

Nitrogen-propane protective atmospheres for annealing and hardening operations in continuous furnaces

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Abstract

Nitrogen (N₂) atmospheres with different, not always optimized levels of reducing and carburizing gases are often used to prevent decarburizing and oxidation of steel parts during annealing in continuous furnaces. The type and concentration of these additives in N₂ should correlate to the extent of air leakage into furnace, entrainment of air with loaded parts, steel composition, and complex reaction kinetics in the gradients of oxygen (O₂) and temperature existing between the entrance and hot zones of the furnace. This study explores the effect of small, 0.1 vol.% - 0.4 vol.% propane (C₃H₈) additions on composition of air-contaminated N₂ atmosphere in the temperature range of 500°C - 860°C. Microstructures are presented for AISI 1045 steel exposed to the atmospheres produced. Atmosphere compositions compared include those produced by a new type of plasma-activated, *in-situ* reformer for N₂-diluted C₃H₈. The latter method extends the atmosphere protection to the lower range of annealing temperatures. Present results may assist heat treaters in optimizing their neutral hardening operations.

Introduction

A critical consideration in heat treatments is the type, consistency and control of the furnace atmosphere. The purpose of a furnace atmosphere varies with the desired end result of the heat treating process. The atmospheres used in the heat-treat industry have one of two common purposes: to protect the components being processed from harmful chemical reactions that could occur on their surfaces (such as oxidation or decarburization) – that is, to be passive (chemically inert) to the metal surface; and to allow the surface of the parts to be changed (by adding carbon, nitrogen or both) – that is, to be reactive (chemically active) to the metal surface. In the furnace atmosphere, there are a number of possible reactions between the gas species and the metal surface. Steel will oxidize in the presence of oxygen bearing gases. This tendency increases in severity as the temperature is raised. However, the oxidation behavior of steel in ambient air differs significantly from that in a mixed-gas atmosphere in a heat treating furnace. The oxidation of steel has been studied by many authors.^[1-15] Commercial steels contain alloying elements and impurity elements, which behave differently from iron when reacting with O₂ in the atmosphere gases. Generally, the existence of chromium, aluminum, and silicon, which are more reactive than iron, provides oxidation resistance for steel, but the protective effect becomes insignificant if their levels are relatively low. Other elements, that are less reactive than iron, usually accumulate at the scale-substrate interface and have little effect on oxidation kinetics. In addition, O₂, H₂O and CO₂ decarburize steels. Medium- or high- carbon steel suffers from decarburization during steel oxidation. In heat treating practice, O₂, H₂O and CO₂ in the furnace atmosphere must be minimized if carbon retention and a bright steel finish are required.

Billings, Kirkaldy, Reeves, and Smeltzer^[16, 24] studied oxidation and decarburization of Fe-C alloys in carbon dioxide-carbon monoxide atmospheres at 950°C. They focused on oxidation-decarburization kinetics and morphological development of wustite scale as well as development of blisters. Boggs and Kachik^[1] investigated oxidation of pure Fe and Fe-C alloys with 0.05–0.99 wt.% carbon at different O₂ partial pressures (0.92 and 0.013 atm) at 500°C. Similar oxidation kinetics and oxide-scale structures were observed at both O₂ pressures for all alloys examined, irrespective of their carbon contents. The oxidation kinetics followed the parabolic rate law, and the scales formed were found to be compact and free of blisters, similar to those formed on pure iron at the O₂ pressure of 0.92 atm at 500°C. However, in contrast to pure Fe oxidized at the O₂ pressure of 0.013 atm (10 torr), the carbon present in steel suppressed blister formation. Interestingly, it was also observed that the Fe-C alloys decarburized when oxidized at the O₂ pressure of 0.013 atm, but no decarburization was detected under the oxide film formed when the samples were oxidized at 0.92 atm.

Chen and Yuen^[2] reviewed 150 articles published from 1920 to 2001, which examined the iron and steel oxidation in O₂ or air at high temperatures. The following were their conclusions. 1) Decarburization is generally observed for steel oxidation above 700°C, particularly for high-carbon steels, whereas carbon enrichment in the steel substrate may occur at oxidation temperatures below 700°C; 2) For Fe-C alloys containing more than 0.1% of carbon, the effect of carbon on steel oxidation varies at different temperature ranges. Below 570°C, an increased carbon content in steel results in increasing oxidation, because the scale formed over pearlite is finer and, generally, more adherent, allowing for a more rapid iron diffusion through the scale. At 700°C, higher carbon contents resulted in a less adherent scale, reduced oxidation rate, and less regular scale structures involving higher oxides; 3) Oxidation of low-carbon steel is generally slower than that of pure iron, and the difference is more profound at higher temperatures. Clearly, the outcome of steel oxidation is dictated by a range of independent variables that need to be characterized: the level of carbon and other alloying additions, temperature, exposure time, as well as the type and concentration of oxidizing gas species.

Neutral hardening treatments are carried out on steels of sufficient hardenability to attain a designated surface and core hardness without additional surface treatments, e.g. carburizing or carbonitriding. When neutral hardening in an atmosphere controlled furnace, the atmosphere carbon potential is matched to the treated part's carbon concentration; thus, the part surfaces are not enriched, decarburized, and/or oxidized. Furnace atmosphere plays a critical role ensuring the desired surface quality. The same atmosphere may be neutral towards one alloy but active towards another alloy. The atmosphere components can be principally divided into two parts: neutral and active gases. Typically, N₂ is the neutral component. The active gases include mixtures of CO, H₂ and hydrocarbon (C_xH_y) as well as undesired H₂O, CO₂, and elemental O₂. Common methods of generating furnace atmospheres for annealing and/or hardening of ferrous metals usually result in inconsistent atmosphere compositions that may lead to decarburization, recarburization, sooting, oxidation, or a combination of these surface phenomena on the metal surface being treated. Stickels and Mack^[8-11] evaluated direct formation of carburizing atmosphere in a batch-type, sealed quench furnace using hydrocarbon and air feeds. They also studied how to control the atmosphere with zirconia O₂ sensor and found, that the logarithm of the weight gain due to carburizing and the logarithm of the surface carbon content varied linearly with the electromotive force of the O₂ sensor (EMF) at 843 °C and 927 °C. In present work, we used the same direct formation approach, although the concentration of reactive atmosphere components and target carbon potential in our tests were markedly lower, the exposure temperatures were graded and exposure time intervals were shorter.

Our tests involved injection of metered quantities of C₃H₈ into a box furnace filled with N₂ and a small amount of air, that simulated an air leakage furnace condition, in order to generate neutral atmosphere for the AISI 1045 type steel products, frequently subject to neutral hardening treatments. Effects of C₃H₈ and O₂ concentration were examined for three different temperatures to imitate the thermochemical conditions of steel parts traveling on a belt in a continuous annealing furnace. The O₂ level in these experiments was set at 1,000 ppm or 2,000 ppm by vol. in N₂, to simulate realistic furnace leakage rates. C₃H₈ was injected into the furnace only when reaching the temperature targeted for exposure test. Thus, the objective of this work was to refine the thermodynamically and kinetically controlled effect of very small, 0.1 vol.% - 0.4 vol.% C₃H₈ additions on the composition of air-contaminated N₂ atmosphere in the temperature range of 500°C-860°C and the interfacial reactions taking place on steel surface. Commercial significance of this work is based on the fact that examined N₂-C₃H₈ atmospheres offer a non-flammable and non-toxic alternative to the conventional, dissociated methanol or diluted endothermic atmospheres most frequently used in the neutral atmosphere hardening operations. Consequently, new insights gained on the N₂-C₃H₈-O₂ process control may help the heat treating industry become cleaner and greener, faster.

Experimental work

AISI 1045 steel was chosen for experimentation. Its composition is listed in Table 1.

Table 1. Chemical composition of AISI 1045 Steel (wt%)

C	Mn	S	P	Fe
0.45	0.80	<0.05	<0.04	balance

The material was received as a hot-rolled, 1-inch diameter rod. As-received microstructure, shown in Fig.1, included a fine-grained and somewhat banded ferrite and pearlite. Test samples were cut into 0.5-inch thick rod slices and surface-ground to remove scale and surface imperfections.

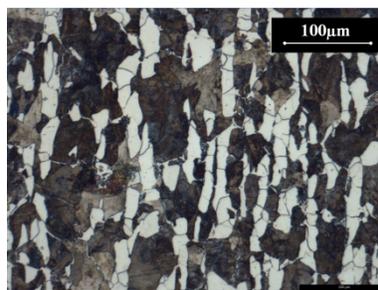


Fig.1 As-received material, AISI 1045 steel, orig. magnif. 200X, Nital etch.

During experiments, the steel samples were treated in a box furnace (16.5 inch × 13.5 inch × 12.5 inch), which featured 40 double-sided electrical resistance heaters ensuring temperature uniformity. Apparatus configuration and temperature profile during treatments are sketched in Fig. 2. Samples were placed in the box furnace before heating up. In all the tests, the heating up step lasts 30 minutes, and the holding time at desired temperature is 30 minutes as well. Note, that N₂ gas quenching is used at the end of our heat treatment cycles instead of the conventional oil bath quenching in order to preserve the surface reaction products intact; martensitic transformations were outside the scope of this study.

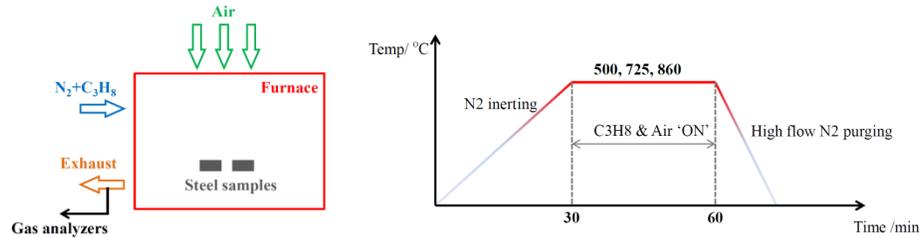


Fig.2 Apparatus configuration and heat treatment schedule

Listed in Table 2, are the combinations of air and C₃H₈ flow rates tested; N₂ flow rate used was always fixed as 100 scfh. The test furnace has two separated inlets. The top inlet admitted air, and the back inlet was used for injecting premixed N₂ and C₃H₈. The furnace atmosphere was analyzed by continuously extracting a gas sample from the back of the furnace. H₂, O₂, CO, CO₂, CH₄, and C₃H₈ gas analyzers were used.

Table 2. Test matrix – feed gas flow rates

Test	Temperature/°C	N ₂ /scfh	C ₃ H ₈ /scfh	Air (O ₂)/scfh	C ₃ H ₈ :O ₂ ratio
1	500	100	-	1.0 (0.2)	0:2
2	500	100	0.2	0.5 (0.1)	2:1
3	725	100	-	1.0 (0.2)	0:2
4	725	100	0.2	0.5 (0.1)	2:1
5	860	100	-	0.5 (0.1)	0:1*
6	860	100	0.1	0.5 (0.1)	1:1
7	860	100	0.2	0.5 (0.1)	2:1
8	860	100	0.3	0.5 (0.1)	3:1

* In continuous furnace, O₂ level will be lower in hot zones than near-entrance and near-exit zones, because main gas inlets are located in hot zones and most air entering furnace comes from the loading end. Consequently, tests involving high temperature, here 860°C, were run using only 0.5 vol.% air, and not 1.0% of air.

Microstructures of processed samples were photographed with optical Neophot metallographer; original magnification of 200X and Nital etching was used in all cases. Leco AMH43 Micro/Macro-indentation hardness system was employed for measuring the subsurface microhardness of processed samples. These measurements were subsequently abandoned as insufficiently sensitive in differentiating between the various heat treating conditions tested.

Results and discussion

Furnace Atmospheres

In industrial operations, air enters furnace with parts and belt, as outlined in Fig.3. To prevent severe oxidation of parts loaded, continuous neutral hardening furnaces include a short transition zone between the entrance and the elongated hot zone. In typical production systems, most of fresh gas is distributed into the hot zones, so the dominant atmosphere flow inside the furnace is from the hot zones to the entrance. The temperature of transition zone is lower than the process temperature. When the part enters the furnace,

it is exposed to atmosphere containing relatively high oxygen but at a reduced temperature. The O₂-temperature shift is sketched in Fig.3. Without a proper furnace atmosphere zoning, there is a risk of simultaneous oxidation and carburizing in the hot zones. In our box furnace experiments, temperatures of 500°C and 725°C (tests 1-4) can be associated with the transition zone, and temperature 860°C (tests 5-8) with the hot zones.

Table 3 presents product atmosphere compositions for all 8 tests, where CO, CO₂, CH₄, and C₃H₈ were determined using IR spectrum analyzers, H₂ with a thermal conductivity analyzer, and trace level O₂ with an electrolytic cell analyzer. The results show that there was no reaction between C₃H₈ and O₂ at 500°C; i.e., adding C₃H₈ to the front side of the transition zone will not be effective in preventing surface oxidation of parts at 500°C. We did observe the surface oxidation in test 2, which will be discussed later in this paper. When comparing results of test 2 and test 4, we can see that the residual O₂ in the furnace dropped significantly to 54 ppm from 1022 ppm with the increase in furnace temperature from 500°C to 725°C. For the same feed compositions at 860°C, no residual O₂ was detected, because it reacted with C₃H₈ more completely, forming CO, H₂, and CO₂ as well as H₂O that was not analyzed in present tests. H₂ concentration provides for the most striking difference between test 4 and test 7 suggesting that C₃H₈ and, to some extent, even a more thermally stable CH₄ dissociated and reformed at 860°C.

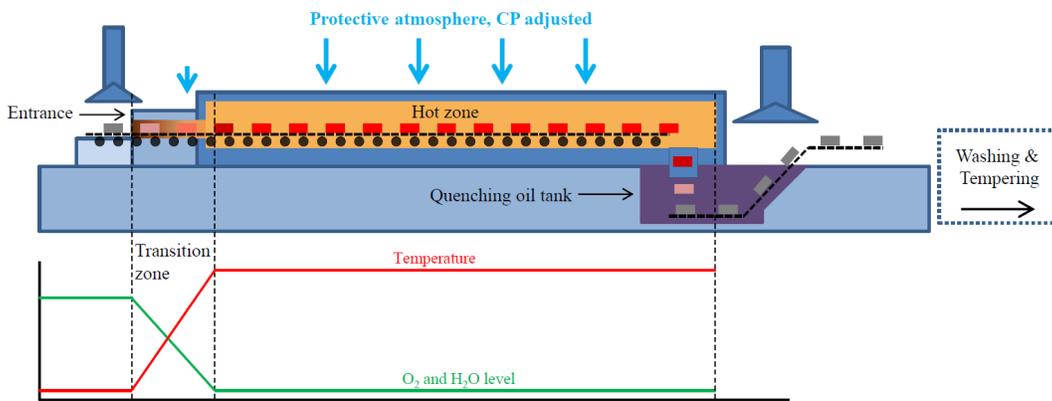


Fig.3 Neutral atmosphere hardening furnace with typical, temperature and composition profiles

Table 3. Furnace atmosphere as measured with extractive gas sample analyzers

Test	Temperature, feed ratio		Atmosphere products					
	Temp./°C	C ₃ H ₈ :O ₂	H ₂ /%	CO/%	CO ₂ /%	CH ₄ /%	C ₃ H ₈ /ppm	O ₂ /ppm
1	500	0:2	0	0	0	0	0	1985
2	500	2:1	0	0	0	0	2002	1022
3	725	0:2	0	0	0	0	0	1993
4	725	2:1	0	0.19	0.02	0.09	606	54
5	860	0:1	0	0	0	0	0	1004
6	860	1:1	0	0.14	0.07	0.05	61	0
7	860	2:1	0.21	0.29	0.01	0.06	92	0
8	860	3:1	0.39	0.36	0.01	0.14	191	0

Experimental feed values listed in Table 2 were used for calculating atmosphere products under ideal, thermodynamic equilibrium conditions, Table 4. All gas-phase reactions come to completion according to this model. The difference between the products from Table 3 and 4 illustrates the kinetic departure from the equilibrium and, to a much lesser degree, measurement inaccuracies of gas analyzers. Because each furnace and gas injection method imposes different kinetic conditions, it is clear that calculations can't replace measurements. Moreover, due to inaccuracies between various gas analyzers, test coupons should be used to verify and confirm effects of calculated as well as measured atmosphere compositions.

Table 4. Furnace atmosphere as calculated using thermodynamic equilibrium model, FactSage*

Test	Temperature, feed ratio		Calculated atmosphere products					
	Temp./°C	C ₃ H ₈ :O ₂	H ₂ /%	CO/%	CO ₂ /%	CH ₄ /%	C ₃ H ₈ /ppm	O ₂ /ppm
1	500	0:2	-	-	-	-	-	2000
2	500	2:1	0.73	0.11	0.03	0.01	2.6E-11	5.2E-25
3	725	0:2	-	-	-	-	-	2000
4	725	2:1	0.79	0.20	2.4E-04	6.2E-04	4.2E-13	4.5E-21
5	860	0:1	-	-	-	-	-	1000
6	860	1:1	0.40	0.20	2.1E-05	4.3E-05	4.2E-15	1.1E-19
7	860	2:1	0.80	0.20	2.1E-05	1.7E-04	6.6E-14	1.1E-19
8	860	3:1	1.18	0.20	2.1E-05	3.8E-04	3.3E-13	1.1E-19

* - FactSage^[12] is a chemical thermodynamics software package developed jointly by the FACT Group (CRCT), Montreal, Canada and GTT-Technologies, Aachen, Germany.

Oxidation in N₂-Air atmospheres

Surface oxidation was observed on samples when furnace atmosphere contains residual O₂. Fig. 4 shows the surfaces of 1-inch dia. samples after tests 1, 3 and 5. No C₃H₈ was injected into the furnace in these three tests. Oxide films were uniform except for test 1 where the film blistered and partly flaked off, apparently unable to anchor in the metal matrix. Fig.5 presents the microstructures of samples after tests 1, 3 and 5. There was a dark gray oxide layer covering surfaces of samples in test 3 and 5. With our short, 30 minute holding time replicating a short-time exposure of steel to oxidizing atmosphere inside the transition zone, the resultant oxide films were quite thin, when compared to characteristic features of the metal microstructure. Note, that only 1000 ppm of O₂ was injected in test 5, and this resulted in a thinner oxide than in test 3 (2000 ppm of O₂) in spite of a higher holding temperature in test 5.



Fig.4 Top surfaces of samples processed in test 1, 3 and 5, (from the left to the right).

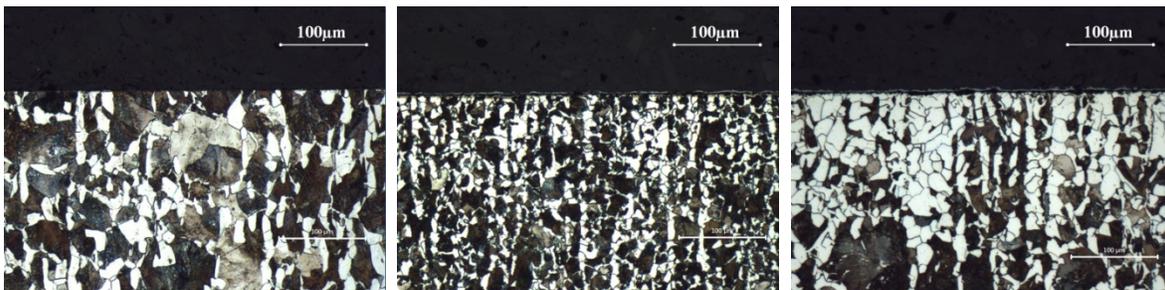


Fig.5 Cross-sections of samples processed in test 1, 3 and 5, (from the left to the right).

In heat treatment, temperature can affect decarburization in three ways^[12,19]. 1) The dissolution rate of cementite and the diffusivity in both phases (austenite and ferrite) increases with temperature, contributing to a deeper decarburized layer within a specified time. 2) The austenite fraction increases with temperature. Since carbon diffuses slower in austenite than in ferrite, and it is more soluble in the former, the presence of austenite reduces the thickness of decarburized layer as a consequence of slower kinetics. 3) The reaction kinetics between oxidizing gases and carbon/iron interface is related to the temperature. As evidenced in Fig.5, decarburization took place at 860°C in test 5. However, at 725°C (test 3), no decarburization was observed, although more O₂ was injected into the furnace. This could be explained by the temperature difference and the 'oxide film' effect.

Reeves and Smeltzer^[24] studied decarburization of steel containing 0.8 wt.% of carbon in oxidizing atmospheres and found that iron oxidation was approximately tenfold more rapid than carbon oxidation at 950°C. In our tests, when O₂ reaches part surface, it instantaneously reacts all elements in the steel, i.e. Fe, C, Mn, etc. If the iron oxide film can form quickly enough, it will provide a diffusion barrier for carbon. Because carbon diffusion in iron oxides is slow and carbon solubility in oxides is low, the decarburization reaction almost stops for moderately thick, adherent and non-blistering oxide films. In test 3, with a thicker and quickly formed oxide film, due to doubling the oxidizing potential of test 5, only a slight decarburization was noted. As we discussed before, temperature plays critical role in oxidation and decarburization. In these tests, 500°C was enough to allow for a continuous supply of iron and carbon to the metal surface. Thus, in test 1 the sample produced only a very thin blister but no decarburization within the exposure time of 30 minutes.

Oxidation in N₂-Air-C₃H₈ atmospheres

As shown in Table 3, when injecting C₃H₈ to counter the O₂ (or air) present in the furnace, the product atmosphere attains different compositions for different ratios of C₃H₈:O₂ and different temperatures. At 500 °C, adding C₃H₈ does not change the residual O₂ level in the furnace, because there is no reaction between those two gases. However, at this low temperature, O₂ does not oxidize the steel strongly. In typical production operations, the exposure time of steel at this temperature in the furnace is short. Consequently, only a light oxidation or decarburization takes place in the transition zone, even for atmospheres containing high O₂. With increasing exposure temperature, oxidation and decarburization reactions in N₂ - air atmospheres are fast. With shifting to N₂ - air - C₃H₈ atmospheres, the O₂ clearly starts reacting with C₃H₈ inside the furnace, as confirmed in the 725 °C and 860 °C tests. The reaction products include CO, CO₂, CH₄, H₂ and H₂O. Minute quantities of residual C₃H₈ and O₂ are also detected. Since CO₂, H₂O and residual O₂ are oxidizing to steel, sufficient quantities of CO and H₂ need to be also generated in order to counter-balance these oxidizing gas products.

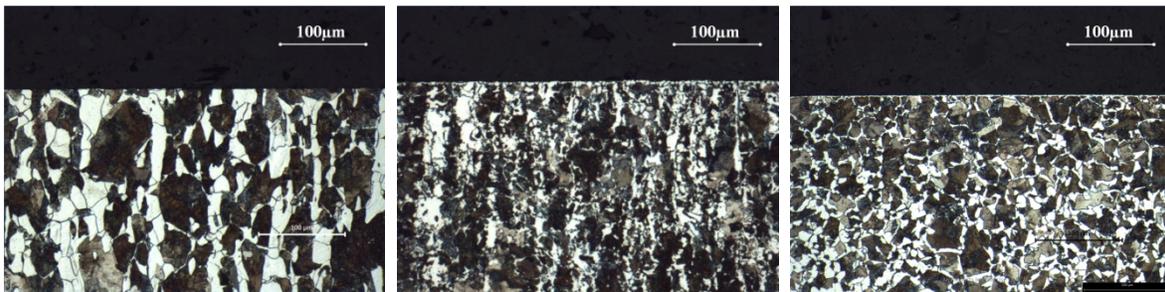


Fig.6 Cross-sections of samples processed in test 2, 4 and 7 (C₃H₈:O₂ = 2:1, 500°C, 725°C, 860°C)

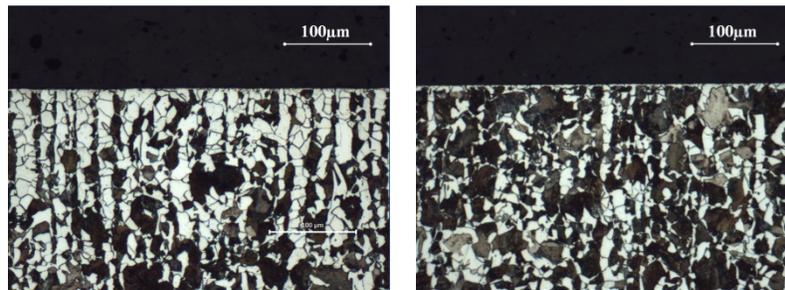


Fig.7 Cross-sections of samples processed in tests 6 and 8 (C₃H₈: O₂ = 1:1 and 3:1, 860°C.)

As Fig.6 shows, the N₂-Air-C₃H₈ atmosphere with the C₃H₈:O₂ ratio of 2:1 assures a neutral hardening condition for AISI 1045 steel, also at the high temperature end of 860 °C. Fig.7 presents the subsurface structure of samples produced in tests 6 and 8. Decarburization in test 6 took place even though there was no residual O₂ in the atmosphere (Table 3), just an elevated CO₂ level. Results of tests 7 and 8 show that a small in absolute terms, yet excessive addition of C₃H₈ can bring about carburizing. Consequently, a precise atmosphere control is critical in neutral hardening operations.

Plasma activation of N₂-C₃H₈ stream

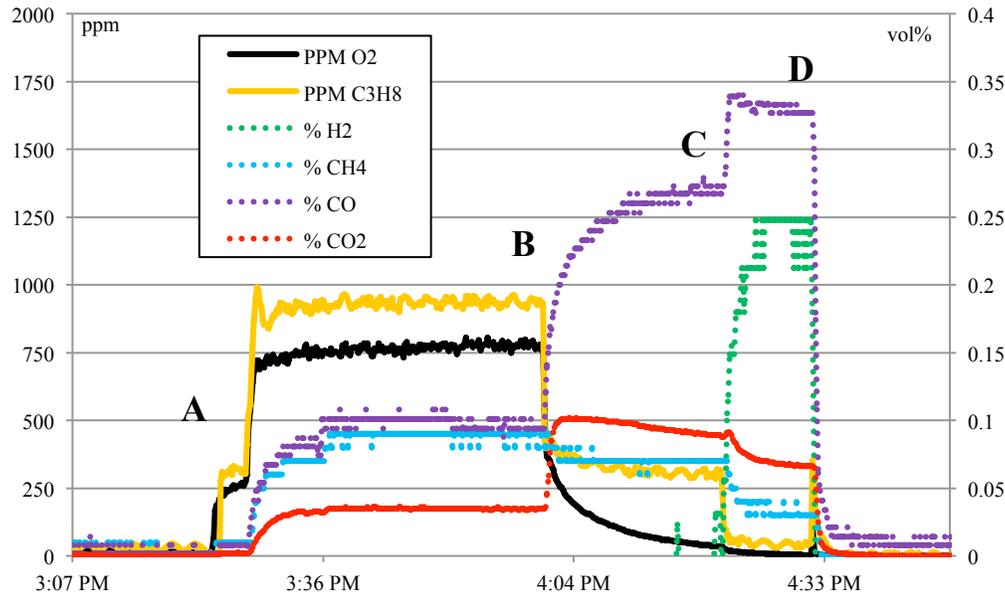


Fig.8 Changes in atmosphere composition at 725 °C: A-B - without plasma activation, B-C - after turning plasma to lower power setting, and C-D - after turning plasma to higher power setting (N₂-100 scfh, Air-1.0 scfh, C₃H₈-0.2 scfh.)

The reactions of C₃H₈ with O₂, just like other hydrocarbon reforming reactions, suffer from sluggish kinetics or incomplete conversion rates at reduced temperatures that are encountered in various heat treating operations. For the 30 minute exposure time inside the 725 °C transition zone assumed in this study, the neutralizing effect of C₃H₈ reactions was not critical, however, the result may be different if the exposure time is longer, like in the case of lower belt speeds and larger loads used in some continuous furnaces.

To address the issue of forming neutral atmosphere at these reduced temperatures without excessive and, potentially, sooting C₃H₈:O₂ ratios, we decided to test the method of plasma-activation described elsewhere^[23-24] and involving injection of the N₂ – C₃H₈ feed to the furnace across of a high-voltage, electric discharge confined inside a patented gas injector^[25]. Conditions of test 4 were modified: twice as much air was used to halve the C₃H₈:O₂ ratio from 2:1 to 1:1. With 2000 ppm of O₂ and 2000 ppm of C₃H₈ injected into the furnace at 725 °C without plasma power on, the resultant, residual O₂ recorded was about 750 ppm, definitely enough to oxidize steel samples. Low power plasma setting, segment B-C on Fig. 8, reduced this residual O₂ level to about 40 ppm. Increasing the power setting resulted in a complete elimination of residual O₂ as shown in the segment C-D on Fig. 8. Concurrent compositional changes included an increase in H₂ and CO, and drop in CO₂, CH₄, and residual C₃H₈, all confirming an improved reforming and conversions. Fig.8 details these changes in time.

Summary

Neutral annealing of steel in continuous furnaces under air-infiltrated N₂ atmospheres can be successful if small quantities of propane are added to counter oxidizing effects. For the air leakage of up to 1 vol.% and the 30 minute exposure times in the transition and, then, the high heat zones, an addition of 0.4 vol.% of C₃H₈ is more than enough to prevent decarburization of steel. Interestingly, the role of C₃H₈ additions is not as critical for decarburizing in the lower temperature zones, because a thin oxide film, formed there in the absence of reducing gases, serves as a diffusion barrier. If formed, the oxide film can be subsequently reduced in the high heat zones, containing sufficient concentrations of the H₂ and CO reformat products in the atmosphere. When longer exposure times are necessary, e.g. for lower furnace belt speeds, an injection of plasma-activated N₂-C₃H₈ stream could be used instead. Present results show, that with the activation, the reactions between the C₃H₈ and the O₂ leaking into furnace are more complete, even if the temperature is reduced to 725 °C and the C₃H₈:O₂ ratio to 1:1.

FactSage calculations show that the atmospheres produced in this study did not attain an ideal equilibrium. This is a prevalent case for all atmospheres produced under industrial conditions; gas products always diverge from those predicted by the Gibbs free energy minimization due to time constraints and fast changes in process conditions. Nevertheless, with H₂, CO, H₂O and CO₂ products measured at certain levels, the neutral atmospheres generated inside furnace display the behavior enabling determination of a transient equilibrium carbon potential, i.e., the most conventional process control methods and instruments can be used here, such as zirconia (oxygen- or carbon-) probe or gas analyzers. Consequently, neutral carbon annealing in continuous furnaces can be effectively run and controlled when using only minute C₃H₈ additions to N₂ atmosphere, thus, offering heat treaters a safer and cleaner alternative to the conventional, endo-generated or dissociated methanol atmospheres.

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