Debinding and sintering of low carbon stainless steel MIM parts

Vacuum Industries
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Debinding and sintering of low carbon stainless steel MIM components is complicated by the large volume fraction of hydrocarbon binder, the ease of formation of chromium oxides, the high surface area of the stainless steel powder and the low carbon specification. D. Duncavage and C.W.P. Finn of Northeastern University, Boston, Massachusetts, USA, and S.J. Donahue, for Centorr/ Vacuum Industries of Nashua, New Hampshire, USA, discuss the chemistry of the processes occurring during debinding and sintering.

Metal injection moulding (MIM) combines the well known plastics technology of injection moulding with powder metallurgy (PM). A mixture of up to 65% by volume of metal powder with particles of diameter less than 20 µm is blended with a mixture of thermoplastic binders and injection moulded to form a green part. The choice of binders is based on their rheology. The early MIM parts were made from iron or iron-nickel alloys. The application of MIM technology to stainless steel is complicated by several factors: the stability of Cr_2O_3, Cr_2N and $Cr_{23}C_6$, and the low carbon specification for stainless steels of the L series of less than 0.03%.

Binder removal

The most common binders used in MIM are mixtures of low melting point waxes, such as paraffin and stearic acid, and higher melting point thermoplastic polymers, such as polyethylene and polypropylene. Paraffin is a natural product produced from petroleum. The melting points and vapour pressures of paraffins have been well known for many years and are shown in Figure 1. Paraffins can be removed from MIM parts by several techniques, including wicking, solvent extraction and vacuum evaporation. It is important that paraffin be completely removed in a controlled manner to avoid distortion of the MIM part. It must also be removed at a temperature less than 300°C to prevent charring. Stearic acid is a natural by-product of the food industry. Its vapour pressure data are shown in Figure 2.

The higher molecular weight polymers do not evaporate but breakdown or depolymerize to lower weight species. Hydrogen gas is often used to assist in depolymerization and for the reduction of Cr_2O_3 which has formed on the surface of the stainless steel powder. Other gases such as nitrogen or argon are used as carriers to sweep away the polymer decomposition products.

Chromium compounds' stability

Of the major elements of Fe, Cr and Ni present in stainless steel, chromium forms the more compounds. Chromium oxide is extremely stable from room temperature to sintering temperature as shown in Figure 3. Chromium oxide is stable at temperatures and oxygen pressures above the line shown in the figure while metallic chromium is stable at temperatures and oxygen pressures below the line.

The vapour pressure chart of Figure 4 shows that chromium is very volatile. The vapour pressure of chromium is higher than the oxygen pressure necessary to cause the decomposition of Cr_2O_3. This means that a vacuum cannot be used to remove the chromium oxide coating from stainless steel powders. The reaction between chromium oxide and hydrogen is shown below.

$$Cr_2O_3 + 3H_2 \longrightarrow 2Cr + 3H_2O$$

Figure 5 shows that this reaction can reduce the oxide coating on stainless steel powders if the water vapour content is maintained at a very low level. Under a hydrogen atmos-

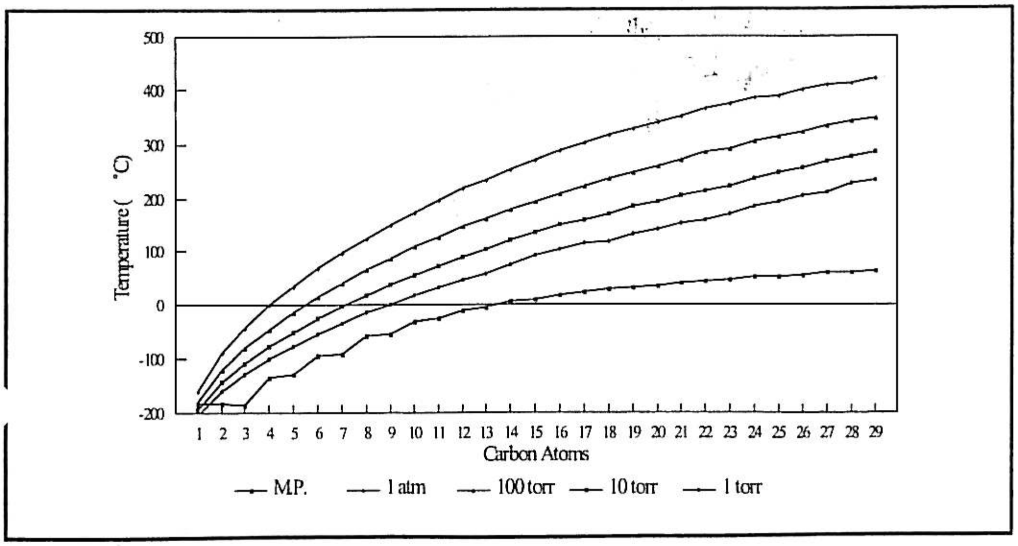

FIGURE 1: The melting point and vapour pressure of normal paraffins (Carbon 1 to Carbon 29)

phere of 10^5 Pa a dew point of -75°C, which is equivalent to 1ppm of water vapour, is necessary to reduce chromium oxide.

Nitrogen gas is often used as a protective atmosphere either alone or in combination with hydrogen, when it is called forming gas. Care must be taken as chromium nitride can form via the reaction:

$$2Cr + 1/2N_2 \longrightarrow Cr_2N$$

Figure 6 shows nitrogen pressure at chromium/chromium nitride equilibrium where the nitride is stable above the line and chromium metal is stable below the line. Above 1000°C chromium nitride is not stable under an atmosphere of pure nitrogen at 10^5 Pa while at lower temperatures sub-atmospheric or diluted nitrogen is necessary to prevent nitride formation. Naturally, in the production of low carbon stainless steel, it is common sense that graphite should be excluded. However, vacuum sintering furnaces with graphite heating elements and insulation are in common use for sintering. If hydrogen is used to assist with binder removal and oxide reduction in a graphite furnace at sub-atmospheric pressure, it is possible to transfer carbon to the stainless steel powder via the following coupled reactions if the methane concentration for the first reaction is greater than that for the second reaction:

$$C + 2H_2(g) \longrightarrow CH_4(g)$$

and

$$23Cr + 6CH_4(g) \longrightarrow Cr_{23}C_6 + 12H_2(g)$$

The equilibria for these reactions are a function of both total pressure and temperature. Figure 6 shows the ratio of methane pressure to total pressure at a total pressure of 130 Pa.

At all temperatures methane equilibrium with graphite is three orders of magnitude higher in concentration than methane equilibrium with the chromium carbide. Hydrogen acts as a carrier to transport carbon from the furnace to the stainless steel powder. These data only indicate the equilibrium conditions, so it is possible that the kinetics for this pair of reactions is slow enough at a binder breakdown temperature of less than 400°C to allow hydrogen to be used.

Finally, it has been observed that during vacuum sintering of low carbon stainless steel the carbon content decreases. A proposed mechanism, which is also under investigation is the reaction of chromium carbide with chromium oxide at sub-atmospheric pressure. The reaction is given by

$$Cr_{23}C_6 + 2Cr_2O_3 \longrightarrow 23Cr + 6CO$$

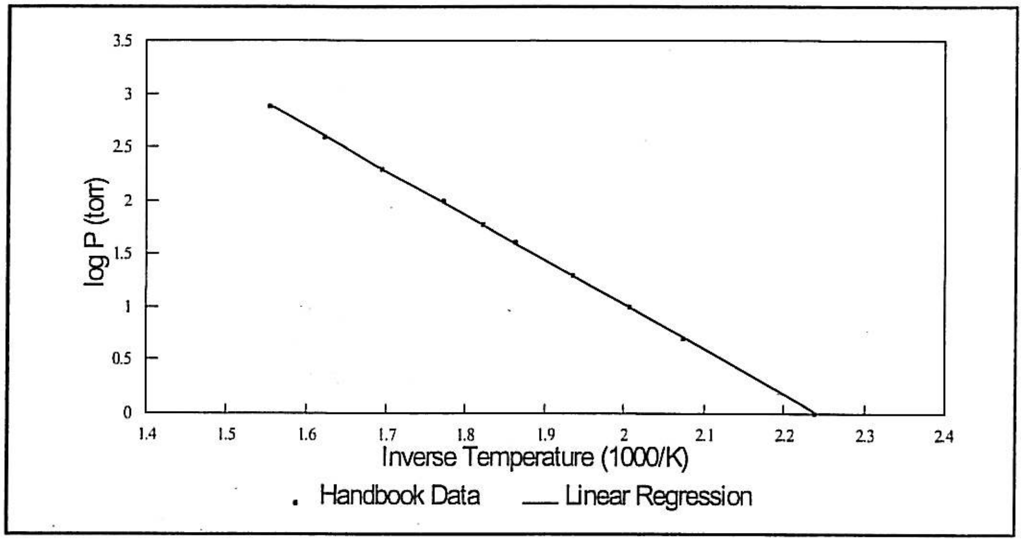

FIGURE 2: The vapour pressure of stearic acid (Ref: Chemical Engineering Handbook, 4th Ed, p. 3-57)

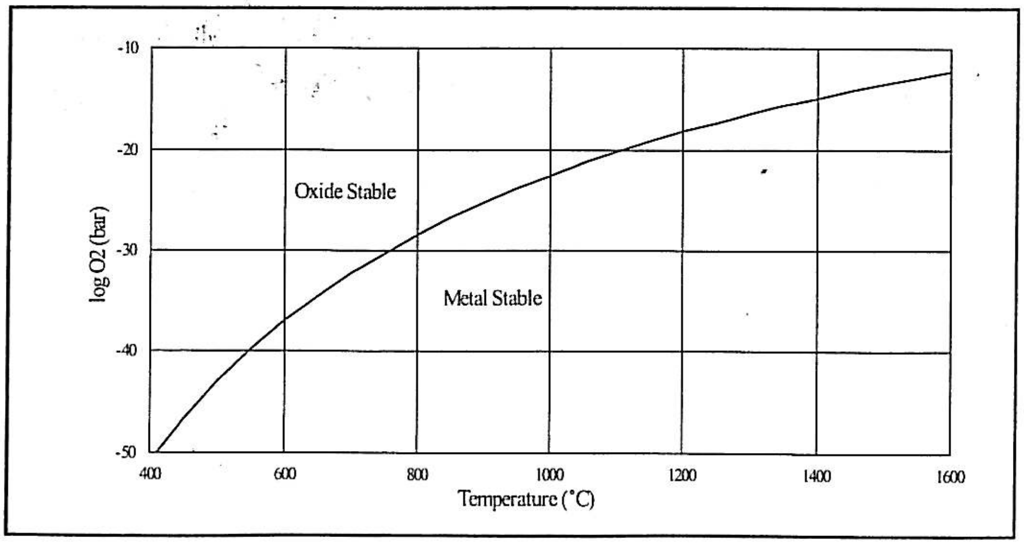

FIGURE 3: Equilibrium oxygen pressure (at Cr/Cr2O3 Equilibrium)

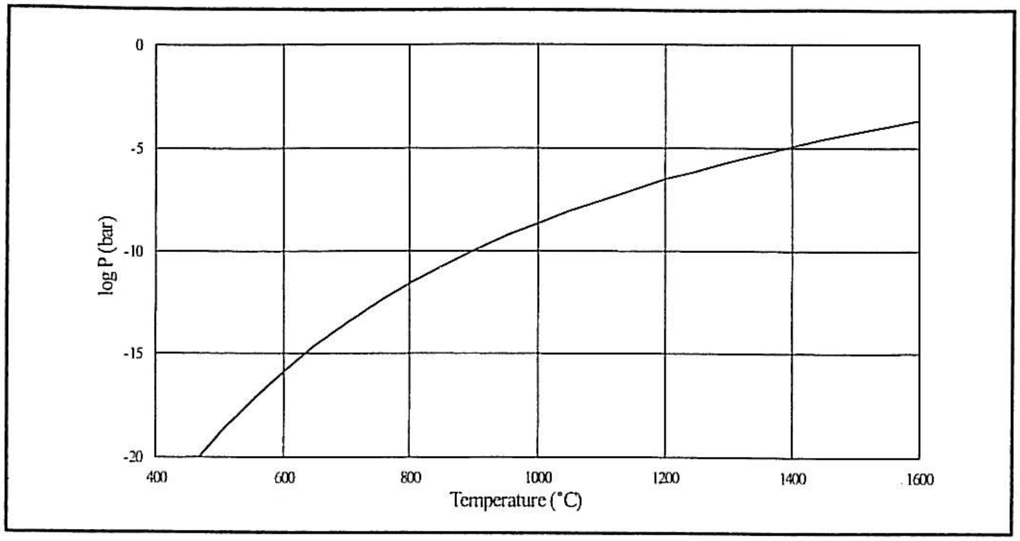

FIGURE 4: Vapour pressure of chromium

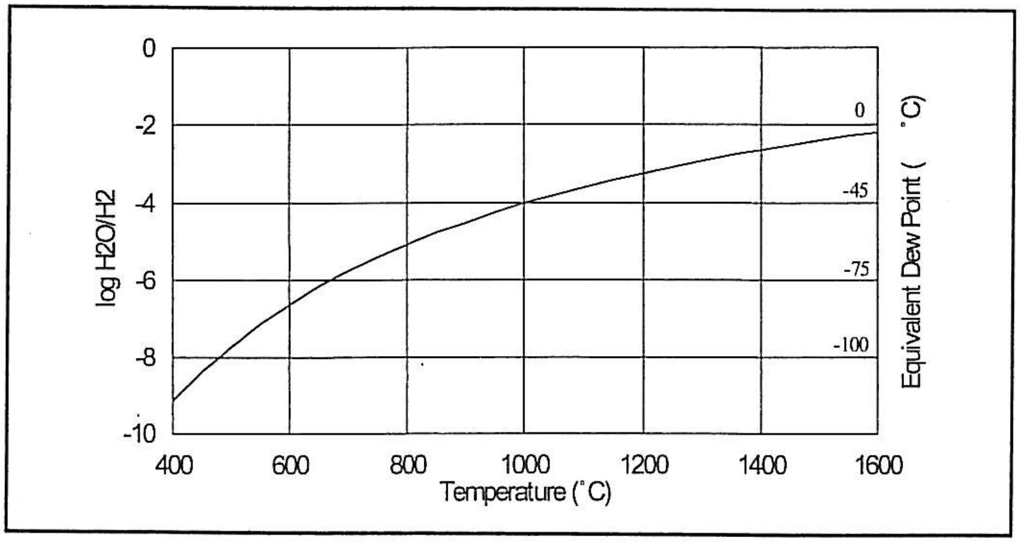

FIGURE 5: Water vapour/hydrogen ratio (at Cr/Cr2O3 Equilibrium)

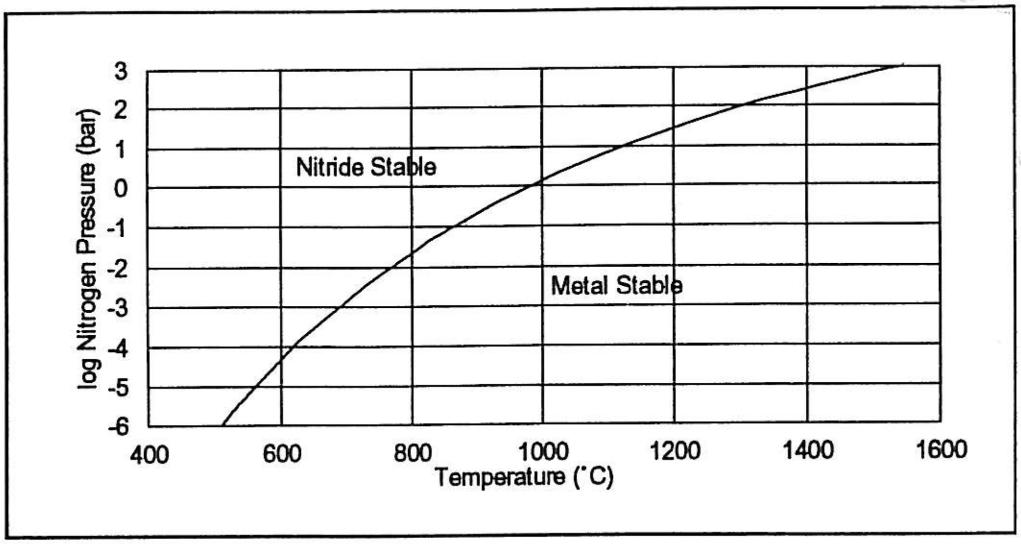

FIGURE 6: Decomposition pressure for chromium nitride (Data: Barin 1989)

Figure 7 shows that the carbon monoxide pressure for this reaction at equilibrium is easily attained with only moderate vacuum equipment. Hence it is possible to vacuum decarburize and deoxidize stainless steel simultaneously if the conditions are just right.

The debinding and sintering of MIM stainless steel parts involves complex chemical reactions among the binder, furnace lining and the stainless steel parts. Care must be taken to avoid the formation of oxides, nitrides and carbides of chromium as well as to suppress the loss of chromium by evaporation. With these goals in mind, it is recommended that: nitrogen be excluded during debinding and sintering to avoid the formation of nitrides; hydrogen be excluded from graphite furnaces to avoid carburization; special care be taken to maintain low oxygen potential to avoid oxidation; and special care be taken to remove all binder breakdown product to avoid carburization.

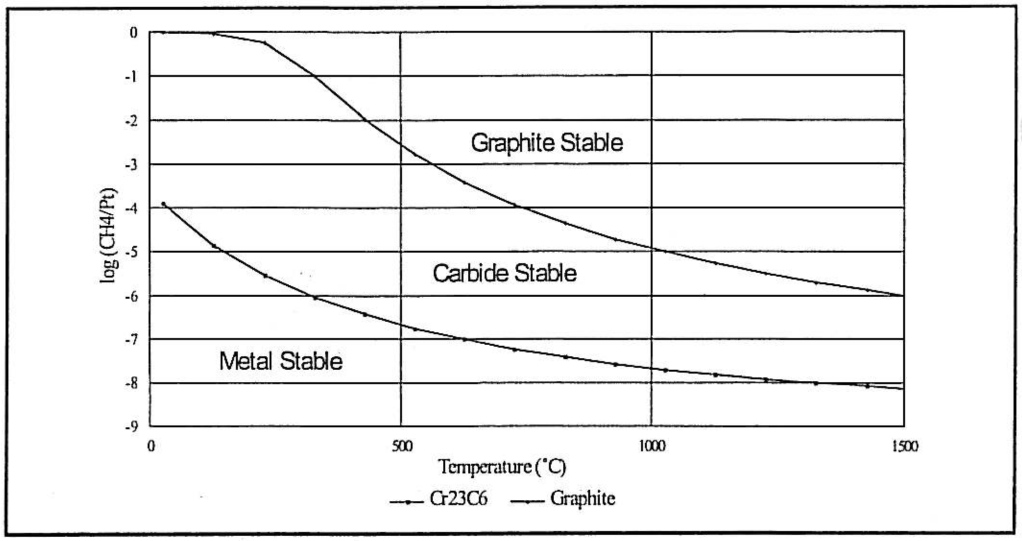

FIGURE 7: The methane-hydrogen-graphite-chromium carbide equilibrium at a total pressure of 130 Pa

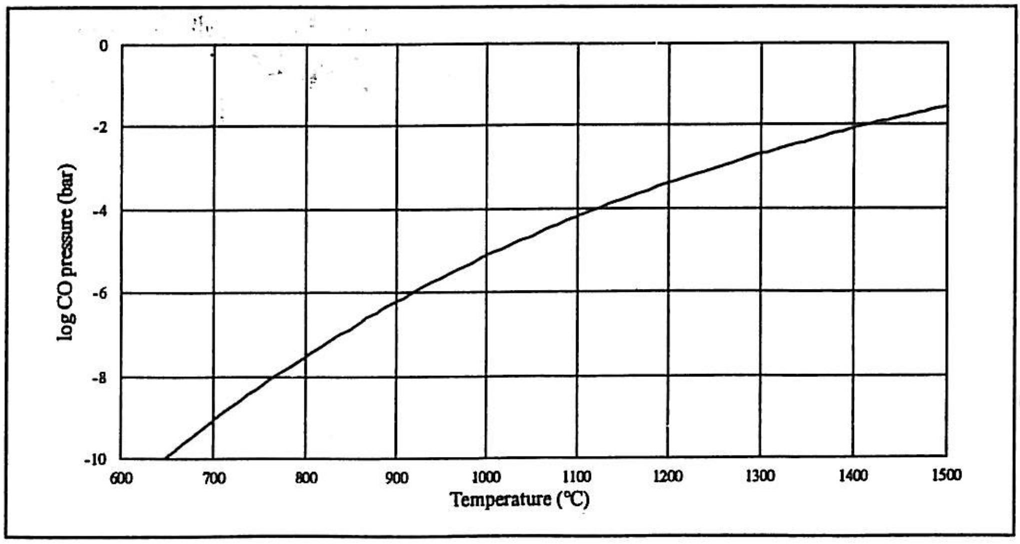

FIGURE 8: The CO pressure for the chromium-chromium oxide-chromium