

gies can change during liquid phase sintering, since they depend on solubility, surface contamination and temperature.⁴ Hence the microstructural parameters shall be shifting with time during liquid phase sintering. A proper development of microstructure during liquid phase sintering is very important for attaining mechanical properties, particularly ductility. A typical example of Fe–P alloy can be cited for this.

6.8 Sintering Atmosphere

Nearly all metals of technical importance react with the gas of their surrounding atmosphere even at room temperature, but more so when treated at higher temperatures. The most important reason for using special sintering atmospheres is to provide protection against oxidation and re-oxidation of the sintered metal powders. There are many other ways in which a sintering atmosphere can influence the basic sintering process. By reducing the oxides the atmosphere may create highly mobile metal atoms. Gas atoms of the sintering atmosphere can enter the sintering compact via interconnected pores. They may later get trapped in closed pores, thus hindering their shrinkage. Gas atoms of the sintering atmosphere may also diffuse into the metal. At times these atoms might also alloy with the metal. In the following sections the details of different sintering atmospheres are given.

6.8.1 Hydrogen

Reducing atmospheres are, by far, most commonly used for sintering metal parts. Pure hydrogen is an excellent reducing gas, but it is not economical except in case of high valued products. Hydrogen is very flammable, having an extremely high rate of flame propagation. Because of its high flame propagation, hydrogen burns with a short, hot flame immediately upon contact with air. The flame is an almost colourless blue. Hydrogen is the lightest element; its specific gravity being only 0.069 as compared to 1.0 for air. It is easily displaced by air, and rushes out the top of the furnace door openings rapidly when free to do so. The gas has thermal conductivity seven times greater than air. Because of this, it accelerates both the heating and cooling rates of the work in furnaces. The thermal losses in furnaces are higher with hydrogen than when using heavier, less conductive gasses. Typical applications of hydrogen are in the reduction of oxides of iron, molybdenum, tungsten, cobalt, nickel and 18–8 stainless steel, annealing of electrolytic and carbonyl iron powders and carburizing of tungsten powders in lamp black to form tungsten carbide.

6.8.2. Reformed Hydrocarbon Gases

These are low cost gaseous mixtures made by reforming hydrocarbon gases. Widely these can be classified into categories – exothermic and endothermic.

Exothermic Gas: Exothermic gas is produced in specially designed generators, where fuel gas and air are mixed in such a ratio that incomplete combus-

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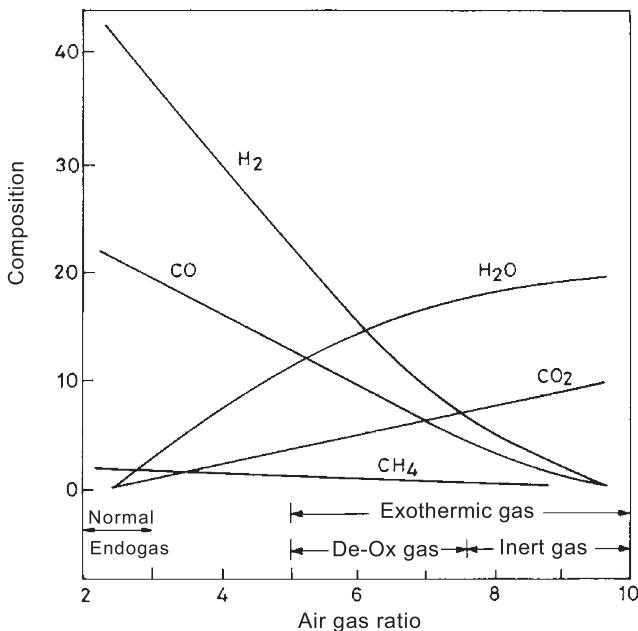


Fig. 6.4 Influence of air gas ratio on exo- and endogas assuming the fuel is pure methane.

tion takes place. The heat generated in the combustion chamber, however, is sufficient to support the reaction. Figure 6.4 shows the common range of analysis for an exothermic gas. This graph is based on the assumption that the fuel gas is pure methane, which corresponds reasonably well to a natural gas. In all cases, nitrogen is actually the largest single constituent. At an air to fuel ratio of 10.25:1, there is practically complete combustion. This gaseous mixture is relatively inert to metals such as hot copper, tin or silver. It will however oxidize hot iron and the reactive metals because of the high proportion of CO_2 and water vapour as opposed to extremely low percentages of reducing components hydrogen and carbon monoxide. This gas is known as 'lean exothermic gas' and has very little application in powder metallurgy.

The exothermic gas generator is a refractory lined, water jacketed combustion chamber that operates at 1100–1425°C. The internal temperature of the chamber depends on (1) the ratio of air to fuel gas, (2) the volume of gas being burned and (3) the effectiveness of the heat transfer from the inside of the chamber to the water jacketed exterior.

The water content in the gas mixture is very important for sintering. Upon leaving the combustion chamber, the gas has a water vapour content of approximately 5 to 15%. This makes the atmosphere oxidizing on most types of sintered products. The gas has, therefore, to be dried to at least below 1% H_2O . This may be accomplished, for example, in a refrigerant cooler by lowering the gas temperature to approximately 10°C. In many cases

Table 6.1 Composition of common sintering atmospheres

Factor	Endothermic	Exothermic	Dissociated ammonia	Nitrogen based
% nitrogen	39	70–98	25	75 to 97
% hydrogen	39	2–20	75	20–2
% carbon monoxide	21	2–10	-	-
% carbon dioxide	0.2	1–6	-	-
ppm oxygen	10–150	10–150	10–35	5
dew point, °C	-16 to 10	-25 to -45	-30 to -50	-50 to -75

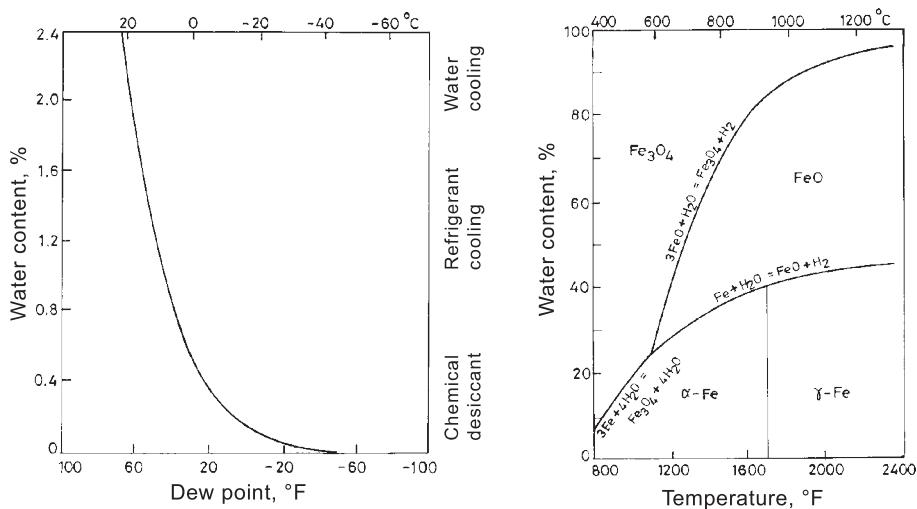


Fig. 6.5 Water content % by volume/versus dew point.

Fig. 6.6 (right) Equilibrium diagram for the system Fe–O–H. %H₂O in H₂/H₂O mixture (100 %) versus temperature.

when a stronger reducing atmosphere is needed a chemical desiccant agent is used, by which the dew point of the gas is lowered to -40°C , or approximately 0.1% H₂O. This dry gas is especially useful in a continuous belt furnace where air may enter from both ends of the furnace. Table 6.1 shows the compositions of some of the principal furnace atmospheres according to the classification of the American Gas Association (ACA).

The correlation between the dew point of the gas and water vapour content is shown in Fig. 6.5. Figure 6.6 illustrates the amount of water vapour which can be present in a pure mixture of water vapour and hydrogen, without oxidizing iron. The slope of the curve in this figure shows that water vapour is more oxidizing at low temperature than at high temperature. This means that even a fairly low water vapour content – which may not be

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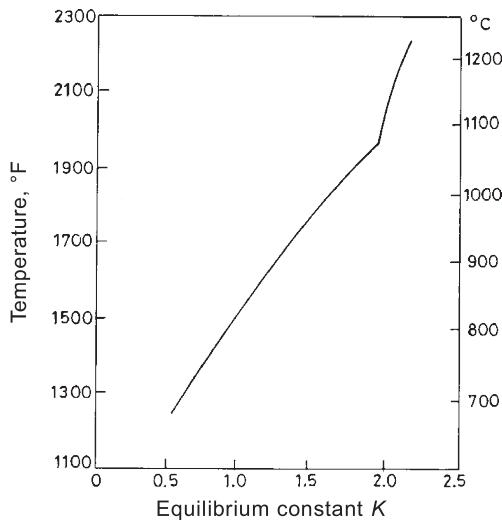
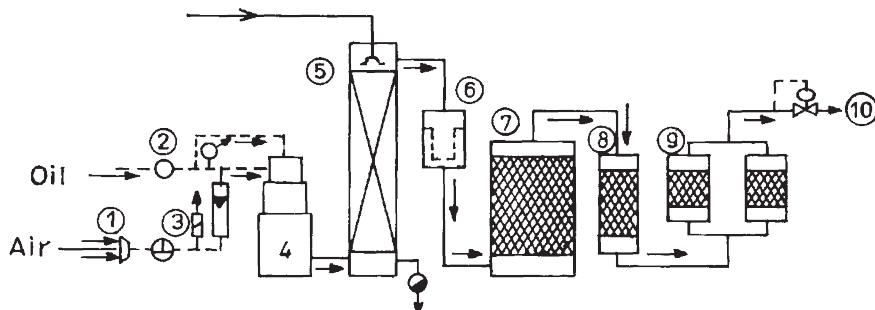


Fig. 6.7 Equilibrium constant K of water-gas reaction $\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ versus temperature.

dangerous at the actual maximum temperature in the furnace – might very well oxidize the compact in the cooling or in the preheating zone. Figure 6.7 shows the equilibrium constant (K) for the water gas reaction as a function of temperature. High temperatures favour the creation of CO and water vapour whereas low temperatures stabilize CO_2 and H_2 .

Production of exogases from hydrocarbon (petrol, crude oil, LPG) has become widely used. From crude oil, an exogas containing 20–30 % CO and H_2 can be obtained. Figure 6.8 shows a schematic diagram of an exothermic gas generator operating with crude oil. The air and crude oil enter the system at points 1 and 2, respectively, and then pass to the retort 4 through flow meters. A pressure gauge 3 is provided to check the air pressure. The oil is burned in the retort and the generated gas passes to the cooler 5 and filter 6. The crude oil contains about 1% sulphur in form of H_2S or



1. Air inlet, 2. Inlet for crude oil, 3. Pressure gauge, 4. Retort, 5. Gas cooler, 6. Filter, 7. Sulphur removal unit, 8. Oxygen removal unit, 9. Absorption dryer, 10. Gas outlet.

Fig. 6.8 Schematic flow diagram of an exothermic gas generator operating with crude oil.

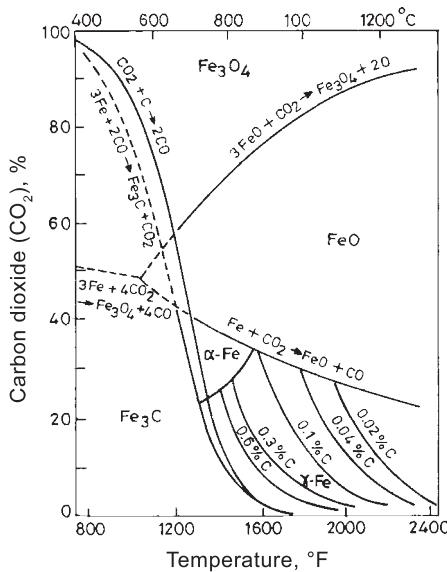


Fig. 6.9 Equilibrium diagram for the system Fe–O–C.%CO₂ in CO/CO₂ mixture (100%) versus temperature.

SO₂ and is removed to a level of 1 ppm. The gas then passes to the O₂ removal unit 8 and hence to the dryer 9. The gas finally leaves the system at point 10 ready to use.

Endothermic Gas: Endothermic gas is produced at a lower air:gas ratio, and heat must be supplied to support the reaction. It is richer than exogas in CO, H₂ and CH₄. This gas is not only strongly reducing, but is also carburizing. Endothermic gas is most suitable for sintering compacts of mixtures of iron–carbon and other alloy steels. The composition of the endogas is controlled, so that it is in equilibrium with the carbon potential of the steel to be sintered. The gas formation is facilitated over a clean catalyst such as nickel oxide in an externally heated chamber. Typically the generator operates at temperatures at about 1060–1100°C. The factors that influence the composition of the produced endogas are:

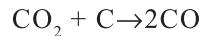
1. Temperature in the cracking zone
2. The air-to-gas ratio
3. The efficiency of the catalyst
4. The time in the cracking unit.

The temperature of the cracker should be kept close to the maximum temperature in the sintering furnace. Otherwise, the gas may not be stable in the sintering furnace. This could cause sooting or uneven properties of the sintered steel.

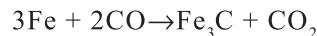
Figure 6.9 illustrates how at lower temperatures the CO is strongly carburizing and reducing. At higher temperatures, however, the action of gas is weaker. The two almost parallel inverted S-shaped curves show

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the producer gas reaction:



and the carburizing effect of CO on iron:



At lower temperatures, the producer gas reaction is generally the most prevalent and results in the soot deposition on the sintered parts. However, at higher temperatures, say at 800°C, the carburizing action is dominant. Soot deposition can be suppressed by fast heating and cooling in the furnace. The effect of methane is different from that of CO. Methane, with increasing temperature, increases the reducing action and the rate of carbon deposition. Figure 6.10 presents the equilibrium between a methane–hydrogen atmosphere and iron with different carbon contents, at various temperatures.

The extent of decarburization and re-carburization determines the finished carbon content at or near the surface of the sintered steel. Carbon content can be controlled by the dew point or the carbon dioxide content in the endogas. Most sintering under endothermic atmosphere is done at dew point ranging from –5 to 15°C. Endogas is reducing to iron above 260°C, because its typical 40% H₂ and 0.8% H₂O (dew point 5°C) contents

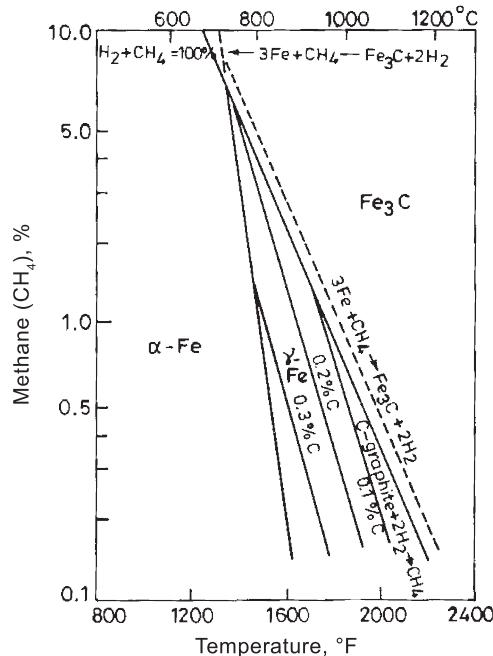


Fig. 6.10 Equilibrium diagram for the system Fe–C–H. CH₄ content in CH₄/H₂ mixture versus temperature.

provide a hydrogen to water ratio of 50 to 1. Although this ratio achieves acceptable oxide reduction, other atmospheres notably those based on hydrogen or dissociated ammonia or synthetic nitrogen based atmospheres – can provide higher ratios.

Figure 6.11 illustrates a schematic diagram of an endothermic generator. The air and gas enter the flow meters (2 and 4) and then the mixing unit 5 through filter 1 and valve 3 respectively. The mixture is then passed in the catalyst filled reaction chamber of the generator by means of the compressor 6. The retort 7 is heated to the desired temperature by heating equipment 9. The gas leaving the retort is cooled to about 200 to 300 °C in the cooler 8 and leaves the system at point 10.

Table 6.2 gives the main characteristics of exo and endo gas generators showing different output capacities.

6.8.3. Nitrogen and Nitrogen-Based Atmospheres

Nitrogen is inert to most of common metals and alloys. Because it is non-flammable, it is also used as a safety purge for flammable atmospheres.

The main constituent of the nitrogen-based system is molecular nitrogen. Molecular nitrogen is obtained from air, which consists of approximately 78% N₂, 21% O₂, 0.93 % argon, 0.03 % carbon dioxide and a small amount of such rare gases as neon and helium. Nitrogen is most commonly produced through air separation, i.e. liquefaction and fractional distillation. Air is filtered, purified, compressed to drive it through the rest of the sys-

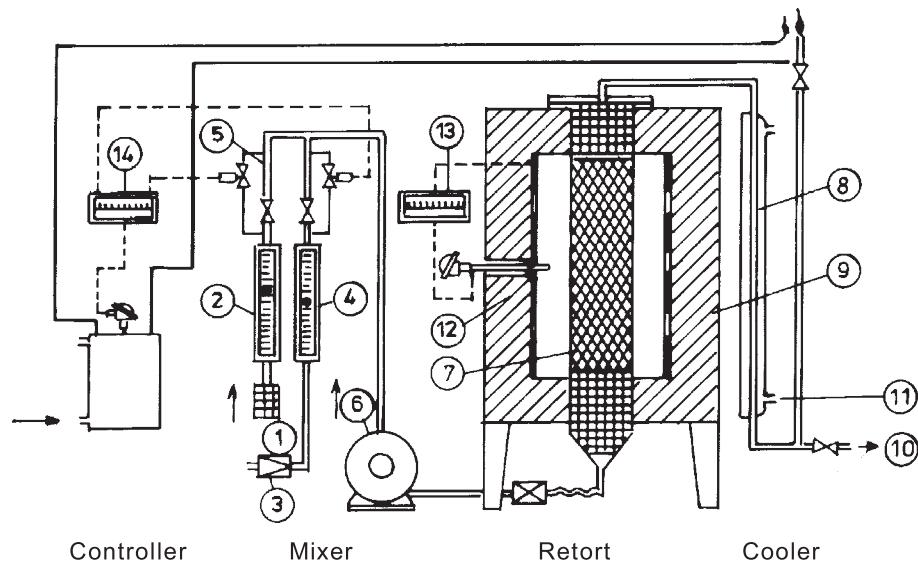


Fig. 6.11 Schematic flow diagram of an endothermic generator: 1 – Air filter; 3 – valve; 2 and 4 – flow meters; 5 – mixer; 6 – compressor; 7 – retort; 8 – gas cooler; 9 – heating equipment; 10 – endogas outlet; 11 – cooling water; 12 – thermocouples; 13 – dew point analyser.

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Table 6.2 Main characteristics of exothermic gas generators

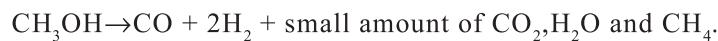
(m ³ /h at NTP)	Overall dimensions (m)			Base gas demand (m ³ /h at NTP)		
	length	width	height	propane	natural gas	town gas
20	1.5	1.4	2.2	1.1–1.6	3–4	6.5–10
80	1.8	1.7	2.4	3.5–5	10–13	22–30
300	2.6	2.9	3.8	14–19	37–48	85–115
500	3	3	3.8	23–31	60–80	140–180

tem, and cooled to remove H₂O and CO₂. After being liquefied it is distilled into major constituents, the most abundant being nitrogen. In addition to being plentiful and independent of natural gas, the nitrogen thus produced has the following characteristics:

- It is very dry, having a dew point of less than –65°C.
- It is very pure, having less than 10 ppm of oxygen.
- It is essentially inert to materials most commonly sintered and to furnace components such as muffles, conveyer belt, heating element, radiant tube, fixtures, etc.

In actual practice, furnaces are not very tight and some air does get in. Nitrogen by itself does not control the resulting surface oxidizing and decarburizing. Chemically ‘active’ gases are, therefore, added to the nitrogen, when the atmosphere has to perform functions requiring transfer of some element such as carbon from the atmosphere to the component being treated or such as oxygen from the oxide to the atmosphere. These active ingredients can be divided into the following categories:⁷

(1) Oxide reducing agents – The most desirable ingredient for reducing surface oxides is hydrogen. It can be derived from liquid hydrogen storage tanks or dissociated ammonia. It can also be derived from endogas or dissociated alcohols. Methanol dissociates or cracks at temperatures above 815°C to produce H₂ and CO in the same ratio (2:1) as normally found in the endogas generated from natural gas:



Dissociated or cracked methanol when mixed with appropriate amounts of nitrogen can produce an atmosphere almost identical to endogas.

(2) Carburizing Agents – The most desirable ingredient to carburize is CO. It can be derived from endogas or dissociated alcohols such as methanol, or by reacting a hydrocarbon such as natural gas or propane and an oxidant such as water in the carburizing zone. It is generally found that in order to maintain effective carburizing rates, the CO level in the carburizing zone should not be less than 10 percent.

(3) Oxidant – Small but controlled amounts of oxidants such as CO₂, H₂O, O₂ or some combination of them can be added to nitrogen at selected sections of the furnace to provide decarburizing, oxidizing or burning of lubricants just before sintering P/M parts.

Manufacturing the nitrogen consumes less energy than producing an equivalent volume of endogas: 44% less energy in the liquid storage process and 80% less energy in the ‘on site’ separator process. Nitrogen allows smaller volumes of atmosphere to be used because it permits reduced flow rates, increase in production rates, lower part rejection and increased furnace utilization.

With the proper choice of enrichment gas, nitrogen based atmospheres can be used to sinter and infiltrate iron, carbon steel and other ferrous and nonferrous alloys. Stainless steel and refractory metals can be sintered in nitrogen based atmospheres when nitriding is not critical.

6.8.4 Dissociated Ammonia

Dissociated ammonia consists of 75 % hydrogen–25 % nitrogen by volume. Liquid ammonia from the tank enters a vaporizer at high pressure where heat converts the liquid in vapour. The pressure of the vapour is then reduced in an expansion valve and the low pressure vapour passes through a dissociator element filled with catalyst. Heated at a temperature in the range 900–1010°C, ammonia is dissociated into hydrogen and nitrogen. Figure 6.12 illustrates the flow diagram of an ammonia dissociator. Normally the gas contains only a trace (0.05% or less) of uncracked ammonia, which can be eliminated by passing it through either water or activated alumina. The dissociated gas at elevated temperature is highly flammable. Its specific gravity is 0.295 and thermal conductivity 5.507 compared to air, which is unity. Typical applications of dissociated ammonia include sintering of brass, copper, iron–copper, tungsten and tungsten alloys, aluminium and its alloys, and stainless steels.

6.8.5 Argon and Helium

Argon and helium are nonflammable and are inert to all application. They are used for sintering refractory and reactive metals and also as a back fill in vacuum furnaces. Argon is cryogenically produced from air. Its purity is

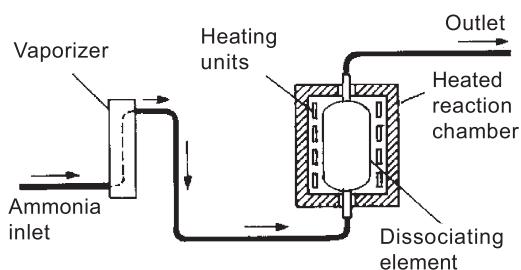


Fig. 6.12 Flow diagram of an ammonia dissociator.

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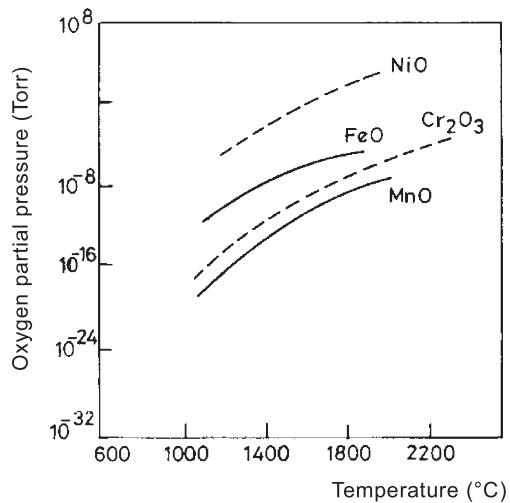


Fig.6.13 Variation of equilibrium O_2 partial pressure with temperature for selected metal oxides.

very high, less than 0.0005 % oxygen and a dew point lower than -68°C . Its specific gravity is 1.379 g/cm³, while thermal conductivity is 0.745.

6.8.6 Vacuum

Vacuum retains the proper chemistry of the parts during sintering. It is often more economical than atmosphere gases, particularly bottled gas. The only operating costs involved in producing the vacuum are for electrical energy and oil for the pumps. Vacuum pumps commonly used are mechanical pumps and oil vapour pumps. Vacua are generally classified with four ranges: rough (>1 to 1 torr), medium (1 – 10^{-3} torr), high (10^{-3} to 10^{-7} torr) and ultimate vacuum ($< 10^{-7}$ torr). Most sintering furnaces are medium or high vacuum furnaces and such vacua are readily created by oil vapour pumps backed by a mechanical rotary pump.

All metallic oxides have a so-called dissociation pressure which is equal to the partial pressure of the oxygen present in the gas atmosphere at equilibrium with the oxide. If the partial pressure of the oxygen is lower than this, the compound will be transferred into a lower value oxide or metal and oxygen. If the partial pressure of the oxygen is higher than the dissociation pressure, the metal or the metallic oxide will oxidize. Figure 6.13 shows the dissociation pressure of some of the metal oxides as a function of temperature. During sintering an alloy, the selective evaporation of some alloying elements, due to the different vapour pressures of the individual metals, must also be taken into account. This naturally depends on the duration and temperature of vacuum sintering. Table 6.3 gives data of vapour pressures of some common metals.

Table 6.4 illustrates the dew point existing at different degrees of vacuum

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Table 6.3 Vapour pressures of some common metals

Vapour pressure, torr	Temperature, °C						Melting point, °C
	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	
Aluminium				1210			660
Carbon		2100	2250	2430			3730
Chromium	1060	1160	1270				1875
Cobalt	1160	1260					1495
Copper		1030	1140	1270	1430	1620	1083
Iron	1110	1210	1320				1537
Lead	490	550	630	720	830	980	327
Manganese	700	770	850	950	1070	1230	1245
Molybdenum	1990	2170					2610
Nickel	1140	1250	1360				1455
Niobium	2190	2360	2500				2470
Silicon	1180	1280	1360	1550	1720	1930	1410
Silver	760	830	920	1030			960
Tantalum	2400	2590	2810				3000
Tin			1090	1230	1400		231
Tungsten	2550	2760	3010	3330	3650		3410
Vanadium	1430	1551					1900
Zinc		250	290	340			420

Table 6.4 Dew point as a function of water vapour content for different vacua

Vacuum (torr)	Dew point (°C) for different volumes percent of water vapour in the gas		
	20 %	70 %	100 %
1	-35	-21	-17
10^{-1}	-55	-43	-40
10^{-2}	-70	-61	-58
10^{-3}	-86	-77	-74
10^{-4}	-92	-90	-89

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for different levels of water vapour in the gas. From the Table it can be seen that for a vacuum of 10^{-1} torr the dew point is between -40 and -55°C , depending upon the water vapour content.

Most of the vacuum sintering is on the reactive metals which are highly susceptible to the formation of hydrides, nitrides or oxides in gaseous atmospheres. Refractory metal carbides, stainless steels, beryllium, titanium, zirconium, tantalum, niobium, vanadium, thorium, uranium and cermets are best examples for vacuum sintering.

6.9 Sintering Atmosphere Analysis and Control

6.9.1 Gas Analysis

Gas analysis is done either by an Orsat type analyzer or infrared analyzer. In the Orsat type the complete analysis of a gaseous mixture is divided into the absorption phase and the explosion or burning phase. The amount of carbon dioxide, oxygen and carbon monoxide are determined by chemical absorption. These units are portable and permit relatively rapid analyses.

The infrared analyzer depends on the principles that different gases absorb infrared energy at characteristic wave lengths. Because of this property, changes in the concentration of a single component in a mixture, produce corresponding changes in the total energy remaining in an infrared beam passed through the mixture. Proper selection of apparatus permits accurate, rapid analyses for such constituents as carbon monoxide, carbon dioxide and methane. Such analyzers are not suitable for measuring oxygen, hydrogen and nitrogen which have no infrared absorption band. Such analysers are highly sensitive and are successfully applied for analyzing gases with high carbon potential, such as purified exothermic gas or dry endothermic gas, and those with high purity such as dry hydrogen or argon.

6.9.2 Specific Gravity Analysis

The specific gravity of gases can be measured and compared against that of air. Since carbon dioxide is much heavier than the other sintering atmosphere constituents, this analysis is especially sensitive to changes in carbon dioxide. In case carbon dioxide appears in the influent or effluent furnace atmosphere, the specific gravity analyser could be used for corrective measures. This analysis is useful for example, in checking sintering furnace atmospheres of purified rich exothermic or rich endothermic gas which are supposed to be free from carbon dioxide. By continuously measuring the specific gravity of the effluent gas from the furnace, the completeness of purge can be established.

6.9.3 Moisture Determination

The moisture content of the sintering atmosphere has significant effect on sintering. One of the simplest method for determining moisture content is by checking the dew point. The device used to determine this is called 'dew