Recent Advances in Binder Removal and Pressure Sintering PM Parts

Vacuum sintering has been employed for many years by tungsten carbide and specialty metal producers because the closed-chamber environment to take advantage of the excellent control of atmosphere and cycle-to-cycle repeatability. Since the early 1980's, the development of new PM production processes such as in injection moulding and pressure consolidation has caused significant changes in the design and appearance of the original batch vacuum furnace. This paper by **Richard H Seymour**of Vacuum Industries Inc, Somerville, Mass., will review how the new processes have resulted in new, improved controlled environment furnaces, and will cover the advantages and limitations of batch furnaces as it applies to these processes.

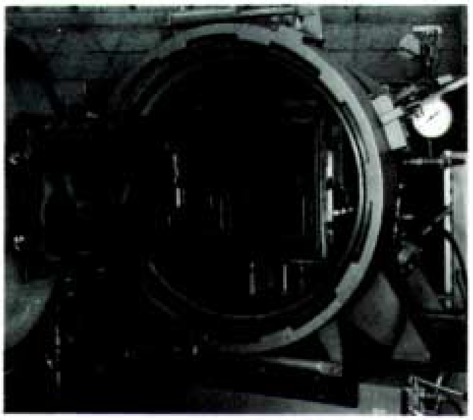

FIG. 1 Refractory metal hot zone with top and bottom heating elements with independent temperature controls.

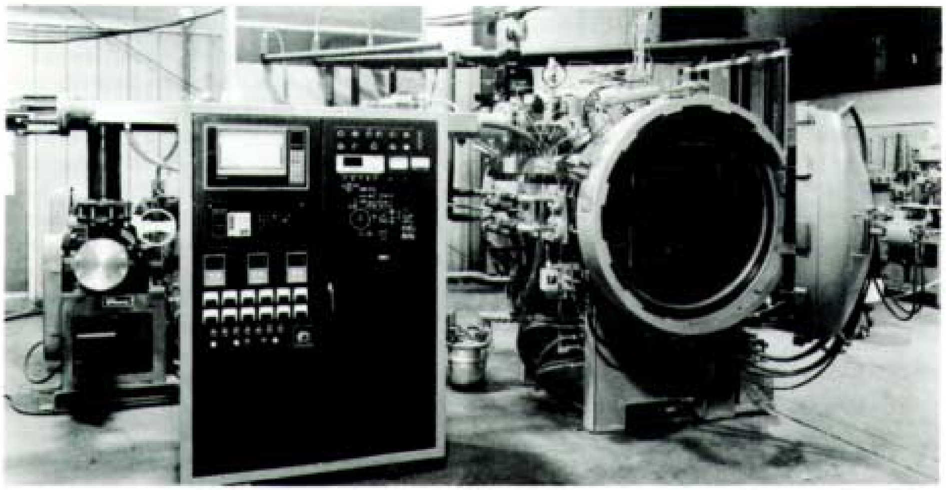

FIG. 2 'Sinterbar' 300 furnace. Temperatures to 1600C with graphite resistive heating and pressure to 400 psig (27.5 bar).

The generic term 'hardmetal' refers generally to a hard carbide of tungsten, tantalum, titanium, or to other metal in a low melting temperature binder such as cobalt or nickel. During sintering of cold pressed powder compacts a liquid phase eutectic is formed, and the compact undergoes a linear shrinkage of approximately 20%. When cooled, the finished parts are near theoretical density with little residual porosity. In the early 1970's, with oil-drilling activity rapidly increasing, competition among producers of down-hole drill bits led to significant improvements in the fracture toughness of the high cobalt, tungsten carbide inserts in contact with the rock face. Analysis of failed parts showed the tungsten carbide tended to fracture at small inclusions and pores not completely removed by conventional vacuum sintering. Hot isostatic pressing after vacuum sintering became a common processing method, particularly for tools destined for most critical drilling applications. It was, and still is, a very expensive secondary thermal process.

Research work begun during the late 1970s' at General Electrics' Mining Products division indicated that applications of lower pressures on the order of 200-300 psi performed during the initial sintering resulted in the same degree of pore closure as HIPing. Further tests showed that the carbide microstructure was improved since only one thermal operation was required. This led to the development of the combination vacuum and pressure sintering furnace referred to at Vacuum Industries as the 'Sinterbar' furnace.

In addition to requiring an ASME-certified pressure vessel, the sinterbar pressure furnace required a completely new approach to heat zone design. During conventional vacuum sintering, heat transfer takes place by a combination of radiation and convention. (Fig. 1). To account for thermal gradients caused by convention currents, it was necessary to design independent upper and lower elements with independent temperature controls.

In addition, an improved lubricant removal method was incorporated using a new condenser which collected the lubricant outside the chamber. This prevented the cracking of hydrocarbon by-products normally associated with a conventional vacuum delube furnace. This modification made it possible to provide an essentially neutral atmosphere which could be easily modified by gas additions during the sintering cycle.

It was also discovered that the new hot zone design resulted in improved temperature uniformity under vacuum conditions - the most critical part of the process cycle. Once parts are fully sintered under vacuum, or with additions of carburizing or reducing gas, a very short application of isostatic gas pressure results in complete pore closure. Cycle times are virtually the same as for conventional vacuum sintering; the extra time required for isostatic pressing is usually offset by a decrease in cooling time under gas pressure.

There are currently five 'Sinterbar' furnaces from Vacuum Industries for tungsten carbide, four of which are shown in Figs. 2 to 5, plus approximately ten from other manufacturers in production in the United States. Equipment costs are about twice that of conventional vacuum furnaces, but are generally one-third the cost of a conventional furnace plus a separate hot isostatic press. Operating costs are only slightly higher than a conventional vacuum furnace, primarily for increased argon gas use. The current design trends are leading to higher pressure furnaces suitable for micrograin carbides with low-cobalt contents and to higher temperature furnaces for structural ceramics.

In 1984, a producer of ceramic wear parts requested sintering tests of some silicon nitride material at positive pressures in a nitrogen atmosphere. It was found that sintering at elevated temperatures under several atmospheres of nitrogen resulted in higher finished densities, improved fatigue

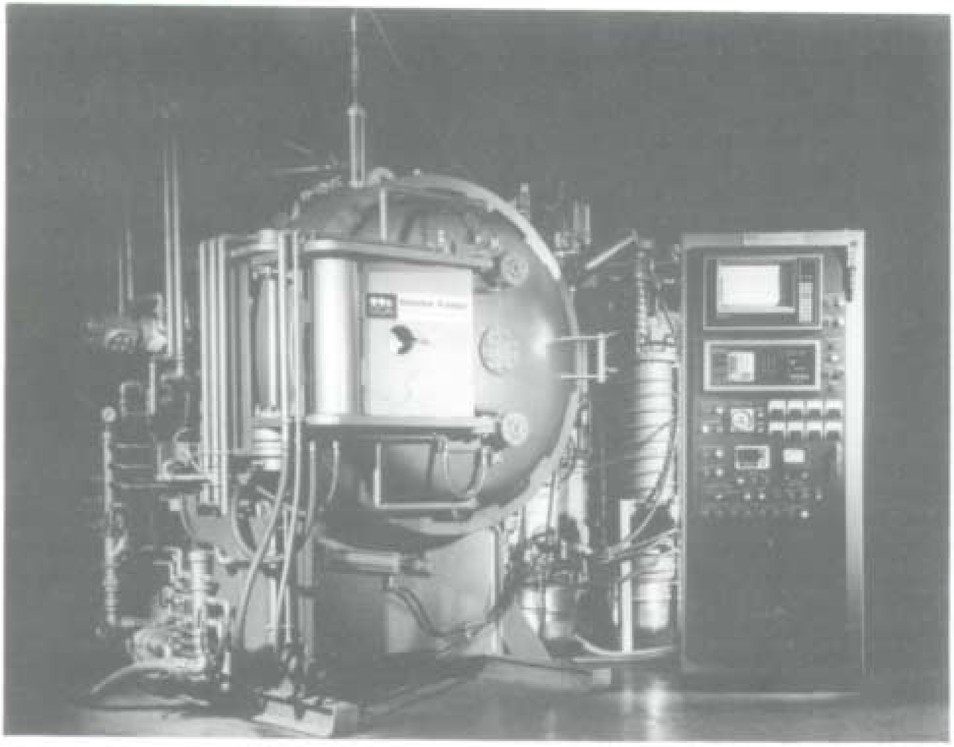

FIG. 3 'Sinterbar' pressure sintering furnace Series 3750 provides work space 12 in. x 18 in. x 12 in. long (300 x 450 x 300 mm) at 2200C and pressures up to 400 psig (27.5 bar).

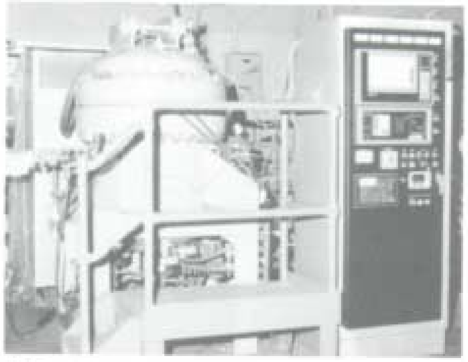

FIG. 4 'Sinterbar' vertical loading furnace with temperature capabilities of 2200C and pressures to 1500 psig (100 bar).

and flexural strength, while at the same time minimizing the decomposition of the base material. One such furnace rated at 2200C and 1500 psi has been recently supplied to the joint TRW/Norton Company Research Programme investigating automotive uses of silicon nitride components.

Another manufacturer of silicon nitride parts has recently installed three 'Sinterbar' furnaces. The first is used for removal of binders from silicon compacts under pressure to prevent excessively rapid evolution of binder decomposition products which could cause the parts to explode. This furnace is also capable of reaching presintering temperatures to give the part some structural integrity. The second furnace is used for reaction bonding of the silicon compacts with nitrogen, and the third furnace is used for high-temperature/high pressure sintering of the reaction-bonded silicon nitride. This development programme is expected to become operational in 1988 and will require installation of several production-size 'Sinterbar' furnaces.

Some initial work has been done using this equipment to process more conventional PM alloys. Improvements in materials properties has been limited because of the very small amount of liquid phase present during sintering and the consequent existence of interconnected porosity. Higher density compacts or additions of sintering aids, which produce a liquid phase, could result in significant improvements in this application.

INJECTION MOULDING

In 1980, a US patent was issued to Dr Ray Weich of San Diego, CA for a process called 'metal injection molding'. this process allows production of extremely complex and intricately shaped parts, such as the bolt lift lever for a sporting rifle shown in Fig. 7.

The process should more aptly be called 'powder injection molding' as some ceramic parts have also been produced by this method. There are currently two separate and competing process techniques: the first, based on the original Weich patent, uses a mixture of very fine spherical metal powders blended with a thermo-plastic resin and wax binder, which is heated before moulding in a cooled die. Binder removal is accomplished by solvent extraction or thermal decomposition.

This method is being used by IBM, Parmatec and Remington Arms, and was licensed by the Brunswick Corporation. Final sintering usually takes place in a reactive or carbonaceous atmosphere to reduce the oxides formed during binder removal.

The second method employs water soluble organic binders which are cold injected into a warm die where the mass solidifies. Binder removal and sintering are accomplished rapidly in either an atmosphere or vacuum furnace, depending upon material requirements. This technique was patented by the Cabot Corporation and is now being used by New Industrial Techniques of Deland, FL. In both processes, although up to 40% volume shrinkage occurs, tolerances of 0.3% are commonly held. It should be noted here that, although it has been forecast that metal injection moulding will become a $200 million industry within ten years, none of the existing producers are yet in full-scale production.

Another version of injection moulding, using much simpler equipment, has been developed by Leco Carbide of Hendersonville, TN. Using a proprietary paraffin-base binder, the mixture is injected into a cold die and solidifies in approximately 30 seconds; binder removal and sintering is accomplished in a conventional vacuum furnace. One of the largest injection-moulded parts made to date is a tungsten carbide grate for an attritor mill, which sells for over $1000.

The most widely used metal injection-moulding process based on the Weich patent has several drawbacks. One is the very long cycle time required for binder removal; another is the difficulty in maintaining proper carbon potential due to varying degrees of

FIG. 5 Three 'Sinterbar' furnaces for binder removal, reaction bonding, and high temperature, high pressure sintering of silicon nitride parts.

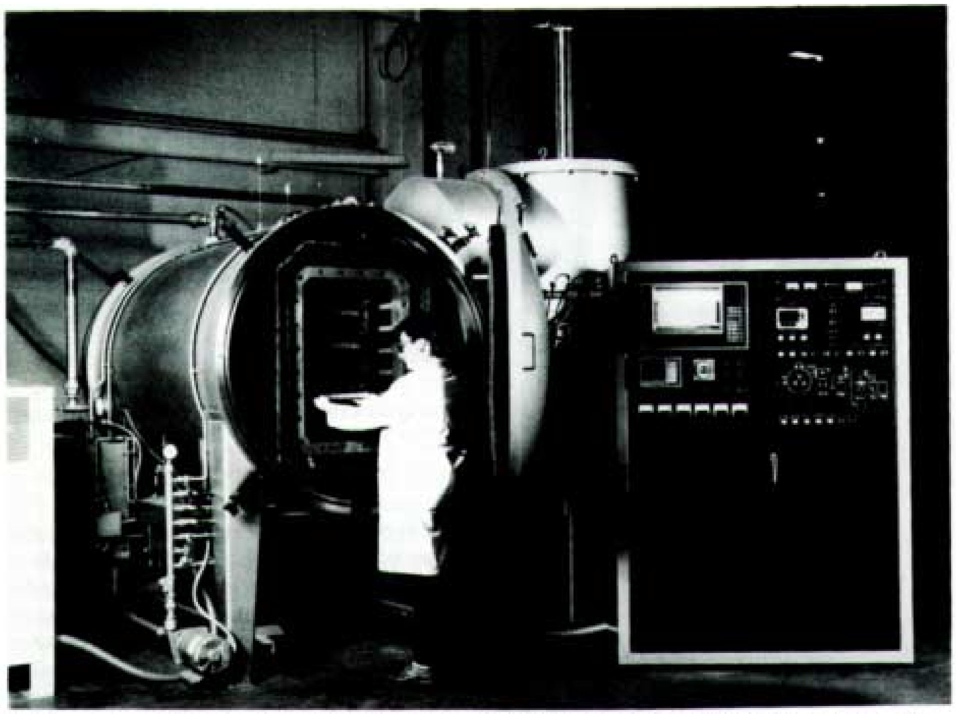

FIG. 6 'Injectavac 500' furnace for combination binder removal and sintering of precision injection moulded PM parts operates at 1400C and provides 280 liter work volume. Automatic operation is achieved with a microprocessor-based program controller and all operating parameters are recorded on a data logger.

FIG. 7 Injection moulded bolt lift lever.

FIG. 8 Stainless steel gyroscope support ring sintering density 7.4 gm/cc.

oxidation. The new 'Injectavac' furnace shown in Fig. 6 overcomes these difficulties. This furnace is especially equipped to allow evaporation of binder materials at low pressures and can complete a full cycle, including sintering, in approximately one-third the time of the previous process.

The neutral atmosphere of the vacuum furnace prevent oxidation and allows close adjustment of the furnace atmosphere for carbon control. For instance, it is practical to control carbon levels with 316 stainless steel to less than 0.01% for corrosion enhancement or to more than 1% for heat treatable steels. Between these two extremes, production lots of parts have been produced with carbon controlled to ± 0.03%. Materials that have been successfully processed include, both high and low carbon nickel irons, 316-L stainless, high-speed steel, and tungsten carbide. Additional work continues on 17-4 PH and 410-L stainless steel.

Part producers contemplating the use of injection-moulding techniques should be cautioned about stepping in prematurely. First, it is a batch process with cycle times determined by the speed of binder removal. Second, the selection of binders is critical, not only for moulding but for binder removal and sintering. For the most part, binders have been chosen more for the moulding process than for ease of removal later. This has led several companies to examine alternate binders more easily removed and less likely to upset carbon balance.

Lastly, no method has yet been developed for sensitive materials such as titanium or zirconium which readily react with the hydrocarbon binder. Development work is underway in both these areas but because of its proprietary nature, is not being discussed publicly.

HIGH DENSITY STAINLESS STEEL SINTERING

In 1985, Vacuum Industries was asked to sinter some 410 stainless steel tensile test bars in order to determine the best manufacturing method for a large stainless steel ring (Fig. 8) to be used as support mechanism for a missile guidance gyroscope. The specifications required a 7.6 gm/cc density, ultimate tensile strength of 120,000 psi, and a minimum 5% elongation. Following several experimental runs and approximately six months of laboratory development, it was possible to achieve or exceed two of the three target parameters. Using a conventional vacuum furnace equipped with special lubricant removal provisions for Acrawax, a part pressed to a 6.8 density was sintered in argon at 1425C to a final density of 7.63. Following a conventional 410 heat cycle, the ultimate tensile strength was measured at 173,000 psi. Elongation, however, was approximately 3.5% less than required.

The great increase in density was the result of a shrinkage of approximately 0.032 in. per inch. The high shrink rate and resulting high density was discovered after almost $20,000 has been committed to hard tooling. A decision was made then to continue with conventional process techniques. It was also determined that vacuum sintering at approximately 1300C produced a part of the correct size which could be repressed to approx. 7.3 density. Five such parts have just successfully passed the first series of operational tests, and although of a lower density, have proved superior to a part machined from stainless tubing. The same parts manufacturer is considering high-temperature sintering for several future applications requiring both 410 and 316 stainless steels.

CONCLUSION

Batch processing has proved extremely successful in a number of applications requiring elevated temperatures at precisely controlled atmospheres. For truly high production, however, continuous vacuum furnaces are needed. Some recently published material specifications for 316 and 410 stainless steel, and several other high-alloy materials, can only be achieved through vacuum sintering. These specifications are currently finding their way into the automotive parts sector where volumes will require much higher production capabilities than currently exist.

Continuous furnaces for these expected large quantities of both conventional and metal-injection moulded parts will require additional equipment development effort. Such efforts are now being made as large scale markets justify the work.

Development of both batch and continuous furnaces requires extensive research in materials in order to minimize cycle time and furnace economics. Vacuum Industries is continuing work in injection moulding and other markets, and these findings will lead to further furnace improvements.

Finally, the structural ceramics market seems ready to move from experimental to production volumes for applications ranging from high-temperature engine parts to cutting tools for high-speed machining. Major efforts in Japan, Europe and the US will undoubtedly result in significant changes in present furnace designs over the next several years.