Understanding the stages to successful delubrication of Powder Metallurgy components

The Gasbarre Furnace Group, a division of Gasbarre Products, offers a comprehensive spectrum of industrial heat treating equipment, engineering, technology and commercial-based solutions through its three companies, Sinterite, C.I. Hayes and J. L. Becker. In this article, Sinterite's Steven Smith discusses the important process of delubrication in the sintering of Powder Metallurgy components.

With products ranging from batch furnaces to continuous belt furnaces, pusher furnaces, vacuum furnaces, humpback furnaces and much more, the Gasbarre Furnace Group has an extensive knowledge and deep understanding of the sintering process. Through many years' experience of supplying sintering furnaces to the Powder Metallurgy industry, the group is ideally positioned to solve any application challenge. Successful removal of lubricants, prior to the final sintering of a PM part, can be one such challenge and the following article hopes to expand on some of the key issues to consider during this important step.

The use of lubricants in the Powder Metallurgy process is commonplace, being vital in terms of protecting components and tooling during the forming and ejection processes. During the sintering process these lubricants are thermally removed. However, this operation can lead to a number of issues with the final component

if not undertaken correctly. Understanding the fundamental chemical forces at play during delubrication can provide process engineers with the proper insight to hone their production process. A well designed delubrication step will result in

higher quality parts and lower equipment maintenance costs.

A recognised industry-leading lubricant is Lonza's Acrawax®, an ethylene bis-stear amide (or EBS) represented by the chemical formula $C_{38}H_{76}N_2O_2$. Acrawax melts

Fig. 1 A well designed delubrication step will result in higher quality parts and lower equipment maintenance costs

$C_{38}H_{76}N_2O_2$	592 g/mole	
Available Carbon		
Parts	350 lbs	
Lube %	0.75%	
Lube Wt	2.625 lbs	*Lbs x Lube %*
	1.19 kg	*Lbs/(2.2lbs/kg)*
	1.193 g	*kg*100*
	2.02 moles	*g lube / (EBS g/mole)*
	76.59 moles	*38 C atoms/molecule EBS*
Lube	919.07 g	*moles C x 12 g/mole*
Carbon	2.02 lbs	*g x (2.2 lbs/1000g)*
Oxidiser required		
Water	1,379 g	*moles C x g/mole*
	3.03 lbs	*g x (2.2 lbs/1000g)*
Water required	**0.38 gallons**	
Carbon	76.59 moles	*38 C atoms/molecule EBS*
Oxygen	21.0% % of Air	*Air Composition*
Air required	731.16 moles	*(2 x moles C) / 0% Air*
Air	21,182 g	*g/mole of air x moles of air*
	46.60 lbs	*g x (2.2 lbs/1000g)*
Air required	**585 ft³**	

	g/mole
Carbon	12
Water	18
Oxygen	16
Hydrogen	1
Air	28.97
O_2	32

A mole is the amount of pure substance containing the same number of chemical units as there are atoms in exactly 12 grams of carbon -12 (i.e. 6.023 X 1023)

Table 1 Water or air required to form CO_2 from available carbon

at 144°C (291°F) and vaporises at 260°C (500°F). In the 510-565°C (950-1050°F) temperature range the methane (CH_4), carbon monoxide (CO) and C_xH_{x+2} molecules decompose to soot via these reversible reactions:

- 2CO <-> 2C (soot) + O_2
- CH_4 <-> C (soot) + 2 H_2
- C_xH_{x+2} <-> xC (soot) + (x+2) H_2

This decomposition to soot is accelerated by the presence of elemental nickel, zinc oxide (ZnO) from zinc stearate and high surface area iron powder. This is the primary source of unwanted carbon in a sintering furnace. This carbon is carried by the belt through the high heat section into the cooling section, causing a variety of problems - which will be discussed later in this article.

Decomposition to soot

When the decomposition to soot occurs outside the part, black soot is deposited on the parts and in the furnace. Soot that forms inside the part inhibits atomic motion over the iron particle surfaces and prevents the development of necks or bonds between the particles. Soot build-up can even rupture the surface of the part. To prevent this blistering, all of the high carbon potential gas molecules should be removed from the part before they can decompose into soot. This can be accomplished by oxidising the carbon atoms to CO_2 and water vapour - noting that this has to occur below 510°C (950°F).

Inspection of the EBS molecular formula $C_{38}H_{76}N_2O_2$ clearly shows there is not enough oxygen to oxidise all of the carbon. For a one-kilogram part with 0.75% EBS we would need

1.5 wt.% oxygen. Oxidation can be accomplished by injecting water vapour, CO_2, or air directly into the delube zone. Blistering is more prevalent in higher density compacts and parts containing nickel.

Calculating oxidation requirements

Table 1 demonstrates how to determine the minimum amount of oxidiser needed to combine with the present carbon to form CO_2, again keeping in mind that this reaction needs to occur below 510°C (950°F). In this example we shall be looking at 158 kg (350 lbs) of compacted powder metal parts that were pressed with 0.75% by weight Acrawax® lubricant. This means that the parts would have

Element	Sample	314 SS Spec
C	0.06	.25 Max
Mn	1.3	2.0 Max
P	0.027	.045 Max
S	0.01	.030 Max
Si	1.0	1.5 Max
Cu	0.29	.35 Max
Ni	20	19.0/22.0 Max
Cr	14.8	23.0/26.0 Max
Mo	0.15	
Al	<0.1	

Table 2 Material sample analysis of slugs

1.19 kg (2.625 lbs) of lube present which would need to be removed prior to sintering. The parts contain 1,193 g of lubricant, which has 592 g per mole of EBS. We need to combine 2.02 moles carbon with enough oxygen in order to form the necessary CO_2, avoiding sooting.

Since there are 38 carbon atoms in every molecule of EBS, this particular example has 76.59 moles of carbon requiring 153.18 moles of oxygen to form the CO_2. Water, having two oxygen atoms per molecule, would require the same number of moles as the carbon that is available. In this example 1.73 litres (0.38 gallons) of water is the minimum amount. If air is the oxidiser, the percentage of oxygen in the air and the need for two oxygen atoms per carbon atom must be taken into account. With the details shown, the minimum amount of air required would be 16.57 m^3 (585 ft^3). This type of calculation is required to determine the air or water flow rate settings for the preheat delubrication section of the furnace. If insufficient oxidiser is provided, soot will form as the lubricant moves into the higher temperature sections of the furnace.

Consequences of improper delubrication

Now we will review several of the many adverse consequences of sooting caused by improper delubrication. Possibly the most

Fig. 2 Belt melting

significant impact is on the physical property performance of the sintered part. Soot remaining in the part will interfere with neck development between the particles, which may result in inferior strength properties. The soot can also alter the chemistry of the alloy, affecting both static and dynamic part properties - particularly troublesome in highly engineered, high-performance parts. Soot will also cause problems with the furnace, especially the belt, muffle, and accelerated cooling units. Carbon soot in a stainless steel wire mesh belt furnace will result in premature failure of the belt, as shown in Fig. 2.

Material slugs

Material slugs similar to those shown in Fig. 2 are commonly found in sintering furnaces, occasionally being pulled out of the furnace and deposited around the unload table. In order to determine how they are formed, a first step is to perform a chemical analysis to determine their composition.

Table 2 is taken from a study of a sintering furnace using a 314 stainless steel wire mesh belt. Shown is the material sample analysis of the slugs. Carbon, manganese, phosphorus, sulphur, silicon, copper, nickel, chromium, molybdenum and aluminium were measured and compared to the
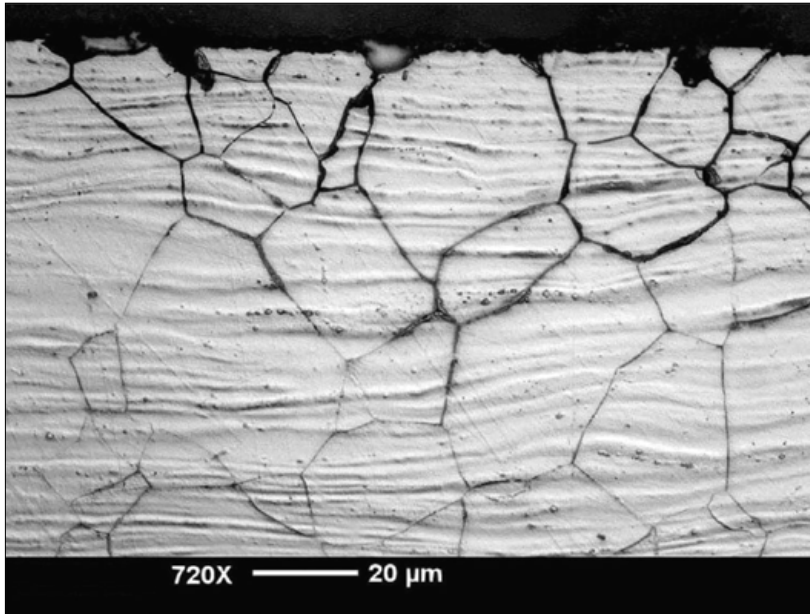
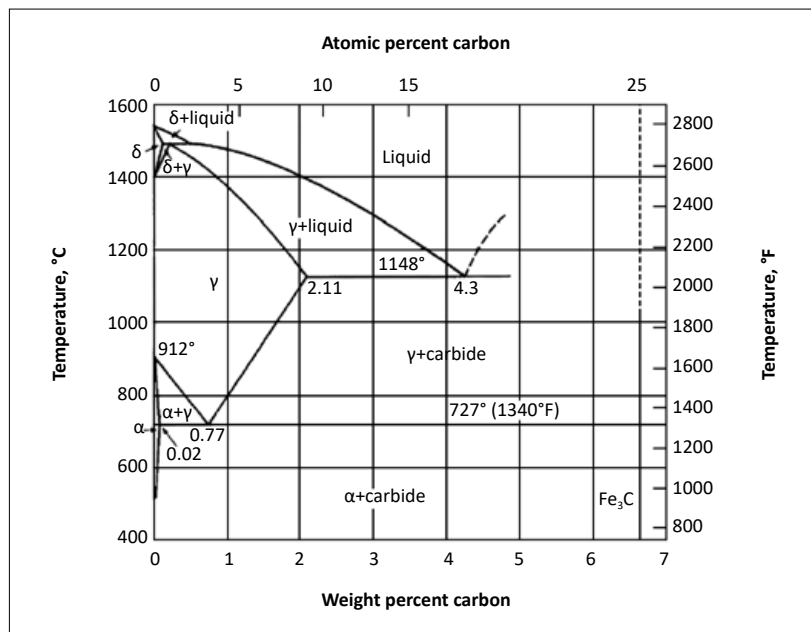*Fig. 3 Inter-granular corrosion attack in austenitic cold rolled stainless steel sheet*

Fig. 4 Iron-carbon (Fe-C) binary phase diagram, showing at temps > 1150°C (2100°F), iron and carbon react to form a low melting liquid

free crystallites. Then, the available carbon in the muffle enables eutectic melting of the stainless steel crystallites which cumulatively forms the slugs. Therefore the root cause of the problem is available carbon in the high heat section due to the inadequate delubrication of the PM part in the preheat section of the furnace.

Intergranular corrosion

An example of intergranular corrosion in a stainless steel is shown in Fig. 3. The missing spaces at the top of the sample are the missing crystallites that collect on the muffle floor, encounter carbon soot, melt eutectically and add to the build-up of the slugs. As the intergranular corrosion and loss of material progresses, the belt weakens - shortening its service life.

Iron comprises the bulk of a 314SS alloy and eutectic melting can occur, even at the molecular level. Fig. 4 is the iron-carbon binary phase diagram showing that at temperatures around 1150°C (2100°F) iron and carbon can react to form a low melting point liquid. The normal operating temperature of the high heat section of a sintering furnace is above 1093°C (2000°F), enabling melting with the right amount of available carbon. Later discussion will show a similar response of carbon with nickel, particularly in the presence of silicon.

Chemistry of carbon soot

Next we will explore the chemistry of carbon soot in the high heat section of a sintering furnace that uses a silicon carbide ceramic muffle. Carbon that is carried into the high heat section of a sintering furnace mixes with silicon carbide that has been worn from the muffle surface by the sliding of the belt. Hydrogen, in certain conditions, can combine with the carbon in the silicon carbide molecule, forming methane which flows out of the furnace - leaving free silicon. The availability of carbon and silicon causes another mechanism for eutectic melting that shortens belt service life. The silicon nickel phase diagram shown

formulation of 314SS. All tested elements were within range of the 314SS specification with the exception of chromium, which was nearly half of what is required. Given that the source material for the belt had tested within specification, it was concluded that the chromium had been depleted from the belt material during processing in the furnace.

The current best theory that explains the formation of the slugs is that available carbon in the high heat model forms chromium carbides in the grain boundaries of the stainless steel belt. This carbide formation consumes chromium, reducing its content in the samples. Additionally, the chrome carbides cause intergranular corrosion of the crystallites of stainless steel, making available

in Fig. 5 exhibits the temperature and resulting phase as a function of mole fraction of silicon and nickel. The red outline section of the phase diagram is shown expanded to the right. Liquid phase can be achieved in the 1150-1200°C (2100 to 2200°F) temperature range for a band of mole fraction ratios. With the introduction of carbon to the nickel silicon system (Fig. 6), the phase diagram shows that eutectic melting can occur below 1150°C (2100°F). This eutectic melting is the mechanism that forms the slugs shown earlier in Fig. 2.

Accelerated cooling

Many modern sintering furnaces are equipped with some form of an accelerated cooling unit used to achieve sinter hardening of the parts as they leave the high heat section of the furnace. Common to all accelerated cooling units is the use of an atmosphere to water heat exchanger that cools the atmosphere after it has pulled heat from the parts. Since these units rely on high velocity atmosphere flow and recirculation, if carbon is present in the cooling chamber it will be pulled through the heat exchanger, resulting in a buildup of carbon on the heat exchanger fins. As the carbon coating increases in thickness the cooling rate for the atmosphere diminishes as does the atmosphere flow rate. Both of these degradations adversely affect the cooling rate of the parts, which in turn reduces part hardness. Long-term degradation of sinter hardened part properties occurs as the carbon buildup increases in the heat exchanger.

Summary

Part delubrication, arguably the most critical step in the sintering process, requires certain time, temperature and atmosphere design. To ensure proper de-lubrication the part must be maintained in a temperature range of 260-510°C (500-950°F) for sufficient time for the lubricant to vaporise and leave the part.
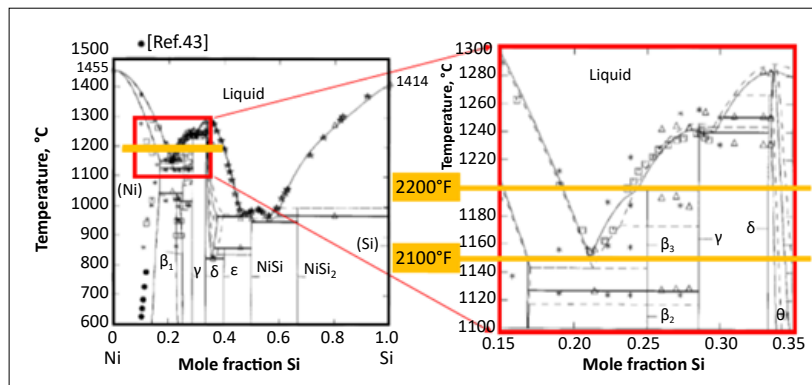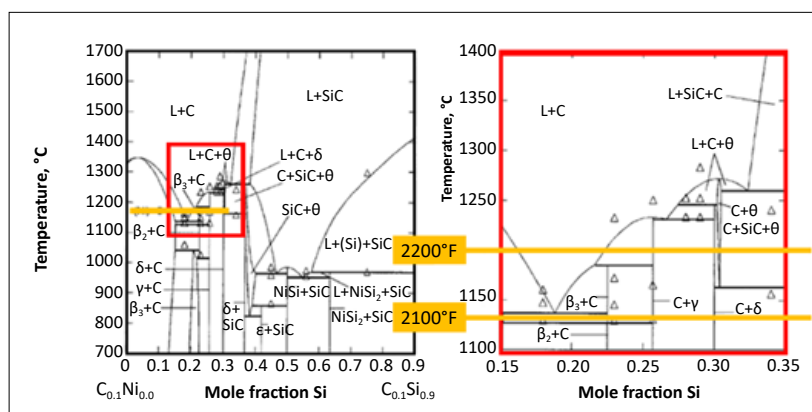

Fig. 5 Silicon (Si) nickel (Ni) phase diagram

Fig. 6 Silicon (Si), nickel (Ni), carbon (C) phase diagram

While some parts makers have found positive outcomes with the use of accelerated delubrication systems (ADS), adjustment of these units can be difficult and time consuming in order to tune in the process. More common (especially in North America and Europe) is the use of longer delube preheat chambers or zones.

Whatever the length, during this period of vaporisation the atmosphere must contain sufficient oxygen to combine with the escaping carbon atoms so that CO_2 forms and flows out of the furnace. Failure to achieve these conditions will result in the formation of soot, causing a variety of problems for both part quality and furnace life.

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