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Ni-Ti ALLOYS BY POWDER METALLURGICAL METHODS

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ABSTRACT

Various powder metallurgical methods for producing nickel-titanium are reviewed, including combustion synthesis, zinc menstruum, mechanical alloying, rapid solidification, and atomization. Though none of these processes has achieved production status, several appear to offer promise in niche applications by providing unique properties. Perhaps the most interesting of these types of applications are the porous NiTi implants used in Russia, made by the combustion synthesis process.

INTRODUCTION

Since the discovery of NiTi in 1962, researchers have applied nearly every known synthesis method in efforts to achieve a consistent and "inexpensive" product. The ingot methods that are by now well-known include:

1. Vacuum Induction Melting (VIM) in both ceramic and copper crucibles,
2. Vacuum Arc Remelting (VAR) with both consumable and non-consumable electrodes,
3. Electron Beam Melting,
4. Electroslag remelting,
5. Plasma Arc Melting, and
6. Hollow Cathode e-Beam Melting.

It is fair to characterize at least the first three of these methods as successful on a production basis, but still problematic compared to conventional materials. Control of M_s, for example, is satisfactory for most purposes, but still imperfect and expensive due to achieve due to yield problems.

Powder metallurgical methods have also been used with the intent of achieving consistent product, reducing costs and/or improving properties. Although no powder approaches can really be thought of as having achieved production status, there are many lessons to be learned and at least some indications of potentially fruitful directions for future work. The purpose of this paper is to review some of these less well-known and more innovative approaches. Strictly speaking, not all the methods reviewed here should be considered powder metallurgical approaches—more accurately, the bounds of this summary should be defined as non-ingot methods of synthesis. In fact, the variety of methods that have been tried is surprisingly broad, perhaps because of the great cost incentives provided by the difficulties of conventional ingot processes, and the difficulty in machining and cold forming (providing a great cost incentive in achieving near-net shape parts).

We can consider non-ingot methods in two general categories: those beginning with pre-alloyed powder, and those synthesizing directly from elemental components.

PRE-ALLOYED METHODS

We treat here all non-ingot methods of synthesis that result in alloyed powder of nickel and titanium of the correct composition. Once one has achieved this, the powder must be compacted and/or sintered, but this turns out to be by far the easier step. For this reason, we will concentrate on the production of pre-alloyed powder and only discuss compaction briefly at the end. Generally speaking the intent of these methods is to reduce the costs of achieving near-net shape geometries and not to modify or improve properties, though there are, as will be described, exceptions.

Gas atomization methods have been the most common methods for producing NiTi from a prealloyed melt (1,2). In this case one begins with a molten pool of the correct composition and blasts it with a high pressure jet of inert gas. Of course the entire operation must be carried out in a high purity inert atmosphere.

In general, transformation temperatures have proven difficult to control due to the high surface area of the resulting powders. Titanium powder in particular has a high affinity for oxygen, and the greater the surface area of the powder, the greater the oxygen content of the finished part. Since oxygen forms TiO and Ti_4Ni_2O, it preferentially removes titanium from the NiTi matrix and suppresses M_S. Thus particle size and morphology have a large impact on M_s, making accurate alloy control very difficult. One is obligated to use carefully sieved powders and to atomize in highly inert environments—even then it is difficult to achieve uniform product quality.

One solution to the M_s control problem has been used in pre-production quantities. The M_s temperatures of individual lots of powder were measured, and the lots mixed to provide the desired M_s temperatures. Accuracies of ±5°C have been reported using such methods (1). Still, the method was abandoned by the developing company in favor of traditional ingot methods.

High oxygen levels also adversely affect ductility, grain growth and fatigue resistance. Ingot metallurgical methods generally produce and specify oxygen contents well under 500 ppm—usually under 250 ppm. Many reports on powder metallurgy fail to report oxygen, but those that do report levels above 1200 ppm in the fully dense state (1,3). Although basic tensile and shape memory properties are reported to be similar to those of wrought material (2), more current understandings of oxygen effects indicate otherwise.

Rotating Electrode Process (REP) has been studied recently in Japan, though results are inconclusive (4,5). In this case, a bar of the desired composition is rotated at high speed while being impacted with a plasma jet. The resulting powders have been reported to have a size of about 300 microns. The powder was subsequently compacted by HIP'ping, with the resulting material shown to demonstrate expected superelastic and shape memory properties. Detailed comparisons with wrought material were not done and oxygen levels were not reported.

Hydriding and mechanical "shattering" the material has been reported as a means of producing powder from ingot (6). Subsequent vacuum anneals remove hydrogen. Hydrogen diffuses very rapidly in Ni-Ti and solubilities are over 40 at.%—more than enough to fully embrittle the material. One would think that the impurity levels of such powder would be very low. Unfortunately little has been reported regarding the properties and economics of this approach.

Mechanical alloying has also been reported (7-10) as a means of producing pre-alloying powder. In this case, one can start with prealloyed atomized powder, or with pure powders. In either case, the starting powders are mechanically alloyed by either attrition or ball milling.

Reviewing all the reported work, one concludes that a great deal of oxidation occurs during the milling process, and that this may be nearly impossible to avoid. Although the resulting powder is reasonably pore-free and homogeneous, the high oxygen content and work hardening make it very difficult to compact. It is also difficult to reduce the hardness of either the powder or compacted material due to the large number of oxides present. Still, high densities can be achieved, and sintering does not seem to cause the swelling observed in elemental powder mixes. The resulting product is very fine grained (50-100Å in one case (8), and 2µm in another (9)).

In general, more work is warranted in this area. While it is doubtful that this approach will be generally cost effective, it appears that unique strength and creep properties favorable to certain coupling or fastener applications may be obtainable.

As a passing comment, it should be noted that one source has reported that the resulting powder can become amorphous (7) under appropriate conditions. At this time, this appears to be of little practical value since subsequent processing to useable processes results in crystallization.

Zinc menstruum (11) has been successfully used to produce small quantities of Ni-Ti powder and sponge, but is unfortunately far from commercialization. The process involves the dissolution of Ti and Ni in a molten zinc bath, then distilling away zinc to leave a high purity alloyed sponge which can then be mechanically converted to an irregularly shaped sponge. Alternatively, the Zn solution can be atomized and then distilled, leaving a fine spherical powder (12).

There are two approaches for using zinc menstruum to produce useable material. First, one can start with the pre-alloyed Ni-Ti sponge from the menstruum process, then go through normal compaction and VAR methodology. Though the economics do not look attractive, prototype melts made through such a route have been highly successful in terms of M_s control and oxygen content. The second option is to use the powder product and compact it to produce 100% dense material. Though very little work has been done to analyze the product, the high compressibility and low oxygen content of the powder are very positive indications. Moreover, the economics of the process would likely compare favorably with other powder production methods.

In principle it is also possible to produce the Ti-Zn solution directly from ilmenite—if successful this would significantly improve the economics of the overall process, possibly making the process less expensive than ingot methods. This method has been tested and proven with pure titanium and other simpler alloys. One must be concerned, however, about the difficulties in accurately knowing the Ti content of the Zn solution, and therefore in controlling the ultimate Ni/Ti ratio and M_s. No results have been reported at this time.

Melt spinning and then mechanically pulverizing the resulting ribbon to produce a powder-like substance is another method that has been applied to Ni-Ti (13). The conversion of ribbon into powder can be enhanced by hydriding and subsequent dehydriding. As-spun ribbons can have extremely fine grain sizes and strong columnar textures. Some reports indicate that ribbons may become amorphous (14). Cold compacted and sintered material has been reported to have a grain size of 10-20 µm. In general there is a suppression of M_S compared to wrought materials—it is not clear whether this is due to preferential oxidation of titanium, or the fine grain sizes produced.

Some applications may allow the use of melt spun ribbon as is, instead of having to pulverize, compact and sinter. Mechanical testing has shown memory effects comparable to wrought material (15). Improved corrosion and fatigue resistance has also been demonstrated (16). At least one finished device has been made using rapidly solidified strip (17): an optical switch using a thin strip of NiTiCu ribbon operating with a two-way bending shape memory effect. The thin strip allows response times of less than 1 msec.

Various Compaction and sintering methods have been successfully applied to Ni-Ti prealloyed powder, providing very high density parts. Methods include CIP (Cold Isostatic Pressing) plus sintering, the CAP process (18), HIP'ping (3), direct powder rolling (19,20), hot extrusion, etc. In general, best results have been obtained with sintering temperatures of 1100°C to 1200°C.

Shock compaction has been successfully applied to directly produce densities of 98%+ (21, 22) with subsequent sintering producing 100% densities (23). Compacted structures are unique in that they exhibit a bimodal grain structure, with large grains (commensurate in size to the powder size) surrounded by ultra-fine grains less than 50 mm in diameter, and possible amorphous regions.

ELEMENTAL POWDER METHODS

Although the use of elemental powder simplifies the powder production problem, it creates new problems: Kirkendall porosity, and the heat from the strongly exothermic Ni+Ti=NiTi reaction. The Kirkendall porosity results from the more rapid diffusivity of Ti in Ni than vice versa. The heat of fusion for the NiTi compound is very high: 8.51 kcal/g. In ideally adiabatic circumstances, this leads to a self-heating of over 1100°C! These two problems manifest themselves during compaction and sintering in the form of pore formation and swelling. As before, oxygen is a problem, often exceeding 3000 ppm (24). Though it is questionable whether high quality titanium powder is really available at reasonable costs, we will make that assumption and move directly to discuss compaction and sintering methods.

Cold pressing and sintering is not generally successful in producing high quality, high density parts. Cold pressing can generally produce green densities of 80% (for fine powder sizes). Sintering generally reduces density (25); moreover, large pores, or craters, are produced on the material surface (26). The mechanical properties of such materials tend to be quite poor, but the shape memory effect remains (27,28).

Heating rates during sintering can have a very large impact on the self-heating that occurs (Figure 1) (29). Here one can see that the "ignition" of the Ni+Ti=NiTi reaction occurs at about 720°C. Avoiding the large temperature peak reduces swelling and prevents adiabatic heating. Insufficient information exists to know what effect such controls will have on mechanical properties.

Vacuum hot pressing at 1050°C and pressures of 12-20 MPa has been shown to produce densities of 95% and oxygen contents of 2700 ppm (30). Shape memory was demonstrated, with ductilities in the range of wrought materials. Unfortunately the reported oxygen levels are likely too high to allow reproducible M_s temperature control and acceptable fatigue resistance.

Combustion synthesis uses the high heat of formation to synthesize the alloy. Generally there are two approaches that have been used: ignition (31,32), and thermal explosion (33-34).

Ignition, or combustion, methods involve locally heating a cold compacted blank above a critical ignition temperature. The heat given off from the ensuing Ni-Ti formation reaction ignites the surrounding material, causing a synthesis front to propagate through the entire material. Following synthesis, blanks have been extruded (32), or HIP'ped and then extruded (31). No densities have been reported but mechanical properties in one case (31) have been excellent, with full superelasticity after a 6% deformation. In this particular case, 600 ppm oxygen was reported, which is the lowest reported in any powder work, and comparable to ingot methods. It is claimed (36) that oxygen (and hydrogen) is discharged from the compact by the highly exothermic reaction Most indicative of success is that M_s was demonstrated to be predictable (Figure 2). There was some concern expressed that the highest nickel data points are warmer than the ingot samples, and in fact warmer than the data points at 50.4% nickel; this would be expected, however, if the samples were slowly cooled, and thus aged prior to testing. This would seem likely considering the consistency shown at each target composition. Even though no ductility data was reported, this may well be the best quality PM product made to date. It is not known, however, what the properties were directly after HIP'ping so the usual PM near-net shape capabilities may not be realizable.

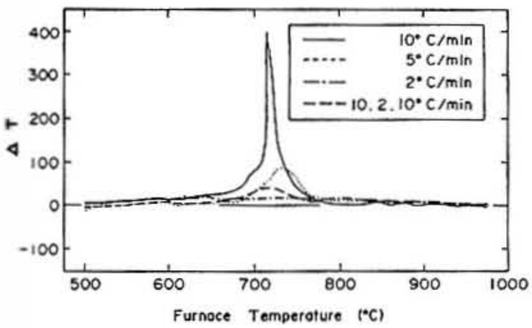

Figure 1: Differential thermal analysis showing the high self-heating occurring during sintering elemental Ni and Ti powders, and the importance of heating rate in determining maximum temperature reached.

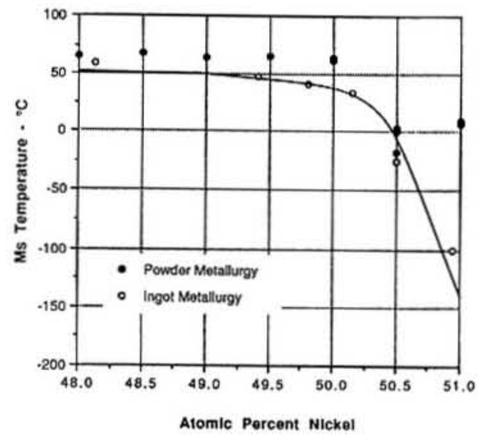

Figure 2: M_S temperature versus composition results for Ni-Ti made by both ingot (Honma et al: J. Jpn. Inst. Metals 39, 1975 p. 175) and powder metallurgical approaches (35).

It is important to note that the as-synthesized structure in this case is highly porous, with a density between 50% and 80% prior to HIP'ping or extrusion. A great deal of work has been done to characterize the utility of these porous structures in medical implants (37-39). Not only does the porous material retain shape memory characteristics, its nature promotes boney ingrowth and provides a more physiological interface between native tissue and metal implant. Such implants have met with particular success in Russia in the field of maxiofacial implants. It has been reported that over 8,000 patients in Russia now have porous NiTi implants (39).

Thermal explosion synthesis more closely resembles a casting process than a sintering process. In this case the entire sample of compacted powders is heated until it reaches an ignition temperature (~900°C) at which point it releases enough heat to exceed the melting point of the alloy (33). The resulting structure resembles a cast structure, with well-formed dendrites and no evidence of prior powder boundaries. This structure can then be hot rolled, swaged, extruded, etc., to produce desired shapes. It is generally not feasible to use the Ni-Ti in an as-cast condition—even after extensive homogenization. More detailed measurements of mechanical properties should be done, however, in order to verify this applies to the as-synthesized state. Again if it is necessary to break down the as-cast structure, the methods may provide little advantage.

SUMMARY

The extraordinary difficulty in achieving finished Ni-Ti shapes with reliable properties has led to several innovative powder metallurgical approaches. The zinc menstruum process beginning with ilmenite offers the potential of reducing the cost of near-net shaped products, but it is very unclear if the correct Ni/Ti ratios are achievable. Mechanical alloying may offer unique high temperature properties, but far too little work has been done. Rapid solidification appears to be a valid method to produce fine strip material, and at least one product has been produced using this method. Combustion synthesis may well be the most interesting methods reviewed here, especially in light of recent results showing utility of porous material in the medical industry.

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