Metallurgia

Light Alloys

N2-Nitrogen On-Site Generation for Heat Treatment of Aluminium

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1. Introduction

In the metals processing industry, heat treatment applications are required for producing parts with the desired mechanical and surface properties, as well as for stress relief after mechanical deformation.

Today some companies use exothermic or endothermic generators or ammonia dissociates to create the necessary atmospheres. Compared with atmospheres composed of technical gases such as nitrogen and hydrogen, these generated gases have serious disadvantages. For this reason, most heat treatment companies use high quality atmospheres based on nitrogen. There are several types of industrial gas atmospheres for the heat treatment of aluminium. For conventional applications such as annealing, brazing and sintering, Air Products provides industrial gas-based atmospheres including pure nitrogen or pure hydrogen and nitrogen/hydrogen mixtures. Since oxidising components are commonly considered harmful for heat treatment processes, most of the operators use very high purity nitrogen, which is delivered and stored in a liquid form in cryogenic tanks and then vaporised on site for gaseous use.

It is becoming increasingly important to produce high quality parts at competitive prices. In a number of heat treatment operations it is technically possible to use nitrogen with lower purities, which means higher oxygen levels compared to liquid nitrogen. This nitrogen can be generated in a gaseous form on the customer's site in so called "On-Site" generators. Depending on the flow conditions and acceptable purity, on-site generated nitrogen can be significantly cheaper than liquid nitrogen.

2. Technical Background

In general, atmospheres are used to provide an atmosphere neutral to the metal, to prevent oxidation on the surface and to provide a bright surface finish. Therefore, air has to be removed from the furnace and, depending on the type of metal, the remaining traces of oxygen have to be reduced by a reactive component in the atmosphere blend. However, the reducing reaction should not produce too many oxidising components such as moisture (1) or carbon dioxide (2), so it is important to provide a sufficient flow rate of a protective atmosphere to prevent air ingress.

$$2\,H_2 + O_2 \leftrightarrow 2\,H_2O \qquad (1)$$

$$2\,CO + O_2 \leftrightarrow 2\,CO_2 \qquad (2)$$

It can be seen that heat treatment atmospheres always have residual amounts or traces of oxidising components. The metal oxidation can be represented by following reactions:

$$2\,Me + O_2 \leftrightarrow 2\,MeO \qquad pO_2 \qquad (3)$$

$$Me + H_2O \leftrightarrow MeO + H_2 \qquad K = pH_2/pH_2O \qquad (4)$$

$$Me + CO_2 \leftrightarrow MeO + CO \qquad K = pCO/\,pCO_2 \qquad (5)$$

Reactions (4) and (5) show that the oxidising or reducing potential always depends on the equilibrium of pH_2/pH_2O or pCO/pCO_2 and not only on the amount of oxidising components. The driving force for reaction 3 is simply the partial pressure of oxygen. This reaction is the most important for pure nitrogen atmospheres. The Ellingham-Richardson-Diagram (Figure 1, appendix) shows the reducing or oxidising potential of the reactions (3), (4) and (5) for several materials and for different temperatures.

3. Heat treatment of aluminium

As shown in table 1, aluminium reacts with very small amounts of oxidants and thereby produces a very thin passive oxide layer anyway.

	Aluminium	
	400°C	**500°C**
pO_2	$2{*}10^{-76}$	$3{*}10^{-65}$
$Kp=pH_2/pH_2O$	$>1{*}10^{+16}$	$>1{*}10^{+16}$
$Kp=pCO/pCO_2$	$>1{*}10^{+16}$	$>1{*}10^{+16}$

Table 1: *Equilibrium constants for aluminium*

For that reason, aluminium was traditionally heat treated in an exothermic generated atmosphere or in air. But annealing in an oxygen rich atmosphere has two drawbacks, firstly increased surface oxidation and secondly the possibility of explosion due to rolling oil vapour mixing with oxygen at high temperature. Exothermic generated atmospheres also have the disadvantage of being toxic and combustible. Furthermore these generators have high maintenance costs and sometimes cause production losses due to breakdown. Consequently, nearly all heat treaters of aluminium use a pure nitrogen atmosphere. Nitrogen purges the oxygen out of the furnace, eliminates the risk of explosion due to oil vapour and avoids the formation of flammable atmospheres with toxic components such as CO, as found in exothermic atmospheres. Since aluminium forms a corrosion resistant protective layer, both with O_2 and H_2O, there is no need to use high purity nitrogen. Trials have shown that there are no differences in the surface quality or oxide layer by using nitrogen of purities 99.5 % and above for pure Aluminium. In case of alloyed aluminium, there might be the requirement for higher purities of nitrogen, but there is still the opportunity to use cost effective on-site generated nitrogen.

4. Nitrogen "On-Site" Systems

Nitrogen can be supplied in different ways and with different purities. For the quantities used normally in heat treatment companies, bulk or on-site supply can be used. Bulk, or liquid stored nitrogen has the highest quality with a purity of 99,9995%. On-site generated nitrogen can be produced in different ways and with different purities. There are three typical technologies, membrane systems, pressure swing adsorption (PSA) systems, and high purity nitrogen (HPN) generators.

Table 2 provides an overview of the different systems, with the range of nitrogen purities, flow rates and pressure for optimal use.

	Liquid Nitrogen	Membrane	PSA	HPN
Flow rates (Nm≈/h)	0 - 600	0 - 4000	20 - 2500	150 +
Purity (% N_2)	99,9995	79 – 99,9	95 – 99,9995	99,9995
Pressure (barg)	0 – 14*	0 – 12*	0 – 7*	0 – 9*

Table 2: *Standard Ranges, Purities and Flow Rates of Nitrogen Supply Modes*

**higher pressures available on request*

5. Commercial Reflection

Since nitrogen flow rates and operational procedures are different in every plant, there can be no general recommendation for any mode of supply. The investment costs for an on-site system increase with higher purities and flow rates. In general, on-site systems are very competitive for continuous and high flow rates, but, the break-even point is different for every customer. In some cases it can be more economic to stay with liquid nitrogen.

Figure 2 shows a typical nitrogen flow profile for a heat treatment plant with several furnaces. On-site systems work most economically when they deliver a constant 100% design flow. It is therefore recommended to specify the on-site system for the base load (grey line) and to supply the peaks by liquid nitrogen. (LIN – green line). The buffer vessel normally used with on-site systems allows short term peaks in demand to be catered for (orange line).

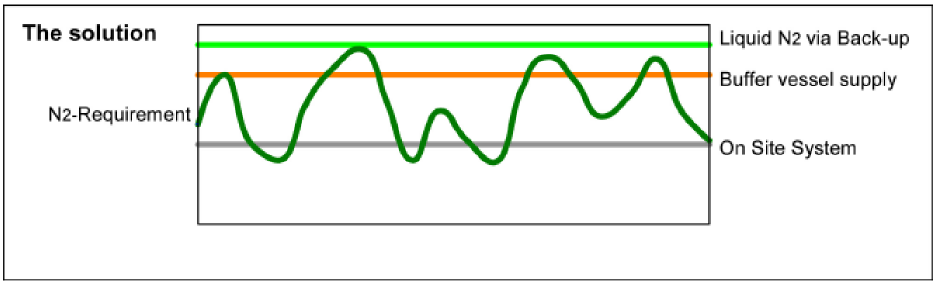

Figure 2: *Specification of an On Site System*

Practical experience on customer sites has shown significant costs savings of up to 50% on total nitrogen costs.

6. Summary

In normal heat treatment processes of aluminium exothermic generated atmospheres or nitrogen atmospheres are used. Due to several disadvantages of exothermic generated atmospheres like high maintenance costs, toxic and explosive atmospheres most of the heat treaters have replaced the generators by nitrogen based atmospheres. In this case the nitrogen is commonly supplied in a liquid form. However, in many heat treatment processes it is possible to use on-site generated nitrogen with a lower purity compared to liquid nitrogen. Furthermore for some applications, although the high quality of liquid nitrogen is required, it still makes sense to convert the liquid to an on-site supply. Practical experience on customer sites has shown significant costs savings of up to 50% on total nitrogen costs. Technical gas suppliers can assist in calculating the real commercial benefits for specific applications.

6. References

[1] Claude Beguin: Einführung in die Technik der Schutz- und Reaktions-gase, Schweizerischer Verband für die Wärmebehandlung der Werkstoffe

[2] D. Garg and B.B.Bonner: Heat Treatment of Ferrous and Nonferrous Metals and Alloys in Non-Cryogenically Produced Nitrogen by an Innovative, Economical System, Industrial Heating, June 1992

7. Appendix

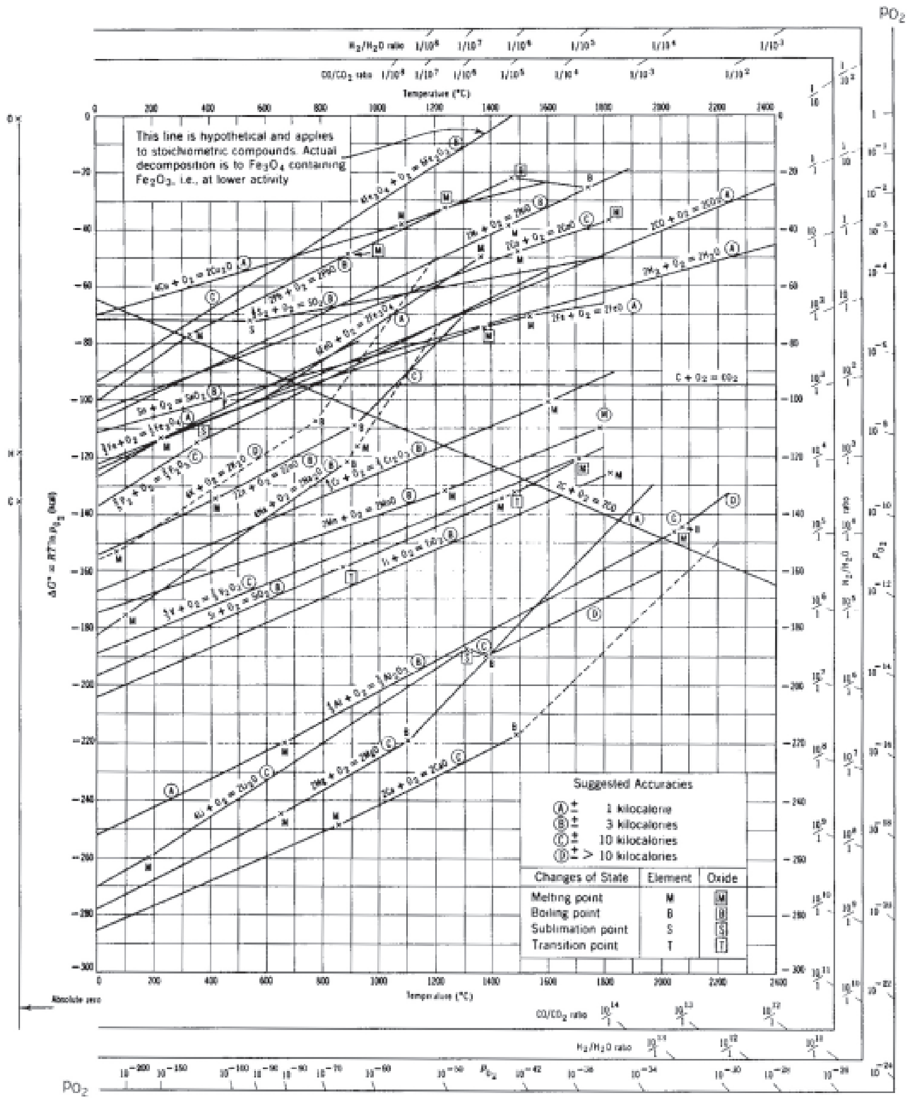

Figure 1: *Ellingham-Richardson-Diagram [1]*

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