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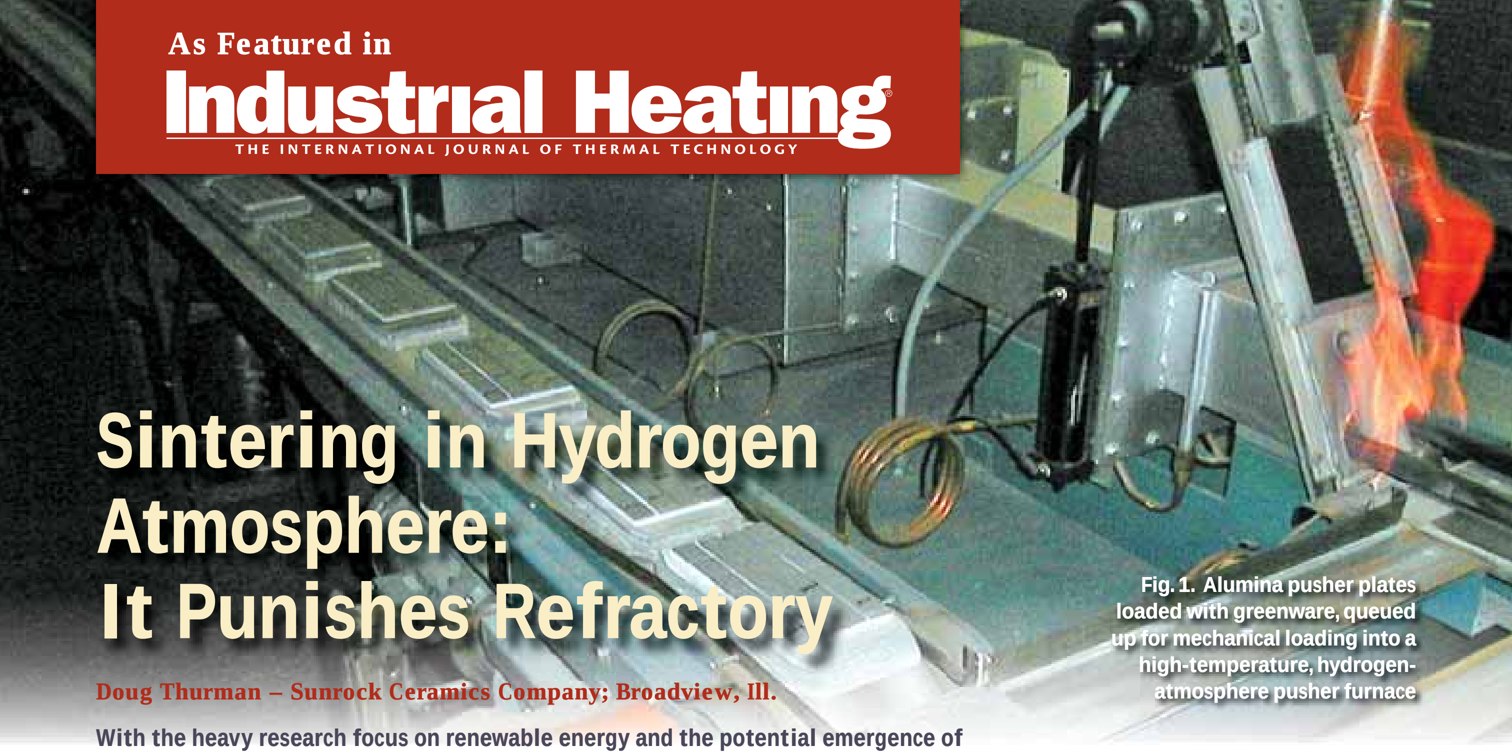

Fig. 1. Alumina pusher plates loaded with greenware, queued up for mechanical loading into a high-temperature, hydrogen-atmosphere pusher furnace

Sintering in Hydrogen Atmosphere: It Punishes Refractory

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With the heavy research focus on renewable energy and the potential emergence of a "hydrogen economy" at some point in the future, the element hydrogen has been in the news a great deal lately. In certain sectors of the industrial heating world, however, hydrogen has been a hot topic for decades.

Pure hydrogen gas (H_2) is often the most effective atmosphere for the high-temperature sintering (i.e. the thermal fusing of powders in compaction to form a solid, usually at temperatures near the melting point) of many powder metallurgy (PM) parts. Stainless steel parts represent a major portion of this business, but a number of other high-performance alloys, such as tungsten carbide and other tungsten alloys, also require high-temperature sintering in hydrogen. There are also many interesting developments in ceramic/metallic compositions, creating a host of new materials with very tailored physical properties.

Many other PM sintering processes, such as dissociated ammonia (75% hydrogen, 25% nitrogen), require less expensive reducing atmospheres. Vacuum sintering also plays a key role in many smaller, very specialized operations. To maximize the performance of low-carbon stainless steel pressed or metal-injection-molded (MIM) parts, however, especially when produced in higher volumes, a sintering temperature of at least 1300°C (2372°F) in pure hydrogen is the preferred firing environment. Sintering temperatures of 1600°C (2912°F) or higher in pure hydrogen are not unheard of when dealing with many specialized alloys, such as tungsten, as well as certain ceramic/metallic compositions.

Hydrogen firing helps maximize the key part properties of density and corrosion resistance. One of the reasons such high temperatures are needed when sintering stainless steels in hydrogen (besides striving to reach comparable densities to wrought parts) is to reduce surface oxides and strip impurities such as silica (SiO_2) from the alloy. For instance, at a dew point of -60°C (at standard atmosphere) the reduction of SiO_2 to the metalloid Si + O_2 occurs at approximately 1350°C (2462°F). See Table 1 for the relationship of the moisture content and temperature necessary to produce this dissociation. From an operational perspective, however, this same silica reduction is problematic for the high-temperature refractory of the furnace.

The Effect on Refractories

Refractories in high-temperature applications are typically based on high-alumina (aluminum oxide, Al_2O_3) formulations. Alumina is exceptionally inert (except against fluorine) and has great compression strength at high temperature. However, its thermal-shock resistance is poor when in pure form. This thermal-shock weakness is typically mitigated by the alumina being combined with silica, usually in the form of an alumino-silicate. Therefore, in high-temperature hydrogen-atmosphere applications great care must be taken with regard to refractory selection because the same chemistry that usually serves to maximize performance and useful life of the refractory (i.e. the alumino-silicates) can and will be reduced by the hydrogen, causing rapid failures and unplanned outages, which never seem to occur at a good time.

Furnace Types

A review of the types of furnaces often used in these applications will help illustrate the issues. The most common sintering furnaces for PM applications are

Table 1. Equilibrium temperature in relation to dew point* for $SiO_2 \rightarrow Si + O_2$ in H_2 atmosphere

	Dew Point				
	-30°C	-45°C	-60°C	-75°C	-90°C
Equilibrium Temperature (approximate)	1850°C	1650°C	1350°C	1150°C	950°C

* At Standard Atmospheric Pressure

Fig. 2. Fully sintered stainless steel parts on alumina pusher plates as they exit the cooling zone of a pusher furnace

continuous furnaces because of their higher throughput. After all, PM production is a means of achieving better throughputs and less waste than casting and machining these same parts. The sintering of some smaller parts – such as in specialized MIM operations – is often done in batch processes, but to achieve high-volume throughput, a continuous-furnace operation is needed. In lower-temperature PM operations, belt furnaces are often used. At elevated temperatures, the belts are not feasible, however, and the most common furnace is a pusher-plate furnace (Fig. 1).

With respect to refractory in these furnaces, the hot-face lining in the hot zone must be a very high-purity alumina with essentially no silica. Since this refractory usage is in a continuous furnace, the temperature in each zone is held more or less constant, so thermal shock is not a significant issue. Therefore, in hot-face linings a very high-purity alumina refractory can last for many years without incident. However, the pusher plates, which form the mechanical conveyor system through the furnace are a bigger challenge. These plates require a delicate balance of the thermal, mechanical and chemical characteristics of alumina ceramics.

The thermal-shock load on a pusher plate can be one of the most severe in industry because PM parts producers often utilize a quench zone straight out of the hot zone to combine sintering of the part with surface hardening, all in one furnace run. As previously discussed, the best formulation for withstanding the chemical attack is a high-purity alumina with no silica, but this would fail on the first pass out of the hot zone and into the quench zone (Fig. 2). Since the lineup of sequential pusher plates provides the mechanical path through the furnace, plate failures can potentially cause unplanned outages. Therefore, having a pusher plate designed specifically for this application is an important consideration.

The pusher plate must be designed and manufactured with adequate thermal-shock resistance for the severe thermal cycle while still having the chemical inertness to withstand, over a reasonably extended period of time, the highly reducing atmosphere. The typical method to achieve this balance is to utilize a form of alumino-silicate in the ceramic that has maximum resistance to the hydrogen attack and the resultant breakdown of the SiO_2. The material in question is mullite (Al_2O_3-SiO_2), a man-made alumino-silicate that is very structurally stable and, therefore, protects the silica via a strong ceramic bond that takes time for the hydrogen to degrade. However, creating a strong, well-formed mullite bond in the production of pusher plates can be a challenging exercise. Alumina formulations that work perfectly adequately in air firings – even at higher temperatures – may perform disastrously in the punishing hydrogen-atmosphere cycles of high-temperature PM sintering furnaces.

Conclusion

Hydrogen-atmosphere furnaces, especially those operated above about 1350°C (2462°F), are very useful for sintering many high-end alloys and ceramic/metallic compositions, but the demands placed on refractory are formidable. In pusher-plate furnaces, the demands on refractory are especially great on the pusher plates. Extremes of thermal cycling, mechanical loading and the chemical attack from such a severe reducing atmosphere combine to create the need for a very specialized ceramic. Great care should be taken and significant testing performed to ensure maximum performance of the system. IH

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