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Advanced High Temperature Equipment Used for New Structural Ceramic Processing

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Kilns of all sorts have been used to fire the common ceramic ware of commerce and industry for centuries. Over the years, control of the time and temperature of firing ordinary ceramic ware in kilns has reached a high level of development. Some degree of atmosphere control has also been achieved. The new advanced structural ceramics, by contrast, can only reach their high performance potential when they are fired or sintered in a strictly controlled atmosphere and by a carefully controlled heating cycle.

Non-oxide ceramics such as silicon nitride, for instance, show wide variations in physical properties unless they are sintered in an atmosphere in which the excess oxygen level has been reduced to 50 ppm or less. Excess oxygen frequently results from water vapor absorbed in the green body before firing. In addition, complete removal of lubricant or binder materials with no undesirable residues has become a major criteria in successful processing of both non-oxide and high-alumina ceramics.

As a result, new ceramic materials are being fired in furnaces mounted within sealed and water-cooled vessels so that precise and consistent time/temperature/atmosphere programs can be achieved. This article will discuss and illustrate the capabilities of some of the batch or periodic furnaces used to develop and produce high performance ceramics.

First the vital role of the vacuum hot press in the development laboratories is described. Then, the problem created by the binders needed for economical production are reviewed. Next, chemical modification techniques and sintering procedures are discussed followed by mention of multi-function combination furnaces and a look at future requirements.

Vacuum Hot Press Sintering Furnaces

The vacuum hot press sintering furnace has been the old stand-by for laboratory work in the creation and characterization of ceramic mixtures. The hot press provides a combination of vacuum to remove contaminates from the powders and work pieces, and the application of uni-axial compacting force to allow the materials scientist to make samples of the highest purity and near theoretical density. In fact, the literature is full of references to the base-line characteristics of hot pressed silicon carbide, silicon nitride, titanium diboride and other materials.

Fig. 1 illustrates a modern version of a laboratory system. A resistance heated hot zone is employed for the extreme temperatures needed as well as, an induction heated hot zone. Temperature is sensed by a two-color optical pyrometer mounted directly on the furnace and aimed at the critical area of the die. A microprocessor based programmer/controller provides a preplanned heat cycle and may also provide a preplanned force program. Feedback of the applied force is supplied by pressure transducers or load cells. Thus the entire process is made to be fully automatic.

Fig. 2 shows a similar press with

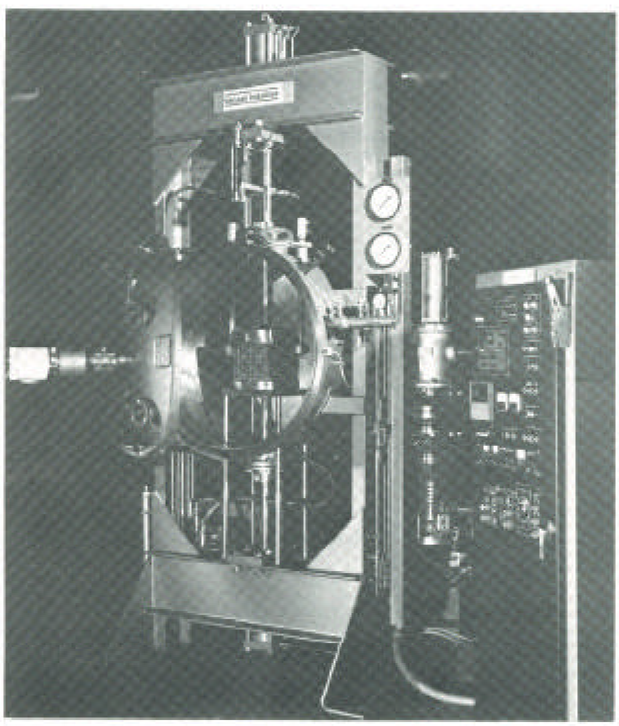

Fig. 1 Modern resistance-heated hot press sintering furnace.

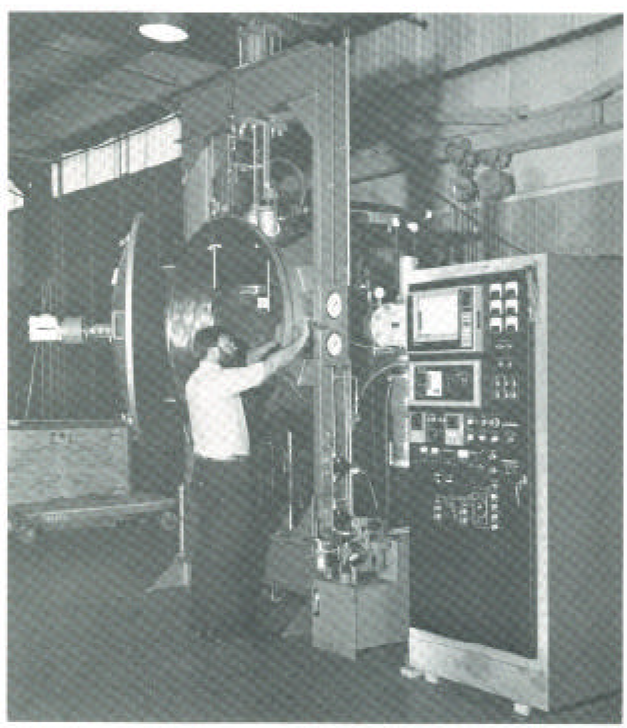

Fig. 2 Modern hot press sintering furnace with automatic control of temperature and pressing force.

full digital data reporting, as well as programming and control of pressure and temperature. In this case, extensometers in the form of LVDT's sense and record ram motion in concert with the record of the forces applied and the temperature. Use of moveable upper and lower rams allows the completed compact to be ejected from the die for the most rapid cooling of both the work and the furnace.

At the conclusion of the sintering portion of the cycle, the lower ram retracts and the upper ram extends to push the sample out of the die while it is still hot. This action also helps to avoid scratches in the die as well as to improve the rate of cooling.

A resistance hot zone can be used in an oxidizing atmosphere as well as in vacuum. One furnace of this type is used for materials which require an oxidizing atmosphere and temperatures up to 1600°C are quite practical.

Thus, the materials scientist is now able to make many more runs and to work with much more varied material than was possible only a few years ago.

Binder Removal

Very few parts can be produced economically on a production scale by hot pressing the raw powders. The need for near net shape in complex part geometries requires parts to be made by economical processes such as cold pressing, slip casting, or injection molding followed by sintering. These cold forming operations require the use of a binder to hold the powder grains together until sintering. Removal of the binder therefore becomes a critical step between the forming operations and the sintering of the work pieces.

For some ceramic materials, binders may simply be burned off in economical ovens at atmospheric pressure either in air or in a non-oxidizing gas atmosphere. After binder removal, the work is transferred to the sinter furnace.

While such procedures are well known and are thought to be economical, they may have disadvantages for the high performance ceramic materials. Binder materials may break down during the debinder heating process and thus leave undesirable residues in the matrix of the parts. Also, after binder removal, the parts are particularly delicate. In the handling between binder removal oven and sinter furnace crumbling may occur at the edges of the parts and in the thin sections. Internal cracks may also occur but be unnoticed at this stage. Thus, the yield of sound pieces is reduced.

In treating higher cost structural and fine ceramics, therefore, it is frequently desirable to remove the binder and to sinter in the same furnace without moving the work piece. This procedure has, of course, already been demonstrated to be the most cost effective in other industries including the hard metal industry.

Since these are sealed chamber, atmosphere-controlled batch furnaces, the vapor of the binder becomes a part of the environment surrounding the work pieces. It should, therefore, be removed completely to avoid its effect upon the parts at the high sinter temperatures. Removal can be accomplished by flowing a carrier gas over the parts to entrain the binder vapor and to carry it completely out of the furnace.

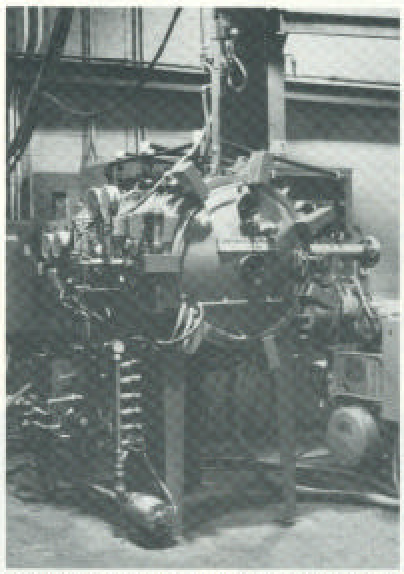

Fig. 3 Horizontal furnace with flammable gas burn-off for debinder and sinter operations.

This technique is used at a pressure just above atmospheric pressure to remove Butvar from fine, thin alumina bodies that are used for co-fired semi-conductor chip carriers, for instance. It is also used to remove poly-vinyl alcohol from thicker bodies made from relatively coarse powders.

Fig. 3 shows a small complex furnace equipped with a flow through flammable gas system which may be used with either hydrogen or dissociated ammonia. The carrier or sweep gas enters the side of the chamber through the complex control system which assures safe operation in a closed vessel, it passes into the hot zone of the furnace where it entrains the binder vapor being released by the parts and passes out of the furnace through an internal manifold to a burner tower where the gas and vapor are oxidized. Combination or inert gases may be used with this technique as well.

Binder removal at sub-atmospheric pressures often assures complete evaporation of the binder or its breakdown products and hence a cleaner matrix in the work piece. Such binder materials as paraffin and other waxes, stearic acid, acrawax and polyethlene glycol are condensed effectively in special condensers outside the furnace. The sweep gas technique then can be used in the range of a few torr pressure instead of being used at atmospheric pressure. The vacuum pump is protected by the condenser and the entire system operates as shown in Fig. 4. Fig. 4 shows the entrance of inert gas into the chamber, the entrainment of vapor from the work pieces and the

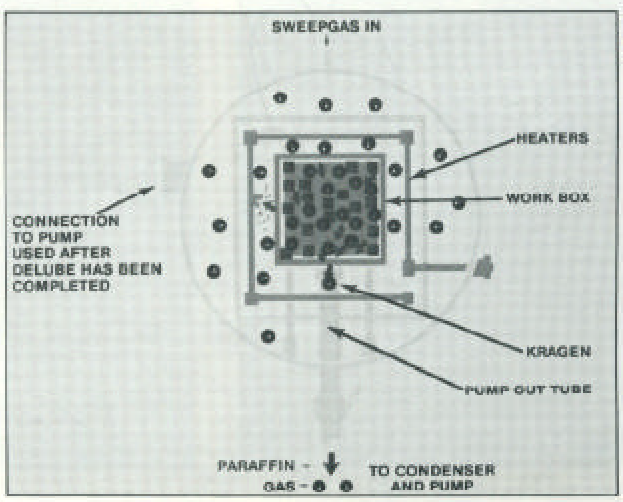

Fig. 4 Sweepgas™ debinder system — mode of operation.

direction of exhaust from the furnace hot zone and chamber.

The use of the Sweepgas system at relatively low absolute pressures presents an opportunity to understand the binder removal process as it applies to a given material or to a given workload. Fig. 5 shows the relation of time, temperature and pressure during a binder removal cycle using a Sweepgas system.

First a flow of gas is established at some typical pressure. The input flow is regulated by a preset needle valve and the output flow is balanced by a valve setting in the manifold to provide a flow usually in the order of about 10 standard cu ft per hour at the desired pressure level. As the temperature rises, binder vapor is added to the flowing gas thereby, increasing the total pressure within the furnace chamber. When the vapor supply decreases, showing the end of the debinder cycle, the pressure again returns to its original value.

Chemical Modification

When a part has been debindered but is still porous, the chemistry can be altered slightly by the introduction of gases into the sealed volume. For instance, fine alumina pieces upon which circuits have been printed with tungsten bearing inks can be fired in atmospheres of alternate wet and dry hydrogen to improve the adhesion of the printed circuit and to help free the alumina from any remaining carbon. Controlled atmosphere furnaces are now available with automatic dew point control for either hydrogen or dissociated ammonia gases. Dew points can be selected either side of the Richardson oxidizing/reducing curve vs. temperature for the metals and gas that is selected and the dew point can be changed automatically by the cycle programmer to suit the need at any portion of the total heating ramp.

Another reaction performed successfully in production quantities is the reaction of nitrogen with silicon metal to form silicon nitride parts. Fig. 6 shows a typical furnace of 12 cu ft volume used for reaction bonding production quantities. The controls in this case are selected for complete reliability since the process must proceed to completion without interruption to avoid damaging the material. The length of the cycle demands unattended operation for obvious economic reasons. Similar laboratory size furnaces are also in operation at several locations.

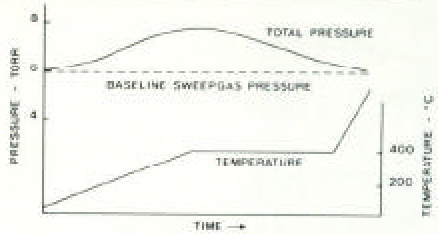

Fig. 5 Sweepgas™ debinder system— schematic relation of time, work temperature, pressure.

Sintering

Sintering high performance structural ceramics is usually done at atmospheric pressure in a gas that is inert to the work such as argon in some cases, or nitrogen. The purity of the atmosphere is maintained to assure consistent work pieces unaffected by contaminants. Sinter temperatures are high—2300°C for silicon carbide and titanium diboride for instance. Resistance furnaces have been developed for production volumes of these materials as is illustrated in Fig. 7.

Control of the furnace temperature at both the low end for binder removal and at the high end for sintering presented a challenge to the equipment maker but has been solved by the use of dual channel controls. The low temperature is sensed by a thermocouple and the high temperature range by optical pyrometer.

The thermocouple is automatically withdrawn from the hot zone before it melts as the temperature increases. At this point the optical pyrometer takes over the control to provide temperature information to the controller and programmer to complete the cycle. In such a dual arrangement an air cylinder operated thermocouple is installed next to a two-color optical pyrometer on the top of a small horizontal high temperature furnace to accurately sense the hot zone temperature through-

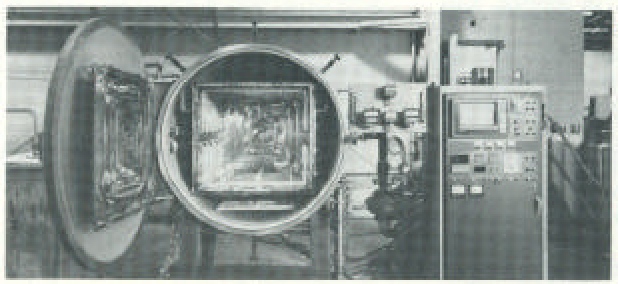

Fig. 6 Reaction bonding furnace for silicon nitride.

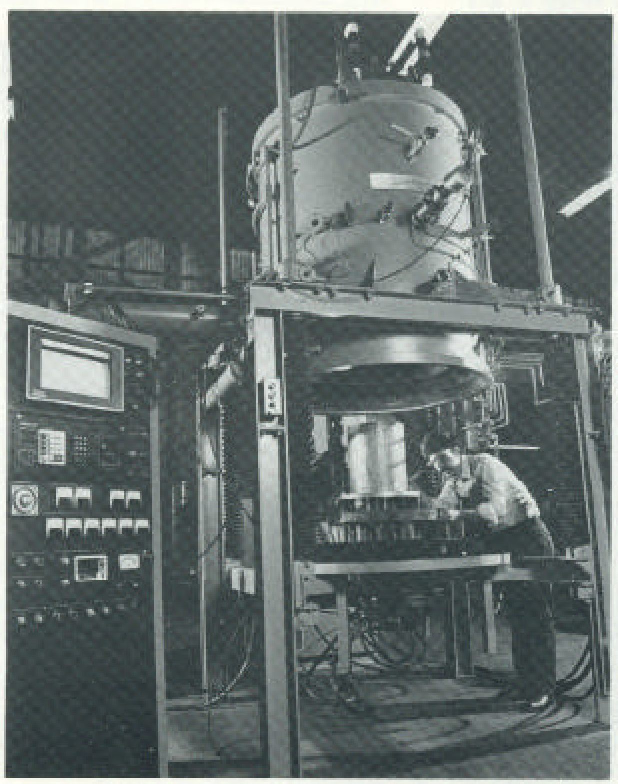

Fig. 7 Vertical elevator type sinter furnace for silicon carbide.

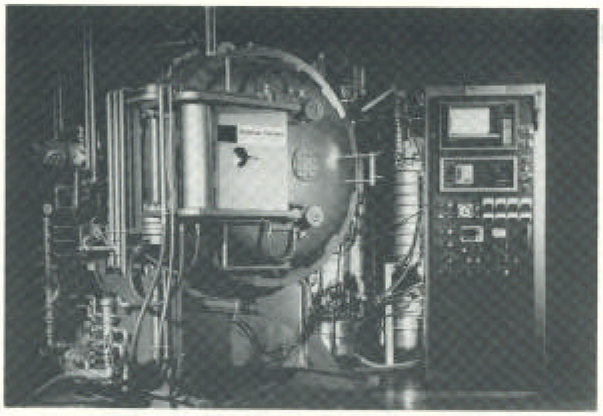

Fig. 8 Combination binder removal, sinter and pressure densification furnace.

out the entire operating range from room temperature to 2300°C.

Pressure

Silicon nitride may be sintered at about 1800°C but the density and strength are usually improved if it is sintered at even higher temperatures. However, the thermodynamics of this material indicates that pressure above atmospheric must be used to prevent a reverse reaction which would result in molten silicon metal and nitrogen gas. Hence the most appropriate equipment for sintering will have the capability of both vacuum and moderate positive pressure operation.

Moreover, a strong suspicion exists that the application of relatively low isostatic pressure to the work pieces during sintering, when any glassy phase in the work is molten, will improve the density and hence the strength. The extreme pressure employed in hot isostatic pressing may not be needed provided there is sufficient silica, yttria and similar glasses in the mixture. Pressure densification up to about 100 atmospheres (1500 psig) can be done during or immediately following sintering and, thus, the addition of this step exacts no significant processing time penalty.

Combination Furnaces

The result of these considerations is the introduction of the furnace shown in Fig. 8. In this furnace, high performance structural ceramic work pieces may be debindered using the Sweepgas system, sintered and densified in one automatic continuous and even unattended cycle. The binder is removed at the most desirable pressure; many contaminants may be evaporated away by the use of vacuum; sintering may be done in the most appropriate environment and finally the piece parts may be densified after the interconnected porosity has closed during sintering.

Conclusion

Significant design advances have been made in high temperature processing equipment for the new era of high performance ceramics. As more structural ceramic products are designed and as more ceramic development work is done, the demand on the equipment must of necessity call for even higher productivity and lower processing cost. Both furnace manufacturers and users have anticipated the need and are laying the groundwork for the development of continuous furnaces to work in this field.

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