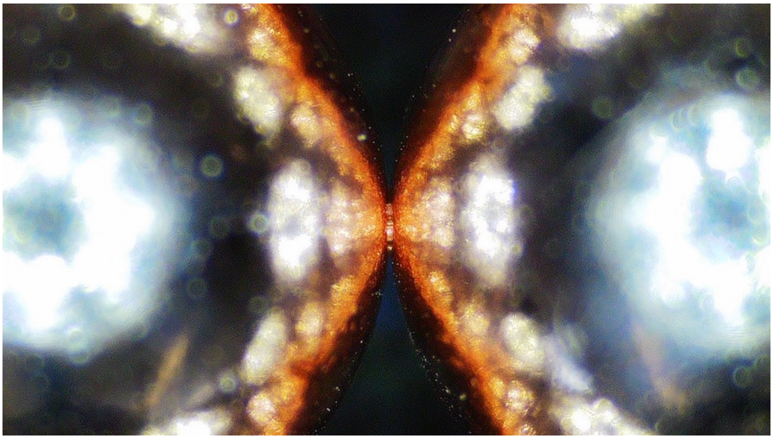


Figure 8: Sintered neck between two 3 mm copper spheres.

The sintered spheres did bond into coherent shapes. All the parts were handleable but quite "soft" and could be deformed easily. Spheres near the edge of the plane and strip could be removed by hand. Figure 9 shows the planar array rolled up to demonstrate the formability. However, even gentle handling would buckle the rings. Figure 10 is a ring shape made from 3 mm copper spheres. Although interesting looking, it does not possess the strength needed to wear.

Referring again to Figure 8, a ¼ mm neck is only about 8% of the diameter of the 3 mm sphere. A rough estimate would imply that the strength could only be expected to be a fraction of that of the sphere (less than 1% based on area). Additionally, a collection of well-packed spheres (packing factor of 74%) could only be, at best, 74% the strength of a solid. Thus, a collection of spheres bonded by small necks should be expected to be weak with respect to larger necks via soldering (larger necks) as per ref. 1 or to a solid mass of material. Further examination of the array of sintered spheres shows that not all contact areas develop into necks as shown in Figure 11. This also decreases the overall strength of the sintered construction. Certainly, larger necks could help increase the strength but at the cost of greatly increasing the processing time.

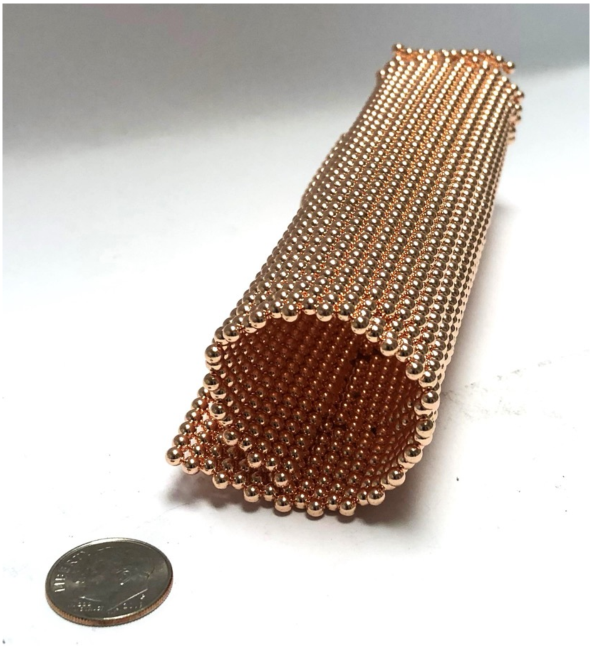


Figure 9: Sintered planar array of 3 mm spheres showing degree of formability.

Figure 10: Ring made from 3 mm copper spheres.

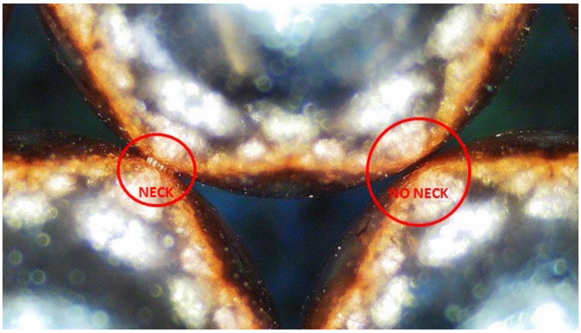


Figure 11: Close up of sintered copper spheres showing regions of neck formation and region with no neck.

TEST PIECES: PARTIALLY DEFORMED MONO-SIZED SPHERES

Deforming the spheres to provide the aesthetic appearance in Figure 5 serves a second purpose: increasing the contact area, and thus the strength of the piece. Deformation can be achieved at room temperature by compacting the piece in a rigid die or it can be done at elevated temperature by hot pressing. If the deformation is done at room temperature, this must be followed by a sintering heat treatment to diffusion bond the newly formed contact area. However, since the deformation creates the increased contact area, the sintering time and temperature can be significantly reduced. In hot pressing, the sintering and formation of the increased contact area occurs simultaneously. Figure 12 shows the ring after compacting approximately 20% at room temperature. The amount of contact area is considerably increased. Although the strength of the piece was increased after the cold deformation, a short-term sintering (60 minutes at 750°C/1380°F) allowed the contact areas to develop metallurgical bonds and the strength increased substantially to the extent where it may be worn as a ring.

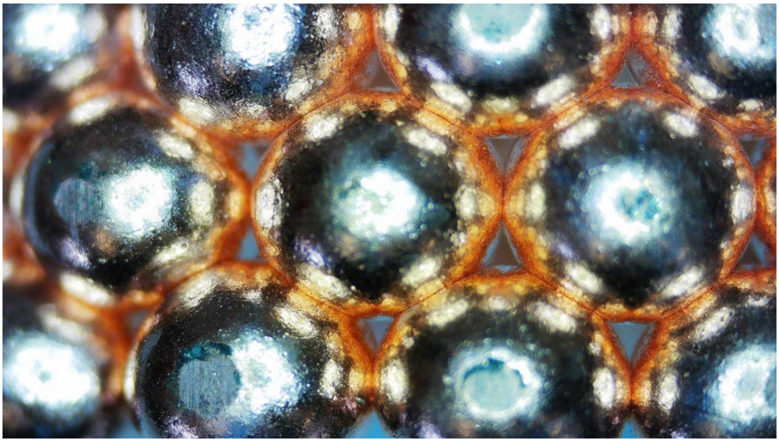


Figure 12: Sintered 3 mm copper spheres after ~20% cold compaction.

The deformation was performed in a rigid (hard metal) closed die. This had the consequence of producing a flat on the spheres where they contact the die or punch face. Attempting to deform the pieces in an open platen press (no support on the OD of the part) caused many of the spheres to break loose. Confining the pieces in a rigid die supported the outer spheres as the contact areas were established. Subsequent sintering produces a very robust part. Figure 13 show cylinders of 3 mm spheres deformed at three levels. Figure 14 shows a ring made from 3 mm spheres compacted approximately 30%.

Figure 13: Cylinders of 3 mm spheres deformed 10%, 20%, and 30% left to right.

Figure 14: Ring made from 3 mm spheres compacted approximately 30%.

TEST PIECES: MIXED SIZE SPHERES

The CAD image in Figure 5 shows that there are spheres of about 4 sizes with a ratio of roughly 3.3:2.2:1.3:1. Given the sizes of spheres that were available, this was approximated using spheres with diameters of 3 mm, 2 mm, 1.2 mm, and 0.9 mm. The number ratio was also roughly duplicated.

Particle mixtures are known to separate due to differences in density and size.[5] Although all the spheres had the same density (copper; 8.96 g/cm^3), the difference in size and the lack of interparticle friction due to the size, sphericity, and smooth surface finish made maintaining a randomly dispersed mixture impossible. However, the addition of an adhesive significantly helped keep the sizes dispersed. The adhesive used must be able to be removed cleanly during the sintering cycle. Isopars, polyethylene glycols, and petrolatum have been successfully used for this purpose. Still, the dispersion of the 0.9 mm spheres was very difficult as they tended to stick to each other rather than disperse. For this reason, the use of 0.9 mm spheres was eliminated from this study.

Rings and cylinders were made from the mixed spheres and PEG300 (trade name for polyethylene glycol 300 molecular weight). Figure 15 is a sintered ring made of a mixture of sphere diameters. The dispersion technique still needs some optimization. However, in the non-deformed configuration the use of the mixed sizes of spheres causes inefficiencies in packing and many spheres cannot contact their nearest neighbors, producing a weak and fragile structure. In the sintered-only form the ring was very weak and tended to shed spheres easily.

Figure 15: Ring made from a mixture of 3, 2, and 1.2 mm copper spheres.

TEST PIECES: PARTIALLY DEFORMED MIXED SIZE SPHERES

Cold deformation of the pieces made from mixed size spheres was somewhat difficult. The random inefficient packing can produce spheres connected by one point only and they are prone to separating. Figure 16 shows a mixed sphere ring compacted approximately 30%. Figure 17 show cylinders of mixed spheres deformed at three levels. Again, a post-deformation sintering treatment rendered the pieces very robust for handling.

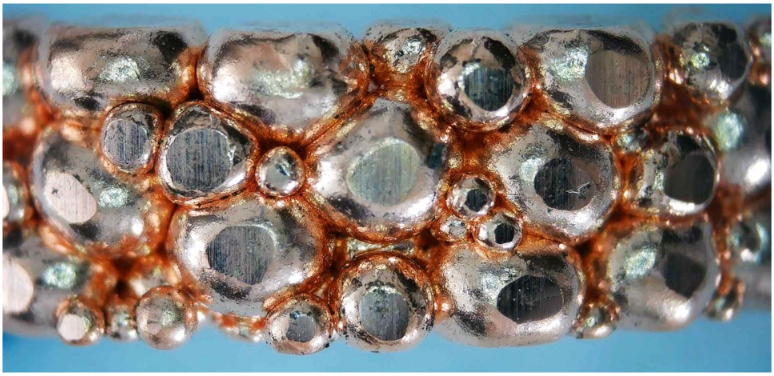


Figure 16: Ring from mixed spheres deformed approximately 30%.

Figure 17: Cylinders of mixed spheres deformed 10%, 20%, and 30% left to right.

HOT PRESSING OF SPHERES

Hot pressing was shown to be able to produce fully dense articles from material forms that poorly pack such as spheres, wire, machine turnings, and powder.[3] In summary, hot pressing entails the simultaneous heating and compaction of material. The pressure applied exceeds the yield strength of the material being pressed and plastic flow becomes the rate controlling factor for sintering. In most cases, full density is achieved in a few minutes.

In this study hot pressing is used just to create sufficient contact area and bonding to yield a part where the spheres are still individually distinguishable and with sufficient strength to function. Hot pressing was performed in graphite tooling at 750°C/1380°F with the pressure applied for 30 minutes. Rather than press to a pressure, the tooling was equipped with mechanical stops to be able to control the amount of deformation. Figure 18 shows a hot pressed piece of 3 mm spheres deformed approximately 30%. A significant amount of bonded contact area was created yielding a very robust piece.

Figure 19 shows a hot pressed item made with mixed spheres and deformed approximately 30%. The increased and bonded contact area made the piece very mechanically robust.

Figure 18: Hot pressed piece made from 3 mm spheres.

Figure 19: Hot pressed piece made from mixed spheres.

All of the pieces that were compacted in rigid tooling, cold or hot, exhibited flats on the surfaces contacting the tooling. Although the deformation produces a high-strength piece, the flats detract from the original objective of the project.

LIQUID PHASE SINTERING

Not all sintering of powder metal parts occurs by solid-state diffusion. Atomic mobility through a liquid is much faster than through a solid. A liquid can be introduced by the addition of another material that has a lower melting point than the matrix phase (powder or spheres). When the melting temperature of this second phase is exceeded, the liquid is formed and is drawn by capillary action to the particle point contacts. This occurs very rapidly (seconds to minutes) and quickly establishes particle-to-particle bonding.

This method is used commercially in the manufacture of WC/Co cutting tools and it is also the mechanism that allows the use of metal dental fillings using an Ag-Cu alloy and Hg as the liquid.

Huycke,[1] in reactive soldering the spheres together, is essentially liquid phase sintering on a macrolevel. It is rapid, forms relatively large necks, and usually involves alloying, which produces a stronger joint. In this application, a similar effect is produced by coating the spheres with Cu8P powder. This was achieved by mixing the spheres with PEG 300 and fine (-635 mesh) Cu8P powder (1% and 1.2% by weight, respectively). This conformally coated the spheres with Cu8P powder. This mixture was loaded into graphite molds and sintered at 750°C/1380°F for 20 minutes in a mixture of nitrogen and hydrogen. Cu8P melts at approximately 715°C/1320°F, so it was fully liquid at the sintering temperature.

Figure 20 is an assembly of 3 mm spheres that have been liquid phase sintered using Cu8P. The necks between spheres are fully formed as the liquid appears to fill all of the gaps that may occur in solid state sintering when there are slight lattice mismatches within the array.

Figure 20: Assembly of 3 mm spheres liquid phase sintered.

Figure 21 shows rings made by liquid phase sintering of spheres in a graphite ring mold.

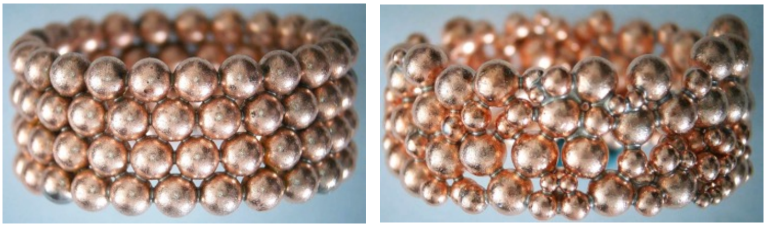


Figure 21: Ring from 3 mm spheres liquid phase sintered (right). Mixed spheres liquid phase sintered (left).

The rings made via liquid phase sintering appeared to be very strong. Rather than deforming them using a rigid die, these rings were deformed in a platen press without any support or constraint on the outside surfaces. The pieces did not break or shed spheres. Figures 22 and 23 show the liquid phase sintered rings after being deformed using a platen press. The pieces exhibit deformation of the spheres but without the flats caused by the constraint of a rigid die.

Figure 22: Ring made by liquid phase sintered 3 mm spheres deformed approximately 20% with a platen press.

Figure 23. Ring made by liquid phase sintered mixed spheres deformed approximately 20% with a platen press.

FUTURE WORK

Pieces made from spheres and mixed spheres were successfully produced by a variety of methods: loose sintering, hot pressing, and liquid phase sintering. Due to the limited strength of the loose sintered pieces, producing the deformed effect required that the deformation be performed in tooling that confined the piece. This produced undesirable flats on the surfaces that contacted the tooling. It was found that the liquid phase sintered parts contained sufficient strength to be able to be deformed in an unconfined manner, which produced a part without flats on the exterior surfaces. It is thought that additional sintering time of the loose sintered pieces may produce enough of a neck to provide the strength needed to survive the unconstrained deformation. This may require sintering times of up to a week at elevated temperatures in a protective atmosphere. While energy intensive, this would be the least labor intensive and least complex method. Another possibility would be to use urethane tooling to support the weaker pieces during platen press deformation. This would allow the part to be deformed without forming flats on the outside surface. The end result would be a robust part made by diffusion bonding of the spheres without the complex addition of a second material.

CONCLUSIONS

1. Sinter-bonding of “macro” spheres was achieved via loose-sintering.
2. The necks formed on 3 mm spheres in 48 hours of sintering did not provide sufficient strength to function as a wearable jewelry item.
3. Deformation of the loose sintered pieces increased the contact area. Subsequent sintering completed the bonding of the additional contact area and yielded a robust piece.
4. Hot pressing provides a compacted form with good mechanical properties.
5. Die compaction and hot pressing produces external surfaces with flats, which were not desirable as per the original goal.
6. Liquid phase sintering produces a strong structure without compaction.
7. Compaction of the LPS structure was possible without confining tooling and allowed the creation of a deformed piece without surface flats.

REFERENCES

1. D. Huycke, “Decorative and Structural Granulation in Larger Silver Artefacts,” *Proceedings of the 34th Santa Fe Symposium*, May, 2022, pp.287-309.

2. G.C. Kuczynski, “Self-Diffusion in Sintering of Metallic Particles;” J. Inst. of Metals, Feb. l949, p. 75.

3. J.T. Strauss and C. Ploof, “Mokume Any Other Way?” *Proceedings of the 25th Santa Fe Symposium*, May, 2011, pp.461-475.

4. C. Herring, “Effect of Change of Scale on Sintering Phenomena,” Journal of Applied Physics, 21, 301 (1950)

5. A. Rosito, K.J. Strandburg, F. Prinz, and R.H. Swensen, “Why Brazil Nuts Are on Top: Size Segregation of Particulate Matter by Shaking,” Physical Review Letters, 1987, vol. 58, pp 1038-1040.