UNDERSTANDING AND OPTIMIZING NITROGEN-HYDROGEN FURNACE ATMOSPHERES FOR ANNEALING

Proper specification, measurement, and control of annealing furnace atmospheres are critical to reduce sooting, oxidation, sticking, and distortion.

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Annealing is a generic term denoting a treatment that consists of heating to and holding at a suitable temperature followed by cooling at an appropriate rate, primarily for the softening of metallic materials. Generally, in plain carbon steels, annealing produces a ferrite-pearlite microstructure. Steels may be annealed to facilitate cold working or machining, to improve mechanical or electrical properties, or to promote dimensional stability[1]. Parts are typically annealed either in batch furnaces such as bell furnaces or continuous furnaces such as mesh-belt and roller hearth-furnaces in the presence of an atmosphere that is non-oxidizing or reducing to components. These atmospheres are either produced by on-site atmosphere generators or supplied by blending nitrogen and hydrogen. Because generated atmospheres are produced by partial oxidation of a hydrocarbon gas in air and the composition of both air and a hydrocarbon gas change continuously with time, it is difficult to produce and supply generated atmospheres with consistent quality and composition. This is the prime reason that most of manufacturers have chosen blended nitrogen(N_2)/hydrogen(H_2) atmospheres for annealing furnaces[2]. Depending on the type of material, different compositions of N_2 and H_2 must be used to achieve the desired, in most cases bright, surface finish.

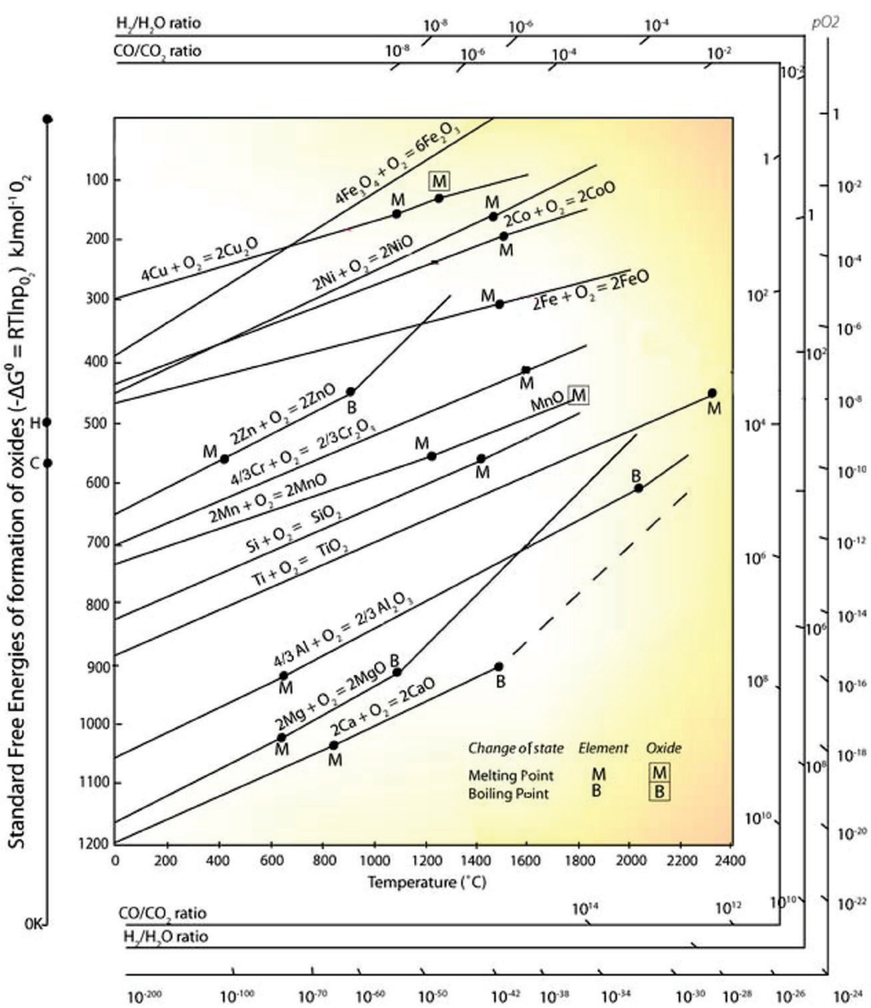


Fig. 1 — Ellingham diagram[4].

Although most people in the industry know how important the atmosphere is, in nearly all annealing processes the atmosphere itself is not closed loop controlled and is just introduced with a fixed blend. This means the introduced gas composition is set-up either for the worst-case scenario or, if any unexpected external influences like air ingress or residual oil contaminates the atmosphere, oxidized and/or decarburized material will be produced leading to rejects or rework[3]. This article describes how to effectively design and utilize a N_2/H_2 annealing atmosphere. Based on years of field experience with N_2/H_2 annealing atmosphere, Air Products has developed an innovative closed loop atmosphere control system, monitoring and regulating the reducing potential of the N_2 based atmosphere for annealing carbon steel.

OXIDATION AND DECARBURIZATION IN ANNEALING

Annealing is a relatively simple heat treatment to perform, but there are still several factors that must be carefully considered and controlled. In the furnace, the material undergoes a temperature gradient during the heating and cooling phases of the process. Due to external influences such as air ingress or oil vaporization in closed furnaces, there are also gradients of atmosphere composition. For example, in a continuous furnace the entry and exit areas are critical. In both areas oxygen (O_2) ingress can create an oxidizing atmosphere. In the low temperature range a direct reaction of the metal with O_2 (reaction 1) can happen; in the hot zone, O_2 firstly reacts with H_2 to water (reaction 2), which impacts the oxidizing potential of reaction 3. In N_2/H_2 atmospheres the oxidation by CO_2 normally can be neglected (reaction 4 and 5):

Oxidation by oxygen:

1) $2\,Me + O_2 \rightarrow 2\,MeO$

Oxidation by moisture:

2) $2\,H_2 + O_2 \rightarrow 2\,H_2O$

3) $Me + H_2O \rightarrow MeO + H_2$

Oxidation by carbon dioxide:

4) $2\,CO + O_2 \rightarrow 2\,CO_2$

5) $Me + CO_2 \rightarrow MeO + CO$

Oxidation-/reducing potentials that need to be monitored/controlled:

for reaction 1: pO_2

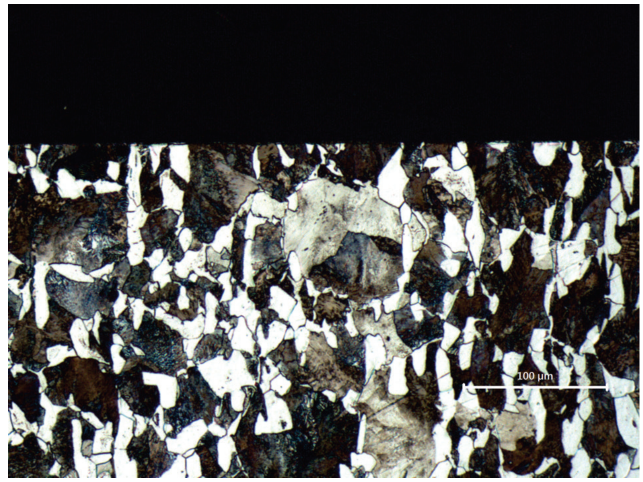
for reaction 3 $K_H = pH_2/pH_2O$

for reaction 5: $K_C = pCO/pCO_2$

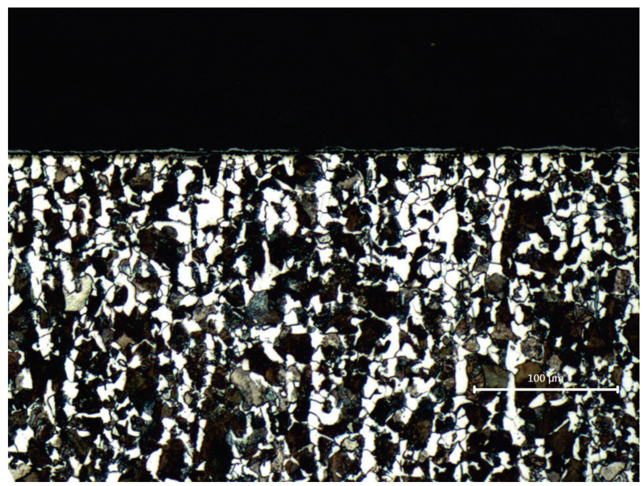
The oxidizing and reducing potentials of the reactions 1, 3, and 5 are different for each element. The Ellingham diagram (Fig. 1) shows the standard free energies for oxide formation for several elements based on the oxidation-/reducing potential of the reactions 1, 3, and 5. Using the Ellingham diagram, process engineers can design the atmosphere after the material and alloying elements are known.

To investigate how oxidation and decarburization happen on steel parts in an atmosphere containing oxygen and moisture, a group of experiments were designed and run in a laboratory box furnace[5]. In Fig. 2 and 3, the surface oxidation and decarburization of different steels in N_2/O_2 and N_2/H_2O atmosphere are observed and studied.

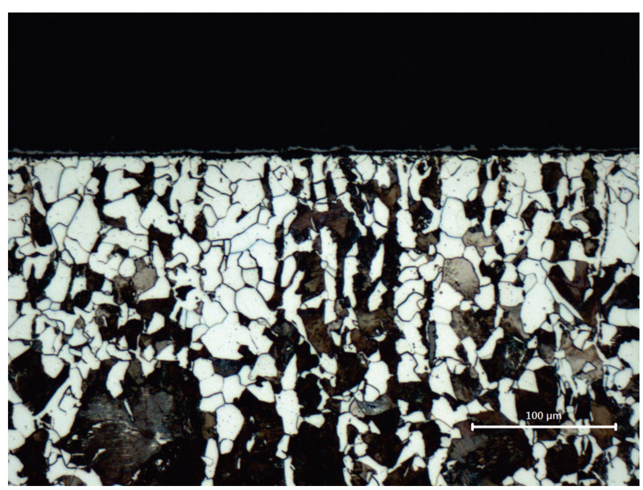
All the N_2/O_2 experiments involve 30 min. holding time at the designed conditions. Gray oxidation surface (oxide scale) is produced on all samples. In heat treatment, the decarburization process is sensitive to temperature[6]. The temperature can affect decarburization in three ways: 1) The dissolution rate of cementite and the diffusivity in both phases (austenite and ferrite) increases with temperature, contributing to a deeper decarburized layer after a given time. 2) The austenite fraction increases with temperature. Because carbon diffuses slower in austenite than in ferrite and is more soluble in austenite, the presence of austenite reduces the thickness of the decarburized layer. 3) The reaction kinetics between oxidizing gases and carbon/iron is related to the temperature.



(1)

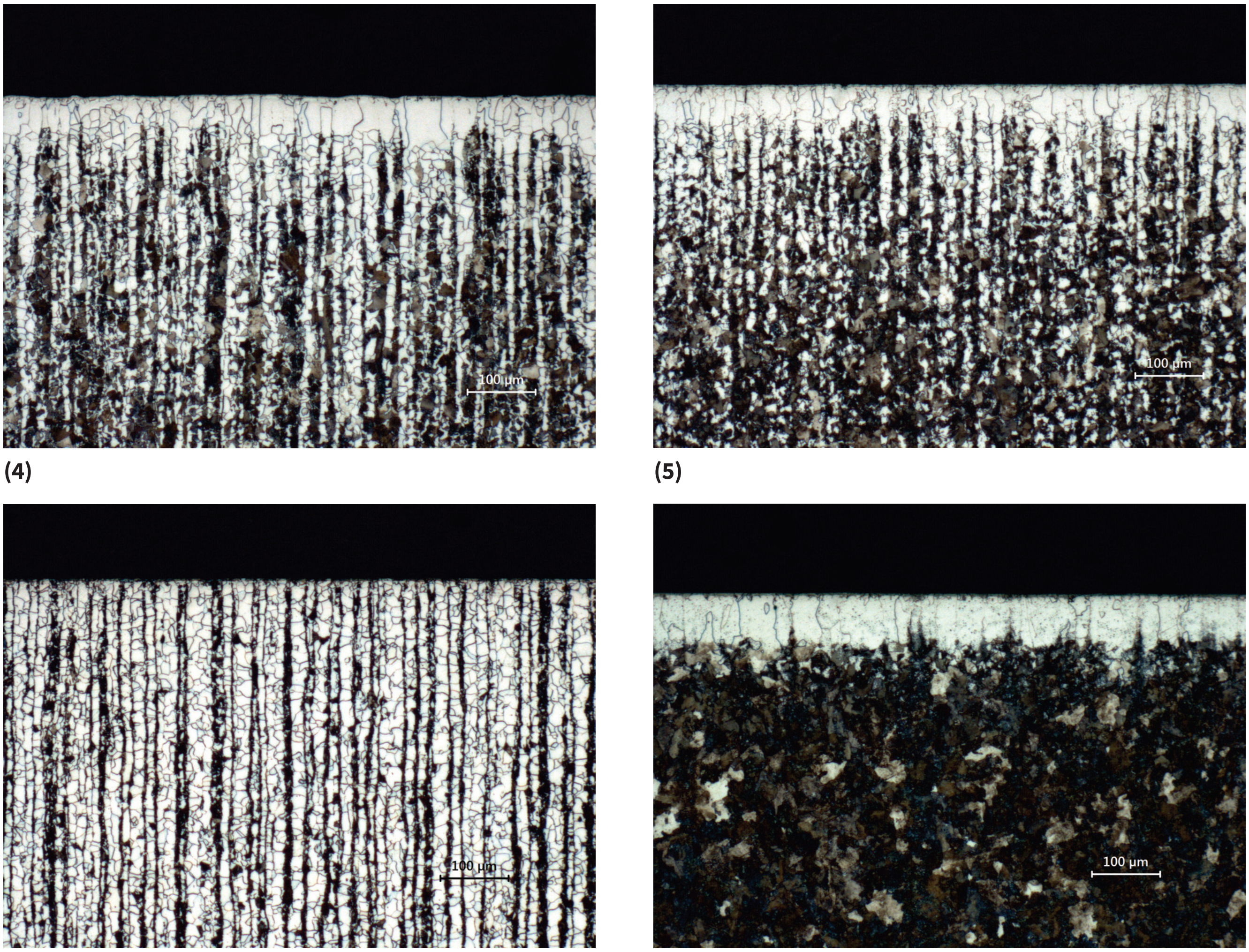


(2)



(3)

Fig. 2 — Surface microstructure of 1045 steel samples after being held in different N_2/O_2 atmosphere for 30 minutes (1. N_2-2000ppm O_2 at 500°C, 2. N_2-2000ppm O_2 at 725°C, and 3. N_2-1000ppm O_2 at 860°C).



(4) (5) (6) (7)

Fig. 3 — Surface microstructure of different steel samples after being held at 850°C for 80 minutes wet N_2 atmosphere, dew point = -4°C. (4. 1045 steel, 5. 4140 steel, 6. 8620 steel and 7. 52100 steel).

The experimental results also show that temperature plays a very important role in the oxidation and decarburization process to dominate the reaction kinetics. 500°C is not high enough to allow steel to continuously supply iron and carbon to the surface to be oxidized. So, in condition-1, the sample only showed very thin blistering at the surface but no decarburization after being exposed to the N_2/O_2 atmosphere for a short period. As shown in Fig. 2, decarburization can be easily observed at 860°C in condition-3. However, at 725°C under condition-2, no obvious decarburization was observed, although more (double) oxygen was introduced into the furnace. This can also be explained by the temperature.

In N_2/H_2 annealing atmospheres, there is no free oxygen in the high-temperature zones because H_2 converts it into water. In the N_2/H_2O experiment, four different steels were exposed to a wet nitrogen atmosphere at 850°C. The dew point of wet N_2 atmosphere was monitored and controlled at -4°C. As each sample has different alloy elements

TABLE 1 – CHEMICAL COMPOSITION OF FOUR STEEL TEST SAMPLES

	1045	4140	8620	52100
C	0.43~0.50	0.38~0.43	0.18~0.23	0.98~1.10
Mn	0.60~0.90	0.75~1.00	0.70~0.90	0.25~0.45
Si	0.10~0.35	0.15~0.30	0.15~0.35	0.15~0.30
Cr		0.80~1.10	0.40~0.60	1.30~1.60
Mo		0.15~0.25	0.15~0.25	
Ni			0.40~0.70	
Fe	rest	rest	rest	rest

(Table 1), the near-surface microstructure is very different although they met the same atmosphere.

From the information in Table 1, it can be seen that: 1) 1045 steel has lowest alloying level, 2) 8620 steel has most alloying elements and lowest carbon content, 3) 52100 steel has highest carbon content, and 4) 4140 steel has medium alloying level and medium carbon content among the four steel samples.

In the wet-N_2 experiments, weight loss (wt%) and decarburization layer thickness (µm) were measured and the results are shown in Fig. 4. By analyzing the measurement results in Fig.4 with the composition information in Table 1, it can be concluded that: 1) higher carbon steel has higher weight loss because more carbon is easily taken out by oxidation reaction with water (52100 steel has about 1% of carbon and showed highest weight loss rate); and 2) higher alloying levels help prevent the evolution of decarburization because the alloy elements help to hold carbon atom in carbides and slow down carbon atom transportation in the steel (8620 steel has highest alloying level and did not show any measurable decarburization after the experiment).

Comparing the two groups of experiments shows the difference between oxidation and decarburization by oxygen and moisture. A.S. Reeves and W.W. Smeltzer[7] studied decarburization of steel containing 0.8% of carbon in oxidizing atmospheres. They found that iron oxidation was approximately tenfold more rapid than carbon oxidation at high temperature. In these tests, once oxidizing gases reaches the part surface, it will react with all alloying elements in the steel, including Fe, C, and Mn. If the iron oxide layer forms very quickly, it becomes a resistance layer for oxidizing gases reacting with C in the steel. Because carbon diffusion in iron oxides is very slow and solubility of carbon in iron oxides is very low, the decarburization process will be almost stopped once there is a relatively thick iron oxide layer. In the experiments, unlike oxygen, moisture is a relatively "soft" oxidizing component in the atmosphere, so there is no thick oxide scale produced in wet nitrogen experiment, which allows continuous decarburization.

OPTIMIZATION OF ANNEALING ATMOSPHERE

The standard set-up of gas supply to the annealing furnace is usually with a liquid nitrogen tank, a liquid hydrogen tank (or H_2-Packs) and a standard N_2/H_2 blender to create a fixed blend to be fed to the furnace. As discussed before, although the flow rate and composition of nitrogen-hydrogen atmosphere introduced into the furnace is fixed, the true

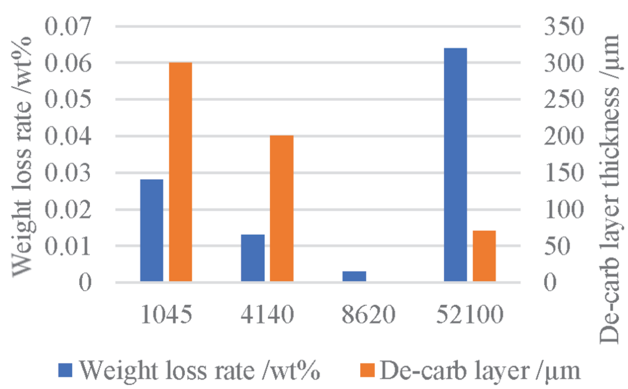


Fig. 4 — Surface microstructure of different steel samples after being held at 850°C for 80 minutes wet N_2 atmosphere.

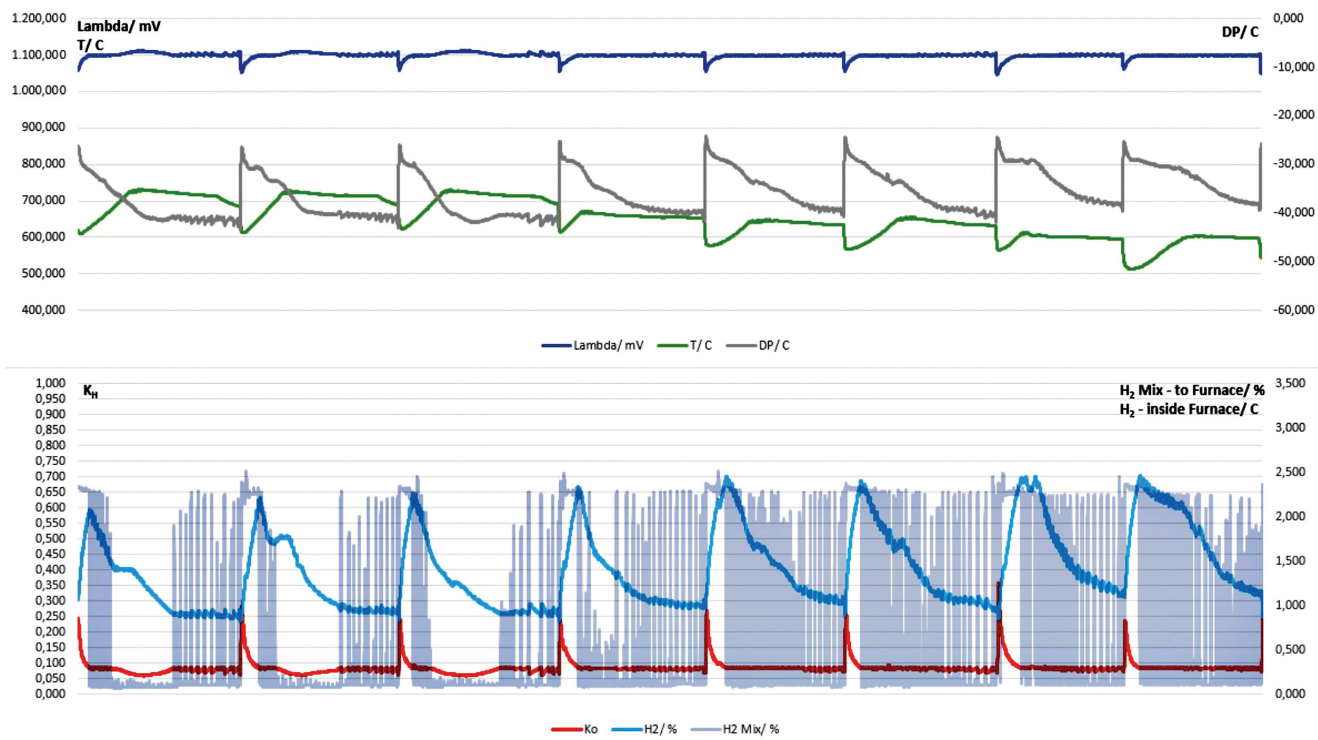


Fig. 5 — Example of optimized N_2/H_2 annealing atmosphere.

atmosphere composition inside the furnace changes continuously with time due to leaks and drafts in the furnace, desorption of impurities such as moisture from the surface of components or decomposition of lubricant.

With the thermodynamic background described before and years of experience on annealing atmosphere practice, Air Products developed an atmosphere control system for annealing atmospheres which measures the oxygen and hydrogen in the atmosphere and calculates the dew-point. To adjust the atmosphere inside the furnace to the desired parameters, the system can either control flow rates or gas composition by opening solenoid valves or mass flow controller. Control set-points can be put in to avoid surface oxidation and decarburization for:

a) Oxygen probe signal
b) $K_H = H_2O/H_2$ ratio
c) Dew point

Figure 5 shows an example of optimized N_2/H_2 atmosphere in a roller hearth furnace with the atmosphere control system, for annealing of steel plates. Top part of the figure shows sensor readings and furnace temperature. Lower part of the figure shows the H_2O/H_2 ratio, H_2% in furnace and H_2% in feeding gas blend during normal operation. The H_2O/H_2 ratio of furnace atmosphere goes up (light blue line) because air and moisture enter the furnace when opening the door. H_2 flow is controlled by turning on/off the solenoid valve to keep the H_2O/H_2 ratio (reducing condition of the atmosphere) at the desired level. In most charges it was possible to significantly reduce the introduced H_2-level over the annealing cycle, as shown by the blue line (H_2 inside the furnace) and light blue line (H_2 in the gas blend to the furnace). Because the H_2 flow is not a fixed setting in the atmosphere control system, the overall H_2 consumption is reduced by approximately 35% in the optimized operation compared to the furnace operation with fixed N_2 and H_2 flowrate.

The atmosphere control system also can be integrated into the cloud-based Air Products' Process Intelligence System for process data management and process optimization by analytical evaluations of the process data based on customized algorithms. This allows further process optimizations to reduce operating costs.

SUMMARY

The present study focused on the better understanding of annealing furnace atmosphere and its control and optimization. Oxidation of metal parts from free oxygen and moisture is different and should be treated differently. Control and optimization of N_2/H_2 annealing furnace atmosphere need both thermodynamic knowledge of reactions inside the furnace and accurate atmosphere measurement solution with a robust atmosphere sensor. With better control of furnace atmosphere, consistent product quality can be guaranteed, and production cost can be reduced. **~HTPro**

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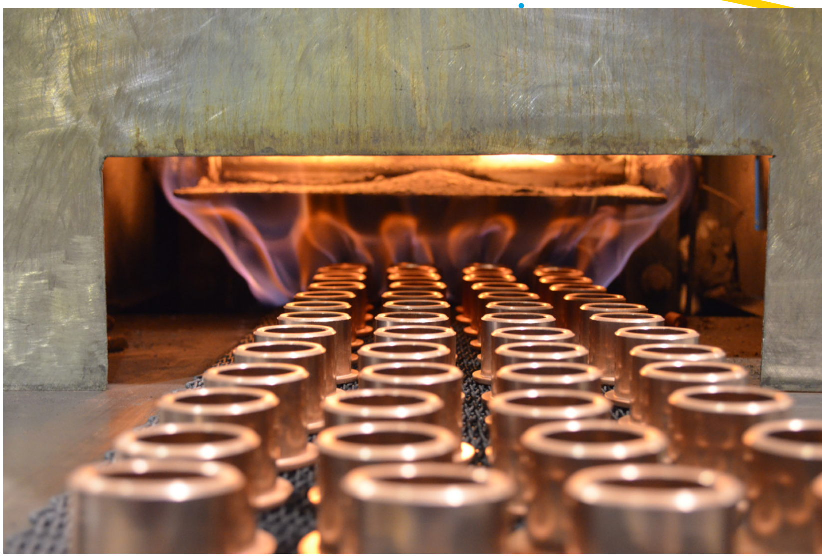

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