Powder Metallurgy

The Idea

Advanced

If you made your way up to this module, you realized that it is not so easy to produce an iron or steel object with a *uniform* structure from "scratch". That is true for sword blades and for about anything else. If you also want the grain size to be very small, say below 1 µm, the task is well-nigh impossible.
Let's review the production processes discussed so far:

- **1. Forging:** With a hammer we can bang a piece of iron into some desired shape. That, as you know now, was the time-honored way to make *all* iron or steel objects for several thousand years. It goes without saying that it takes a bit of practicing before you can shape a complex object like a sword blade by hitting a lump of steel a few thousand times with a hammer. The internal structure obtained in the final product depends on its original composition, how hard you hammered the parts, and in particular on the heating and cooling always going with forging.
  The grain size can never be very small since high temperatures are involved. There is just too much time for grains to grow.
- **2. Casting:** If you can actually melt your iron or steel, casting itself is comparatively easy. However, segregation and different cooling rates of inside and outside will make sure that the structure is not uniform.
  The grain size can never be very small since high temperatures are involved. There is just too much time for grains to grow.

That doesn't look so good. What can we do? Well, for starters, open your eyes and look around you. See any objects with complex shapes that have a rather uniform internal structure? Here are a few:

Classy Ceramics

- If you don't own fine ceramics with artistic value, look at something prosaic like your coffee mug or dinner plates. China (porcelain) has a rather uniform internal structure (look at the pieces when you drop your coffee mug) and certainly comes in complex shapes. How is it made?
  Certainly not like this well-known piece of art:

Essentials of the Venus de Milo

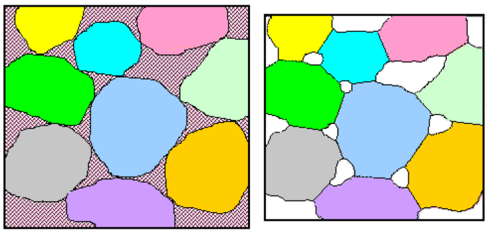
  - The unknown artist who created this masterpiece around 100 BC "simply" did it by taking a big piece of marble and banging away everything not needed. It goes without saying that shaping a complex object like this by banging off the the superfluous material takes a bit of practicing and a lot of time, not to mention a shapely and consenting model.
    Alas, the method is not amenable to mass production (although those ancient Greeks did run some factories producing Aphrodites and the like in quantities) and thus will never be able to produce cheap objects. That doesn't mean that we don't use it to some small extent. Whenever we grind, file or polish, we are scraping off parts of the material but usually only from an almost finished object shape and rarely "from scratch".

- So how do we make relatively cheap china? By **sintering**! And what, exactly, is sintering? Well - let's look at that like 1-2-3:

  1. Produce some powder of the material your object should consist of. For china, it is essentially aluminum oxide, Al_2O_3 and silica. For the time being, you might make a powder the same way you make flour: Run bigger pieces of the material to be powderized through a mill.
  2. Mix your powder with suitable liquids (oil, water, solvents, ...) called a "binder" and produce a kind of viscous goo; just like the mud your kids like to wallow in.
  3. Shape the goo (called "clay" in pottery) into the desired form (called a "green") and "fire" it, i.e. make it really hot for some time. Let it cool down, take it out of the mold if here was one - and here you are!

  - Well - almost. I omitted points 4 - 50 or so of the finer details. It's exactly like pottery, except that here you make your "clay" yourself and don't dig it out of the earth.

- Note that proper sintering does not work by *gluing* the particles of the primary material together. The end product consists *only* of the material itself, there is no glue involved. All the binder material should be completely burned off. You get shiny solid china because the formerly individual particles *grow* together at the firing temperature. This can be visualized like this:



Sintering by diffusion

Before firing: Particles just touch at a few points; in the interstices is (liquid) binder material.	**During firing:** Particles grow together by forming "necks". The binder materials is gone; the volume shrinks a bit.

  - Different colors symbolize different orientations of the (crystalline) grains; the hatched area on the left stands for the binder material (also called "flux" on occasion). "Necks", containing a grain boundary, develop between the grains and grow. Since the volume originally occupied by the binder must shrink as the necks between the particles grow larger, the final product will also be smaller than the mold.

- Do I need to emphasize that atoms need to move for a sintering mechanism as shown above? Obviously, diffusion is the primary mechanism for forming one solid piece of material out of zillions of small particles!

  - Solid, yes. But only up to a point. Getting completely rid of the empty corners in between the former particles would need very long firing times at the highest temperatures possible. Time (and temperature) is money, so we usually stop the process long before "compaction" close to 100 % is reached. Sintered ceramic materials therefore are always porous to some extent.

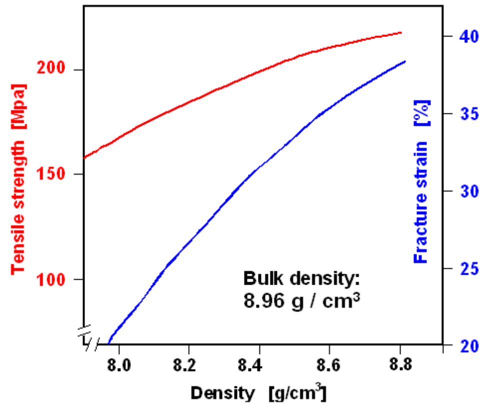
- The question coming up by now is evident:

Can we make a (superior) sword blade by sintering steel particles?

- Well - why not? Diffusion works for metal particles, too, and making mud with metal particles should not be all that difficult either. Or is it?

The Reality

- Making metallic objects by sintering metal particles together is called "**powder metallurgy**". While it's not easy, it is a fast growing branch of metallurgy. So what are the problems? Here is a list:
    - How do you make small metal particles? I'm talking a few µm or even smaller since we want very small grains for added hardness. Simple milling won't work: After some size reduction you are just going to smear the stuff all over the place and you (pressure) weld particles together just as often as you break them up.
    - If you somehow made particles with, say, 50 nm in size, they will immediately oxidize ("rust") if exposed to air. With an oxide layer 5 nm thick (invisible to the naked eye) about 50 % of the volume is now rust and not metal. What will you get when you start sintering? Probably not a superior blade.
    - Are you aware of the fact that powders of many metals (in particular magnesium, aluminum, titanium, ...) are good explosives? No? Then don't try your hand in powder metallurgy if you like to stay attached to it.
    - What kind of properties do you expect for porous steel, full of what I called nanocracks? We know that nanocracks are not so good for fracture toughness - the material tends to be more brittle. If we don't want brittle steel, we need to achieve a very high degree of compaction, far higher than for ceramics that are brittle with or without nanocracks.
- In short: powder metallurgy is a good idea but not so easy to implement. Let's see what we can do about the problematic points mentioned above.
- **Making metal powders**. There are many different methods with a common denominator: they are neither simple nor cheap. I just list them superficially:
    - **1.** Mechanical breaking. We have a real fancy word for that: comminution! As pointed out above, it is not all that great for metals.
    - **2.** "Spray can" method or atomization. Press the *liquid* metal through a nozzle and "atomize" it by exposure to a blast of gas or some liquid. Takes a bit of engineering at the temperatures required; you also can't use gases like oxygen or air that react with the liquid metal.
      Maybe you use "centrifugal disintegration", also known as the "s..t hits the fan" method. A stream of the liquid metal is directed onto a fast rotating cold disc. The stream of liquid breaks up in little parts that crystallize and get thrown off by centrifugal forces. The liquid "stream" can be made, for example, by an electric discharge between the disc and some feed rod of the wanted material held above the disc.
      There are many more variants of these "atomization" methods. They all have in common that you use the molten metal, and that you get particles with a certain range of sizes and shapes. If you need particles with a narrow specification of these parameters, you must filter out the ones that are not kosher, making the process even more expensive.
    - **3.** Reducing oxides or nitrides. You start with a powder of brittle oxides or nitrides that you can produce by regular milling as used for ceramics. Then you reduce this ceramic particles to particles of the pure metal by running them (I leave open how) through a stream of reducing gases like hydrogen (H) or carbon monoxide (CO).
- There are many more methods but you get the point: It ain't all that easy. In particular if you want really small nanoparticles with a defined size and morphology. But now let's look at the oxidation or "rust" problem and the explosion problem
    - Well - those are not real technological problems, just money issues. Run everything in vacuum or in a noble gas atmosphere. If there is no oxygen, no iron oxide can be formed. Neither can the stuff explode because for that you also need oxygen (or nitrogen, or some other reactive gas), too. Implementing these measures will just run up your bill substantially.
- We are left with achieving a high degree of compaction; meaning we must get close to the density of the bulk material. That is the key issue and considerable efforts have been made and are being made to achieve progress at this front. Let's see why:

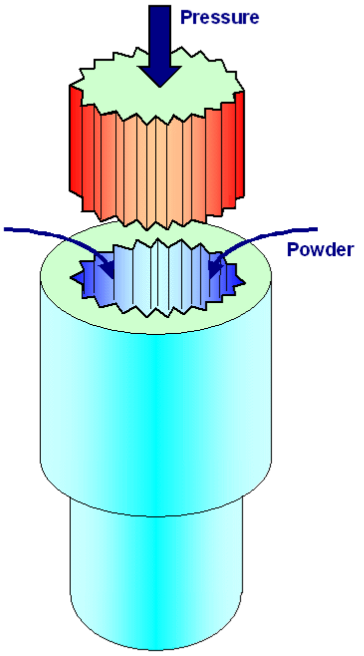


Powder metallurgy: Density and properties for copper (Cu)

Source: Redrawn from illustrations in Kalpakjian et al.; Werkstofftechnik, 5th editions, Pearson

  - While the data given are for copper, they are representative for *all* metals. Note that the density scale in the figure above does not start at zero but at rather high densities.
    The graph makes clear what we suspected all along: you must get close to the density of the bulk material if you want excellent mechanical properties.

- So let's go for high density or very little porosity. The first thing to realize is that the less binder you use, the smaller are the pores to be filled by diffusion. It is thus best to use no binder at all. With luck, just pressing together the metal powder as is, a work piece might be produced that hangs together, however slightly, that can be fired.
  - If you want to make a gear wheel, for example, use a contraption as shown below. Fill a suitable form called a die with the proper amount of the powder, insert fitting pistons, and press like hell. The green thus produced might be one piece that holds together.
    Then fire it.
    Done.

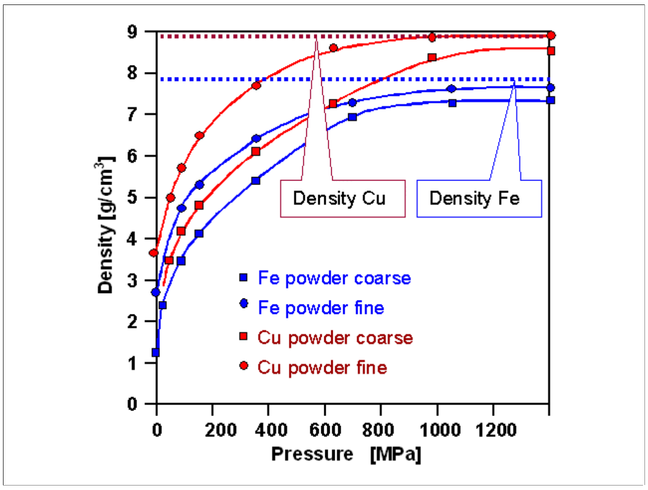


Making a gear wheel by powder metallurgy

- Haha. If you believe that this is all there is to powder metallurgy, you are easy to please. So let's consider the little complications involved.

- **1.** What kind of mixture of particle *sizes* and *shapes* allow most dense packing? That question reminds us of the century old puzzle about the highest packing density for atoms in a crystal. But here we are not trying to achieve the highest packing density for one size of spheres, we want to go for the maximum that is possible with a smart mixture of particles with any possible shape.
  As it turn out the highest packing density can be achieved by having spheres with a large range of sizes. That is easy to see. Pack one size as dense as possible, than take suitable smaller spheres that fit into the interstices. Repeat the process.
  So you want your metal particles to be spheres with some special distribution of diameters? Not really. Spheres touch each other only at points, and a "green" produced this way is not very stable. Irregular shaped powder particles with nooks and crannies stick together much better when squeezed, they just don't give the very highest density.
- **2.** For a more complex piece without an axial symmetry, the uniaxial pressure applicable in a set-up as shown above will not do anything to the powder that is not located in the axis of the pressure direction. That limits the method above to simple axial geometries.
- **3.** The pressure applied by the pistons is not felt much in the depth of the powder. Let's do a simple experiment to understand this. Put your hand on a table and hit it hard with a hammer. Now you know how an impact at high pressure feels like. Now put a heap of sand or flour on top of your other hand, flatten it somewhat, put a planar piece of wood or metal on top of the heap, and have somebody hit the pile with the same hammer (you can't do it anymore). The pressure transmitted through the powder to your hand is far lower then at the place of impact. What's true for your hand is also true for powder deep down: it doesn't feel all that much when someone squeezes on the top.
  Why is that? Because pressure moves the grains of the powder a little bit with respect to their neighbors, and the frictional forces between the particles, and in particular the piston and the die wall, oppose the force from the pressure. At a certain depth no more pressure force is transmitted.

So let's see what we can do with pressure:



Powder metallurgy: Relation between pressure and density (after firing)

Source: Redrawn from illustrations in Kalpakjian et al.; Werkstofftechnik, 5th editions, Pearson

- Shown are examples for copper (Cu) and for iron (Fe). In order to get close to the density of the solid stuff, you need to exert considerable pressure. That's not so easy if your work piece is not very small. Note that 1 MPa is roughly the pressure you get when a well-proportioned lady in high heels puts one heel on your toe and then puts all her weight on that heel. A GPa = 1.000 MPa is what you get if you pile another 999 ladies on top of the first one.
  It's not so easy to persuade all those ladies to compress your powder and not your toe, not to mention keeping them happy up there. That's what makes powder metallurgy so difficult.

What can be done about that? Quite a lot - but at cost.

- As far as the first problem is concerned, you just must compromise. Find the best mixture of particles sizes and shapes that meets all requirements. Then make those particles. That's a long and tedious research program and once more we are graceful that God has made graduate students (unfortunately not enough of the female variety in high heels for the experiment described above).

- The second problem simply calls for the application of pressure from all sides. All you need to do in this case is to make your die from some kind of rubber, fill it with the powder, get out your yacht and immerse the package somewhere deep down in an ocean. The pressure down there acts in any directions and will compact your powder uniformly no matter what shape.
  Unfortunately the people who have the money are typically disinclined to grant yachts as a part of a (non-medical) research proposal. That leaves you with no choice but ~~to get more ladies~~ to put the rubber die in a high-pressure vessel in the lab, fill it with water, and pump it up to very high pressures typically around or even above 400 MPa (around 60.000 psi for you dickheads out there).
  You can even do better by using soft sheet metal for the die and putting the filled die in high-pressure vessel that is filled with ~~water~~ gas (typically noble gases) at very high pressures and *at the same time* is heated to the desired firing temperatures. We are talking "hipping" here; the abbreviation "***HIP***" standing for "**hot isostatic pressure**".
- Hipping almost automatically takes care of the the third problem. Since there are no moving parts, there is no friction between those parts either. You also might grease the mix a bit by adding a drop of "oil", as always when friction is a problem.

We have now reached a point where I could start to go into the intricacies of powder metallurgy, including the many ways of making all those products that I haven't even mentioned yet. I could spend even more time to discuss the many new and complicated issues coming up when you want to go to particle sizes well below 1 µm and do "*nano*" stuff.
I won't do that, however. Powder metallurgy is an old branch of materials engineering. It was, for example, instrumental in working with the "***refractory***" or heat resistant metals like tungsten (W), tantalum (Ta) or molybdenum (Mo) and enabled the modern tungsten-filament light bulb in 1904 that is just now being outlawed in Europe. Powder metallurgy is also an exciting and modern branch of metallurgy, producing the very best products needed for example for critical airplane parts.
However, we won't use powder metallurgy for making swords.
First, because we don't need lots of swords anymore for killing people. We have far trickier things for that, for example predators or reapers: unmanned aerial vehicles commonly known as a drones, with a Nobel Peace Prize laureate at the trigger and likely very expensive hipped parts inside.
Second: I don't think that a sword made by powder metallurgy would be superior to one made by old-fashioned methods. Which parameter, exactly, should be "better" anyway?