

THE CONTROLLED ATMOSPHERE INFLUENCE OVER THE ASPECT OF THE STAINLESS STEEL STRIP

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Abstract. *The aim of this paper is to study the controlled atmosphere influence over the aspect of the stainless steel strip. The use of continuous style, controlled atmosphere bright annealing furnaces to heat treat stainless steels after cold rolling is becoming more common as the aerospace and automotive producers increase the use of stainless steel components on existing designs and explore new designs. Although much of the metallurgy and thermodynamics of Iron, Chrome, Nickel and their compounds are well understood, a review of the application of the fundamentals to the current practices and equipment technology can help with improved product quality, expanded applications, and the optimization of costs for a net improvement in competitiveness.*

Keywords: *stainless steel, controlled atmosphere, bright annealing, hydrogen atmosphere systems*

1. INTRODUCTION

A wide variety of stainless steel strip, wire, tube, and die-formed products are bright annealed in protective atmospheres. Processing in protective atmospheres gives the annealed product a clean, bright surface appearance, and costly cleaning procedures after heat treatment are eliminated. Pure hydrogen atmospheres are required for some stainless grades and for some process and end use conditions. In many cases, however, hydrogen-nitrogen mixtures can be used as economical alternatives to 100% hydrogen systems.

Among the hydrogen and H₂-N₂ atmosphere systems commonly used, a certain amount of hydrogen is required in each case to produce a bright surface appearance. In general, operational economics tend to favor low hydrogen percentage H₂-N₂ mixtures. The hydrogen for these H₂-N₂ mixtures can be supplied from gaseous or liquid storage vessels (H-N System) or from an ammonia dissociator (nitrogen dilution of dissociated ammonia), depending on specific plant economics. In all cases where liquid nitrogen supply is available, 100% nitrogen can be used for low cost furnace idling.

Regardless of system economics, the selection of a suitable atmosphere composition for a specific annealing operation must be based on two key factors:

1. Reducing gas requirements — The amount of hydrogen required to keep the surface bright.
2. Control of surface nitrogen pickup — This involves assessing the effect of certain process conditions on the extent of nitrogen absorption and determining the maximum allowable surface nitrogen content for the particular stainless grade and product end use.

1.1 Reducing gas requirements for annealing stainless

The principal purpose of hydrogen in the atmosphere is to keep the surface of the stainless product in a bright or reduced condition while at annealing temperatures. Ideally, if no oxidizing gases such as water vapor or oxygen were present in the atmosphere, no hydrogen would be required for surface brightness. It is, in fact, possible to anneal 300 series stainless steels under laboratory conditions in high purity argon or nitrogen without significant discoloration. In industrial practice, however, a certain amount of hydrogen is almost always required to insure surface brightness.

Hydrogen is necessary to overcome the oxidizing effect of trace quantities of water vapor and oxygen present in the furnace atmosphere. If an adequate flow rate of high purity gases is being used and if the supply system is free of leaks, the trace oxygen level of a typical retort-lined industrial furnace will generally be below 10 to 15 ppm O₂ in all areas except the entrance and exit region. The water vapor level (generally reported as dew point) will, however, vary greatly with furnace type and process conditions.

Chemical thermodynamics can provide considerable insight into the nature of the hydrogen requirements for bright annealing. Chromium is the most difficult element to maintain in the reduced state of the three major components of 300 series stainless steels. If the atmosphere is reducing to chromium, it will also be reducing to the iron and nickel.

Using published thermochemical methods¹ and data^{2,4} a series of dew point versus %H₂ diagrams can be developed for the reaction of water vapor with chromium dissolved in iron:

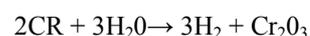


Figure 1 shows the oxidation-reduction diagram for an 18% Cr stainless steel at 2000°F (1095°C). The equilibrium boundary divides the diagram into those atmosphere conditions which are oxidizing and those which are reducing to stainless steels. Note that high hydrogen levels are not required for the atmosphere to be reducing. When the furnace dew point is low, a low hydrogen percentage can be used since it is the %H₂O/%H₂ ratio and not the absolute hydrogen percentage which determines whether the atmosphere is reducing or oxidizing.

The level of oxide contamination on the incoming material has a major influence on the atmosphere dew point and thus the required level of hydrogen. Incoming bright stainless material can generally be processed at a much lower hydrogen percentage than slightly oxidized material such as forgings. Given reasonably oxidefree incoming material, furnace dew points are generally observed to be lower at 20 to 30% H₂ levels than at 75 to 100% hydrogen levels. The points labeled "H-N" and "Dissociated NH₃" in Figure 1 correspond to typical operating conditions for the H-N System and a dissociated ammonia system. Both conditions have the same %H₂O/%H₂ ratio.

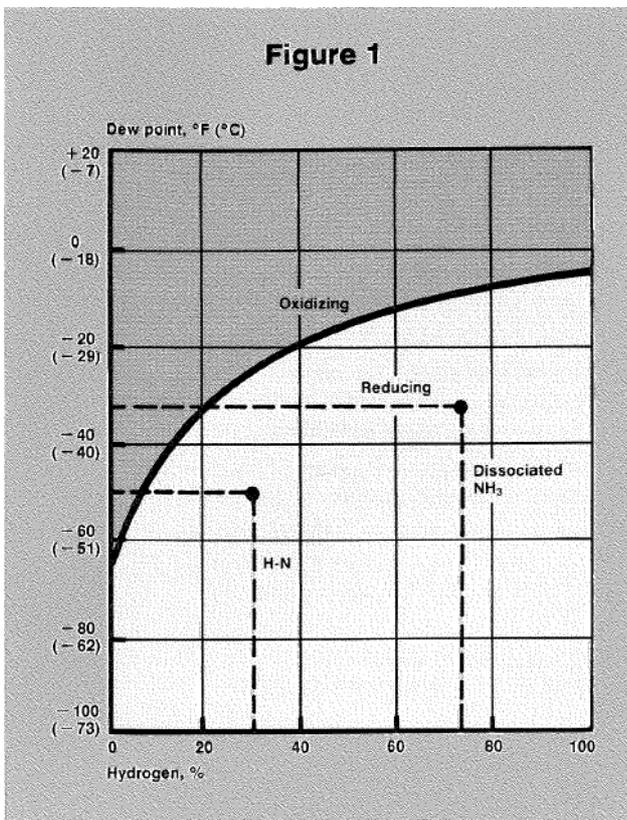


Figure 1 — Oxidation-reduction diagram for 18% chromium stainless steel at 2000°F (1095°C). Also shown are typical operating conditions for the H-N System and a dissociated ammonia system.

The effect of temperature on the oxidation-reduction boundary must also be accounted for. As annealing temperature decreases, the redox boundary shifts downward from the boundary shown in Figure 1. As a result, lower dew points (or higher hydrogen percentages) are required to maintain the same reducing potential. For example, it has generally been observed that brazing at 2100°F (1150°C) can be done at a 20 to 30% H₂ level while annealing at 1900°F (1040°C) generally requires 30% to 40% H₂.

The effect of temperature on the %H₂O/%H₂ ratio can be displayed in another manner which more clearly shows the influence of cooling rate on the reducing requirements. If instead of fixing temperature and varying the hydrogen (as in Figure 1) the hydrogen percentage is fixed and the temperature varied, oxidation-reduction curves can be calculated for a typical part temperature profile. Curves for 75% and 30% H₂ levels are shown in Figure 2. The upper portion of the figure shows a typical temperature profile for a part passing through a continuous annealing furnace. The corresponding lower curves denote the maximum allowable dew point (to remain reducing) for each temperature in the profile.

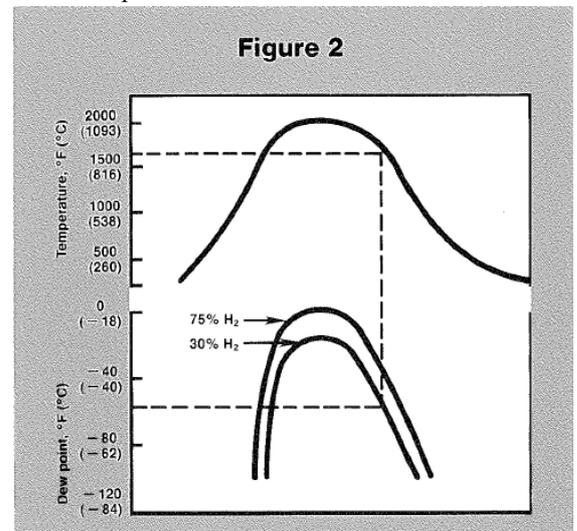


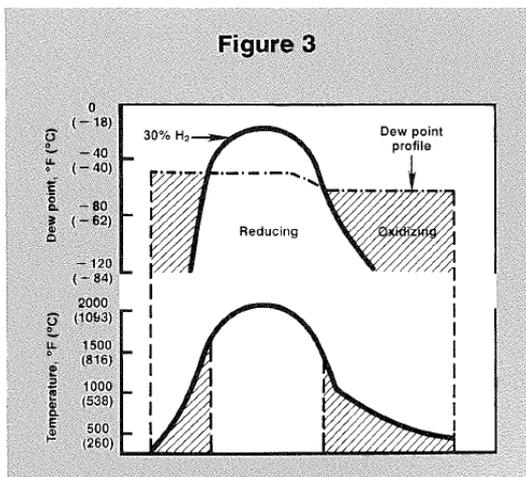
Figure 2 — Oxidation-reduction boundary for typical part temperature profile in a continuous furnace. Top: typical part temperature profile. Bottom: corresponding oxidation-reduction boundaries for 75% H₂ and 30% H₂.

In Figure 3 a typical furnace dew point profile has been superimposed over the oxidation-reduction curve for 30% H₂. The actual furnace dew point exceeds the maximum allowable limits in the areas of the curve which corresponds to the lower temperature. Thus, the atmosphere actually becomes slightly oxidizing to the stainless material below a certain temperature. (These

oxidizing regions have been placed on the original temperature profile on the lower portion of Figure 3.) For the specific dew point profile shown in Figure 3, the 30% H₂ atmosphere becomes slightly oxidizing below 1700 to 1500°F (925 to 815°C).

Examination of the 75% H₂ curve in Figure 2 shows that the atmosphere will still become oxidizing below 1600 to 1400°F (870 to 760°C) for the higher percentage hydrogen atmosphere. It should be noted that the oxidation which occurs during the cooldown is far less severe than would occur in air or in a high dew point atmosphere. For the dew point conditions shown in Figure 3, only 50 to 100 ppm of water vapor are available for oxidation. In addition, the rate of oxidation continues to decrease with decreasing temperature.

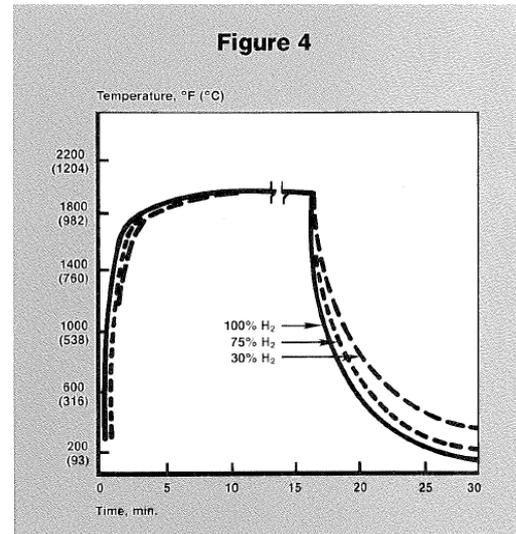
Because the material must pass through this slightly oxidizing region upon cooling, the final surface appearance will be dependent on the cooling rate of the product. As a result, the slower the product cools, the duller or more visibly oxidized it will become. In practice, the final surface appearance of the product will change from bright to dull to a grayish haze as successively slower cooling rates are used. This effect can occur at both high and low hydrogen percentages. It is, however, possible to obtain a bright surface at much slower cooling rates with 100% H₂ than with a 30% H₂-70% N₂ blend. Stated another way, a higher hydrogen percentage (or lower dew point) will generally be required for thick, slow cooling products than for thin, rapid cooling materials.



In addition to being a reducing agent, hydrogen also contributes to the cooling rate of the material.

Figure 4 compares the heating and cooling rate of a 0.5 in. (13 mm) in diameter by 4 in. (100 mm) long bar in 100% H₂ and in two H₂-N₂ mixtures. The curves were obtained by embedding a thermocouple in the bar. Five additional minutes are required to cool the bar to 400°F (205°C) when a 30% H₂-70% N₂ blend is used than

when 100% H₂ is used. Thus, high hydrogen percentages may be necessary in some cases to achieve a rapid cooling rate.



Reducing requirements for a particular set of annealing (or brazing) conditions are, thus, a function of several factors:

1. Furnace dew point and trace oxygen level — purity of incoming gases, oxide contamination level on the incoming product, and type of furnace lining.
2. Product cooling rate — product thickness, product loading rate, and cooling capacity of the furnace.

Any process improvements which will permit the use of lower hydrogen percentages will also result in a reduction of total atmosphere operating costs.

1.2 Another key factor: surface nitrogen pickup

Atmosphere composition cannot be decided solely on the basis of the amount of hydrogen required for surface brightness. Consideration must also be given to the extent and effect of surface nitrogen absorption in the material. Koebel,^{5,6} Scharfstein,⁷ and other authors^{8,9} have shown that appreciable amounts of atomic nitrogen can be dissolved in stainless steels as a result of annealing in atmospheres containing molecular nitrogen. Excessive surface nitrogen pickup can result in detrimental changes in the corrosion resistance and, in some cases, the mechanical properties of the product. The extent of surface nitrogen pickup is, however, highly dependent on the process conditions, i.e., annealing temperature and the composition of the H₂-N₂ atmosphere. In many cases, however, H-N blends or dissociated ammonia can be used without significant

deterioration of product quality. Our initial investigation of nitrogen pickup in stainless steels began in 1975 as a result of a series of preliminary H-N atmosphere tests with thick-walled tubing. During the testing, 300 series tubing samples were annealed in a 30% H₂- 70% N₂ mixture under industrial conditions. The tubing appeared equally bright when compared with material processed in 100% hydrogen. But the tubing turned gray upon immersion in a HNO₃/HF bath. SEM analysis revealed that the gray surface appearance was the result of intergranular attack. Microprobe, TEM, and X-ray diffraction analyses identified Cr₂N and Cr₂(N,C) precipitates at grain boundaries as the cause of the chromium depletion.

A study was initiated to determine the factors which influence the rate and extent of nitrogen pickup under various annealing conditions. A continuous recording microbalance was used for the initial portion of the study.¹⁰ AISI type 302 foil specimens (0.002 in. [0.05 mm] thick) were exposed to various atmosphere compositions. This method allowed the rate of surface deposition to be determined since both gas phase and solid state diffusion were eliminated as experimental variables. The weight gain of the specimen was then correlated to the increase in nitrogen content in the sample.

Figure 5 shows the increase in nitrogen content with time for several H₂-N₂ mixtures at 1900°F (1040°C) and a - 80°F (- 62°C) dew point. The atmosphere dew point was intentionally held at a very low level to obtain a near maximum rate of absorption for each nitrogen percentage.

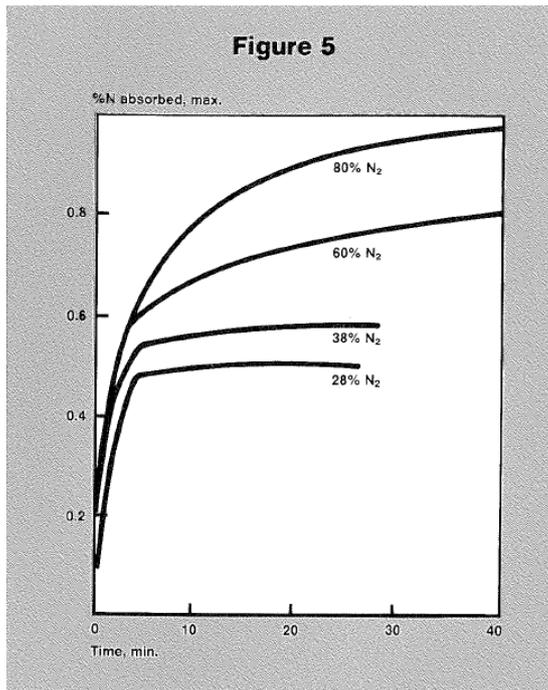


Figure 5 — Rate of nitrogen pickup in type 304 foil exposed to various H₂-N₂ mixtures at 1900°F (1040°C) and - 80°F (- 62°C) dew point. Microbalance method; 0.002 in. (0.05 mm) thick foil.

Figure 6 shows the effect of both annealing temperature and percentage of nitrogen on the extent of nitrogen pickup in the foil. Over this limited temperature range, nitrogen pickup decreases with increasing temperature. For all of the curves, increased nitrogen levels in the atmosphere resulted in increased nitrogen pickup. The curves in Figure 6 were obtained by least squares curve fitting of data from 40 experiments. The dew point was held at - 80°F (- 62°C) throughout the testing. Because the thin foil microbalance method does not take into account nitrogen diffusion into the bulk material, testing was also done using AISI type 304 bar specimens 0.5 in. (13 mm) in diameter. Bars were annealed and cooled in various H₂-N₂ mixtures using a retort lined tube furnace equipped with a cooling section. Leco nitrogen analyses were done on turnings from the bar samples. By pre-machining prior to heat treatment, 0.001 in. (0.025 mm) cuts could be uniformly removed from the radius of the bar for nitrogen analysis.

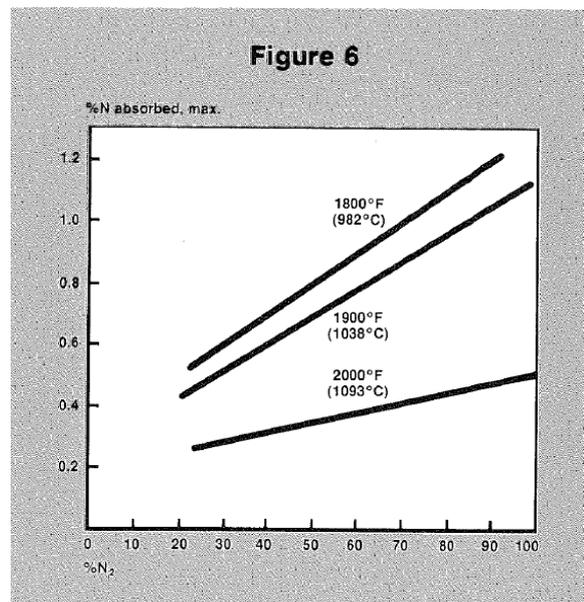


Figure 6 — Effect of %N₂ in H₂-N₂ mixtures on extent of nitrogen pickup in thin foils. Dew point was held below - 80°F (- 62°C) to cause near maximum nitrogen pickup. Microbalance method; 0.002 in. (0.05 mm) thick foil.

A qualitative surface appearance analysis was also done concurrently with the nitrogen study. Samples of 0.002 in. (0.05 mm) thick shimstock and Vie in. (1.6 mm) thick discs were run along with the bar samples to compare the effects of cooling rate on surface

appearance. One surface of each of the samples was polished to a mirror finish to provide a uniform surface finish for comparison.

Figure 7 shows the effect of annealing temperature on the extent of nitrogen pickup after 15 minutes at temperature. The dew point was held at -80°F (-62°C) to permit near maximum nitrogen pickup. Almost no nitrogen pickup occurred below 1500°F (815°C). The samples below 1700°F (925°C) all had a slight yellowish oxide tint despite the extremely low dew point of the atmosphere.

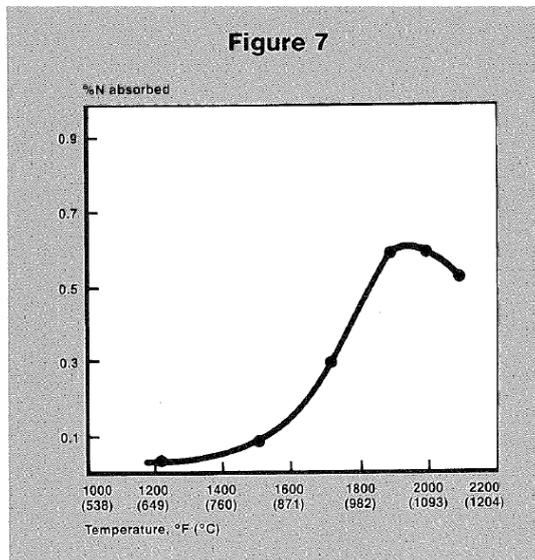


Figure 7 — Effect of annealing temperature on extent of nitrogen pickup. Bar samples were held at annealing temperature and cooled in a 30% H_2 -70% N_2 mixture having a dew point of -80°F (-62°C). Nitrogen levels are for first 0.001 in. (0.025 mm) of surface.

Figure 8 shows the effect of $\text{PH}_2\text{O}/\text{PH}_2$ ratio (where P is the partial pressure) on the extent of nitrogen pickup in the first 0.001 in. (0.025 mm) of the surface. This curve is for a 15 minute anneal at 1900°F (1040°C) followed by a cooldown in a 75% H_2 -25% N_2 atmosphere. As the dew point of the atmosphere is increased, the level of nitrogen pickup decreases. Examination of the surface appearance bars at the top of the figure shows, however, that increasing the dew point too much will result in visible oxidation of the material. Comparison of the surface appearance bars also shows that the extent of oxidation is somewhat dependent on the cooling rate of the product.

It is interesting to note that very high levels of nitrogen pickup can occur when only molecular nitrogen is present in the atmosphere. In the past, some authors have attributed nitrogen pickup associated with dissociated ammonia solely to the trace ammonia present in the atmosphere as a result of incomplete decomposition.

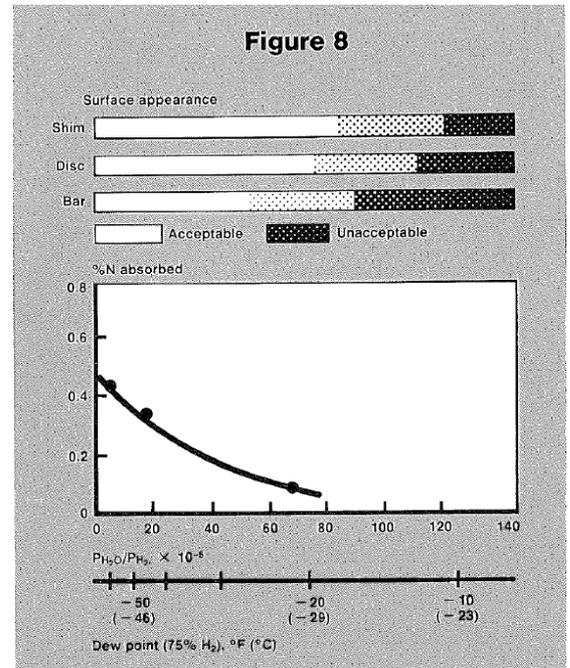


Figure 8 — Effect of $\text{PH}_2\text{O}/\text{PH}_2$ ratio on surface appearance (top) and extent of nitrogen pickup (bottom) after processing in 75% H_2 -25% N_2 mixture for 15 min. at 1900°F (1040°C). Nitrogen levels are for first 0.001 in. (0.025 mm) of surface.

The effect of $\text{PH}_2\text{O}/\text{PH}_2$ ratio is shown in Figure 9 for a 30% H_2 /70% N_2 atmosphere (15 minutes at 1900°F [1040°C]). Again, the extent of nitrogen pickup can be controlled by elevating the dew point of the atmosphere. Grabke's work with iron¹¹ as well as our own with stainless steel indicate that the presence of trace oxidants such as H_2O , N_2O , or CO_2 results in adsorbed oxygen on the surface of ferrous metals. The adsorbed oxygen inhibits the breakdown of molecular nitrogen on the surface of the material and thus slows the rate of nitrogen pickup. In many cases, nitrogen pickup can be limited to acceptable levels without visibly oxidizing the product.

Use of oxidant additions to control nitrogen pickup need not be limited to bright annealing temperatures. Many martensitic and precipitation hardening products are processed in integral quench, rotary, or shaker hearth furnaces. The material generally discolors upon

quenching and requires some surface removal regardless of the atmosphere. In these cases, a 100% N₂ atmosphere can generally be used without product quality deterioration. It is, however, important to control the level of atmosphere oxidant additions in order to prevent undesirable levels of nitrogen absorption.

Time-at-temperature also plays a key role in the extent of surface nitrogen pickup. For example, in nitrogen profiles for 2, 5, and 10 minute exposures to - 50°F (- 45°C) dew point, 30% H₂-70% N₂ atmosphere at 1900°F (1040°C), the amount of nitrogen pickup at the surface was quite small (less than 0.2% N) for the 2 and 5 minute anneal times. Depth of penetration into the surface ranged from 0.002 in. (0.05 mm) for the 2 minute time to 0.004 in. (0.10 mm) for the 10 minute anneal time. Because of this, low hydrogen percentage H-N blends are used more frequently for product requiring only a short time at temperature such as thin strip and small diameter wire than for products which require long annealing times.

Total exposure time can become important for products which require several annealing passes during processing. This type of processing is typically used for tubing because the material must be drawn and annealed several times before the final dimensions are obtained. For instance, in several 3 minute annealing passes, surface nitrogen content increased by 0.05 to 0.1% N with each pass. For noncritical work, at least two to three passes can usually be done in an H-N blend without a significant loss in room temperature corrosion resistance.

For a given set of operating conditions and product quality requirements, a safe "operating window" can be developed with respect to dew point. An example of this is shown in Figure 10 for the 15 minute, 1900°F (1040°C) condition shown earlier in Figure 9. Here the maximum allowable surface nitrogen content has been set at 0.35% N. Because of this specification, furnace dew points below - 50°F (- 45°C) would represent an unacceptable condition.

Examination of the surface appearance bars (top of diagram) shows that the location of the oxidation boundary (right portion of the diagram) is dependent to some extent on product thickness and cooling rate. In some cases, the safe operating zone will be too narrow for practical application to industrial furnace conditions.

This can occur from long anneal time requirements, slow cooling rates, or low surface nitrogen content requirements. In these cases, a lower %N₂-higher %H₂ atmosphere would be required. If no nitrogen pickup can

be tolerated in the material, a more costly pure hydrogen, argon, or vacuum system must be used.

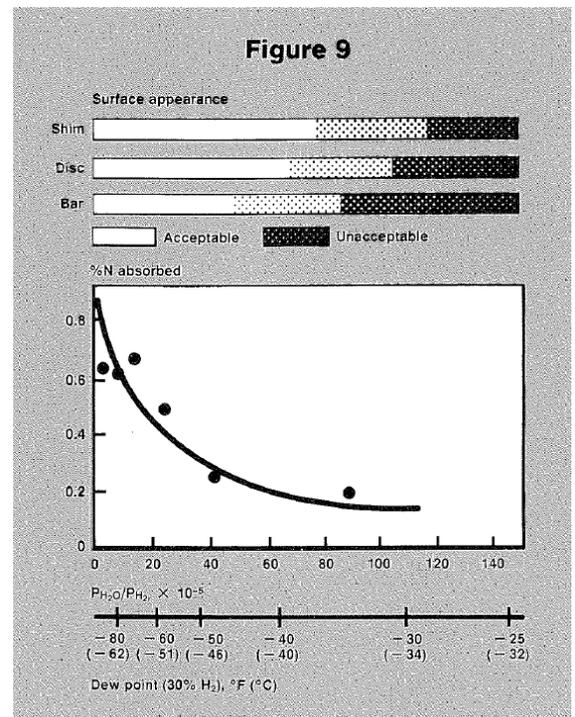


Figure 9 — Effect of PH₂O/PH₂ ratio on surface appearance (top) and extent of nitrogen pickup (bottom) after processing in 30% H₂-70% N₂ mixture for 15 min. at 1900°F (1040°C).

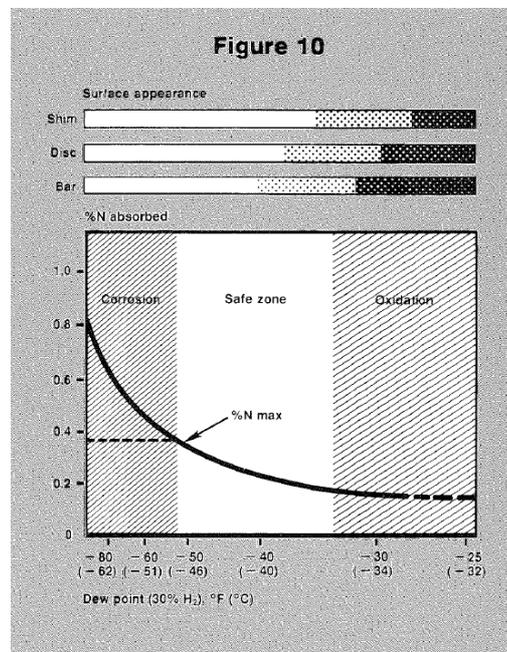


Figure 10 — Safe operating window with respect to dew point can be developed for specific set of operating conditions and quality requirements. Data plotted here are for 15 min. at 1900°F (1040°C) in a 30% H₂-70% N₂ atmosphere.

Grutzner [12] has developed a number of useful time-temperature-transformation diagrams for predicting the effects of various nitrogen levels on the corrosion behavior of austenitic stainless steels. These diagrams can be very useful in establishing the maximum allowable nitrogen content for various end uses of stainless steels. Based on his work, surface nitrogen content should probably not exceed 0.35% N since stainless steels with higher nitrogen contents could probably not be cooled quickly enough to prevent at least some loss in corrosion resistance. In cases where the material is cooled slowly, or used for high temperature service, much lower surface nitrogen contents are required.

1.3 Establishing the atmosphere composition in practice

As can be seen from the previous discussion, a large number of factors influence the degree of surface brightness and the extent of nitrogen pickup which result from using hydrogen-nitrogen mixtures for annealing stainless steels. In specific cases, lower cost H₂-N₂ mixtures can be used without significantly affecting product quality.

Because of the wide variety of process conditions, production practices and material end uses, the atmosphere composition can often be best established through careful inplant testing under simulated industrial conditions. In most cases, small sample lots of material can be used to evaluate the various atmosphere composition options. Corrosion testing and surface evaluation should always be performed, keeping in mind that the effects of surface nitrogen pickup are generally limited to the first 0.002 to 0.008 in. (0.05 to 0.2 mm) of the material.

2. REFERENCES

[1]. O. Kubaschewski and C. B. Alcock. *Metallurgical Thermochemistry*, 5th Ed.: New York, Pergamon Press, 1979.

[2]. I. Barin and O. Knake *Thermochemical Properties of Inorganic Substances*: Berlin, Springer-Verly, 1973.

[3]. F. Miller and O. Kubaschewski: *High Temperatures-High Pressures* "Thermodynamic Properties and the Equilibrium Diagram of the System Chromium-Iron," Vol. 1, 1969, p. 545.

[4]. Y. Jeannin, C. Mannerskanty, and F. D. Richardson: *Transactions of the Metallurgical Society of AIME*, "Activities in Iron-Chromium Alloys," Vol. 227, April 1963, p. 300.

[5]. N. K. Koebel: *Iron and Steel Engineer* "The Role of Externally Prepared Furnace Atmospheres," July 1964, p. 81.

[6]. N. K. Koebel: *Heat Treating*, "Surface Activation In the Heat Treatment of Metals," December 1977, p. 14.

[7]. L. R. Soharfstein: Proceedings of the 69th Annual Meeting of the American Society for Testing & Materials, "Effects of Residual Elements on the General Corrosion Resistance of Austenitic Stainless Steels," June 1966; American Society for Testing & Materials, Philadelphia, No. 418.

[8]. B. M. Estrin: *Stal*, "Nitrogen Absorption During Heat Treatment of Stainless Steels in Cracked Ammonia Atmosphere," November 1970, Vol. 30, p. 1028.

[9]. H. S. Nayar, R. M. German, and W. R. Johnson: *Industrial Heating* "Effect of Sintering on the Corrosion Resistance of 316L Stainless Steel", December 1981, p. 23.

[10]. J. H. Kaspersma and R. H. Shay: *Metallurgical Transactions B*, "Carburization of Iron by CO-Based Mixtures in Nitrogen at 925°C," March 1981, Vol. 12B, p. 77.

[11]. H. J. Grabke: *Archiven fuer das Eisenhüttenwesens*, "The Kinetics of Nitriding Steel as a Function of the Oxygen Activity in the Gas Phase," Vol. 44, 1973, p. 603

[12]. "Intergranular Corrosion Sensitivity of Nitrogen Containing Austenitic Chromium-Nickel Steels Caused by Chromium Nitride Precipitation," by G. Grutzner: *Stahl und Eisen*, January 1973, Vol. 93, p. 9.