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Coat-Nitrocarburizing Using Triazine Polymer Reagent

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A chemico-thermal treatment process, coat-nitrocarburizing, has been developed for use on iron and steel. The process consists of treating the workpiece with a coat that forms on the surface from the gaseous products of sublimation and decomposition of a triazine polymer reagent in a closed volume. The process can be used over a wide range of temperatures, either below the eutectoid transformation temperature in the Fe-N-C system for low-temperature nitrocarburizing, or above this temperature for high-temperature nitrocarburizing in different applications. The process is very simple, easily controlled, and is economic. In addition, it is a nonpolluting process, unlike conventional chemico-thermal treatment processes that discharge harmful gases into the atmosphere.

Keywords:

coating, carburizing, heat treating, polymer reagent, triazine

1. Introduction

NITRIDING or nitrocarburizing has been used for more than 70 years[1,2] as an economic means of surface treatment to increase the hardness, wear resistance, scoring resistance, corrosion resistance, and fatigue life of steels and other ferrous alloys. Because of the excellent combination of surface properties of machine parts treated by nitriding or nitrocarburizing, this process is widely used in modern industry, with many applications in aerospace, aviation, automobiles, machine tools, dies, diesel engines, textile parts, instruments, etc. As this process becomes increasingly important,[3,4] intensive study of different aspects of the process has been conducted. A number of new techniques have been developed; these include high-temperature nitrocarburizing and nitrocarburizing with direct hardening,[5-13] nitrocarburizing combined with subsequent oxidation,[14,15] resource-saving methods,[16] and new impregnating reagents.[17,18] However, more research effort is required to reduce the length of the production cycle, to increase the thickness and improve the properties of the case, and to lower the cost and environmental pollution associated with the current practice. This article introduces a new technique known as coat-nitrocarburizing, which uses triazine polymer reagent. The results show that this very simple process is economic, easily controlled, and nonpolluting.

2. Experimental

Specimens of surface-polished pure iron (99.99%) and AISI 1020 and 1060 steel specimens (size 10 × 10 × 25 mm) were loaded with nitrogen-containing organic triazine polymers into a closed container, then heated up to 500 to 900 °C, and held for 10 to 120 min. After coat-nitrocarburizing, the specimens were quickly quenched in oil. The microstructures were examined, and the microhardness values of the case were measured.

3. Reagent and Its Reaction

Triazine polymers were used as the impregnating reagent for the coat-nitrocarburizing process discussed in this study. This material is well known as a regeneration agent for use in nitriding salt baths.[19,20] It is a nitrogen-bearing organic material and is a mixture of melam, melem, and melone. Compositions of the triazine polymers and ammonia are given in Table 1. The constituent triazine polymers contain about 33% carbon and much less hydrogen. These new reagents (melam, melem, and melone) are extremely stable under normal conditions without any toxic or unpleasant releases. Melam and melem are physically stable up to 350 °C, above which they start to sublime. Melone is stable in air at temperatures up to 600 °C for an extended period. The vapor phase products of the sublimation engage the surface of an iron or steel to form a fine coat during nitrocarburizing.

The nitrocarburizing process consists of four successive steps, namely sublimation, coating, impregnation, and diffusion, as shown schematically in Fig. 1. First, the workpieces and the reagents are heated in an air-bearing closed volume, and the reagent sublimes. Second, the vapor phase products interact with the surfaces of the workpieces and form a coat. Then, as the temperature rises, the surfaces of the workpieces become saturated with active nitrogen and carbon, and finally, diffusion annealing takes place, causing the thickness of the carbonitride case to increase significantly.

Decomposition of the reagents is complex and probably involves the following reactions:

$$C_6H_9N_{11} \rightarrow 11[N] + 6[C] + 4\tfrac{1}{2}H_2 \qquad [1]$$

$$C_6H_6N_{11} \rightarrow 10[N] + 6[C] + 3H_2 \qquad [2]$$

Table 1 Compositions of triazine polymers and ammonia

Material	Molecular formula	Composition, wt% N	C	H
Ammonia	NH_3	82.25	0	17.75
Melam	$C_6H_9N_{11}$	65.51	30.63	3.86
Melem	$C_6H_6N_{10}$	64.21	33.02	2.77
Melone	$[C_6H_3N_9]_n$	62.68	35.82	1.50

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$$[C_6H_3N_9]_n \rightarrow 9n[N] + 6n[C] + \tfrac{3}{2}nH_2 \qquad [3]$$

$$C_6H_9N_{11} + 3O_2 \rightarrow 11[N] + 6CO + 4\tfrac{1}{2}H_2 \qquad [4]$$

$$C_6H_6N_{10} + 3O_2 \rightarrow 10[N] + 6[CO] + 3H_2 \qquad [5]$$

$$[C_6H_3N_9]_n + 3nO_2 \rightarrow 9[N] + 6nCO + \tfrac{3}{2}nH_2 \qquad [6]$$

$$C_6H_9N_{11} \rightarrow C_6H_6N_{10} + NH_3 \qquad [7]$$

$$n(C_6H_9N_{11}) \rightarrow [C_6H_3N_9]_n + 2nNH_3 \qquad [8]$$

$$n(C_6H_6N_{10}) \rightarrow [C_6H_3N_9]_n + nNH_3 \qquad [9]$$

$$NH_3 \rightarrow [N] + \tfrac{3}{2}H_2 \qquad [10]$$

$$2CO \rightarrow 2[C] + O_2 \qquad [11]$$

4. Results and Discussion

The specimens of pure iron and AISI 1020 and 1060 steel were coat-nitrocarburized at 565 and 700 °C for 1 or 2 h. The results are shown in Fig. 2 and 3 and Tables 2 through 6. The microstructure of the nitrocarburized case treated at 565 °C consists of two layers: an outside oxide layer and an ε-γ' phase sublayer, as shown in Fig. 2 (a, c, and e). The ε-γ' phase sublayer appears white on the photomicrograph and is therefore called the "white layer." The thicknesses and hardness of the oxide layer and white layer are given in Table 2. The microstructure of the nitrocarburized case treated at 700 °C differs from that treated at 565 °C. As shown in Fig. 2 (b, d, and f), it consists of four layers: an oxide layer, ζ-phase, ε-phase, and an

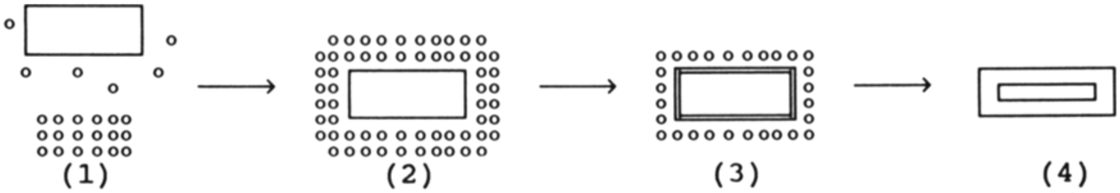

Fig. 1 Schematic diagram of the coat-nitrocarburizing process in a closed volume. (1) Sublimation of triazine polymers. (2) Coating the surface of the article. (3) Nitrocarburizing. (4) Diffusion annealing.

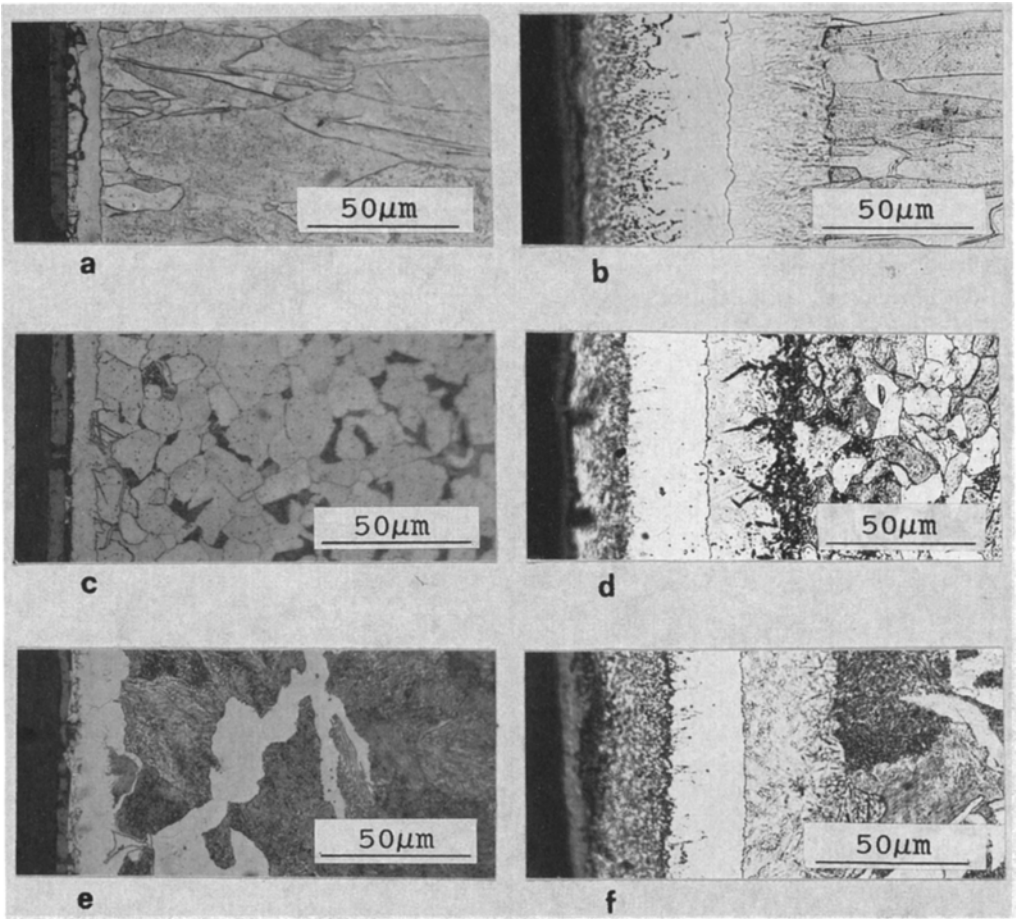

Fig. 2 Microstructure of pure iron (a and b), AISI 1020 (c and d), and AISI 1060 (e and f) after coat-nitrocarburizing at 565 °C (a, c, and e) and 700 °C (b, d, and f).

austenite-martensite layer from the surface to the center of the specimen. Here, the hardness of the austenite-martensite layer represents the case hardness. The thicknesses of each layer and the case hardnesses for various materials are shown in Table 3. The thickness of the case, the related microstructure, and the hardness profiles are strongly dependent on the impregnating temperature and time.

Tables 2 and 3 show that the treatment temperature has the most significant effect on the case thickness and microhardness. When the treatment temperature was increased from 565 to 700 °C, the thickness of the carbonitride case increased about sixfold in accordance with the expectation that the higher the exposure temperature, the greater the diffusion rates of interstitial nitrogen and carbon.

The high efficiency of this coat-nitrocarburizing process is attributed to the high temperature stability as well as the high nitrogen and carbon contents of the triazine polymer reagent. However, up to now, no other such reagents have been found that can be easily, efficiently, and economically applied in the coat-nitrocarburizing process.

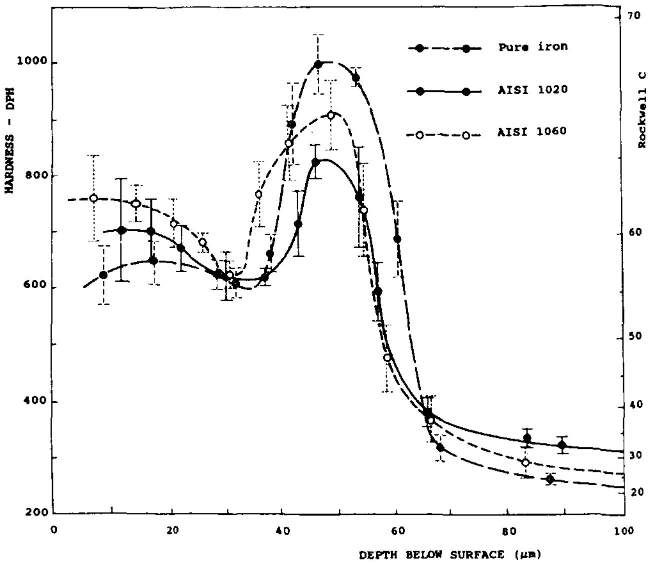

Fig. 3 Hardness profiles near the surface of specimens of different carbon-containing steels after coat-nitrocarburizing at 700 °C for 60 min.

The impregnation time provides another important parameter affecting the thickness and composition of the carbonitride case in coat-nitrocarburizing. Table 4 shows the thickness of the ζ-phase layer (Fe_2N), ε-phase layer ($Fe_{2-3}N$), and the austenite-martensite layer in the specimens after coat-nitrocarburizing at 700 °C for 60, 90, and 120 min. The results show that the thicknesses of the ζ-phase and ε-phase decrease, and the thickness of the austenite-martensite layer increases as the soaking time increases from 60 to 90 min. When the soaking time further increases to 120 min, the ζ-phase and ε-phase disappear, and the austenite-martensite layer increases for AISI 1020 and decreases sharply for AISI 1060. This is because the duration of the effective nitrogen impregnation depends on the consumption of the loaded triazine polymer reagent, *i.e.*, it depends on the time over which the polymer is available to maintain the coat on the surface of the surface concentration of the specimen. The nitrogen impregnation will stop when the polymer vapor is no longer available on the surface. This usually takes about 60 min. Then diffusion annealing, *i.e.*, a denitriding process of the surface layers, starts. The active nitrogen atoms diffuse from nitrogen-rich layers (ζ-phase and ε-phase) towards the body matrix and to the surface, and thus escape into the air. Consequently, in this diffusion annealing step, the layers of the ζ-phase and ε-phase become increasingly thinner, and finally disappear. The thickness of the austenite-martensite layer becomes increasingly thicker. However, extended soaking during diffusion annealing will make the total case soft and the austenite-martensite layer thinner because of the denitriding occurring during the extended process. Consequently, the optimum operating time should be the period required to produce the thickest carbonitride case, usually around 70 min.

Table 2 Thickness and hardness of the case produced by coat-nitrocarburizing at 565 °C for 1 h

Material	Oxide layer, µm	White layer ($\varepsilon + \gamma'$), µm	Hardness ($\varepsilon + \gamma'$), HV
Pure iron	4.3 ± 0.5	12.6 ± 0.5	410 ± 16
AISI 1020	3.7 ± 1.1	9.3 ± 0.9	571 ± 40
AISI 1060	3.4 ± 1.4	8.7 ± 1.2	590 ± 27

Table 3 Thickness and hardness of the case produced by coat-nitrocarburizing at 700 °C for 1 h

Material	Oxide layer, µm	ζ phase, µm	ε phase, µm	$\gamma + \alpha''$ layer, µm	Hardness ($\gamma + \alpha''$), HV
Pure iron	6.1 ± 1.3	17.4 ± 1.4	29.4 ± 1.2	33.9 ± 1.4	999 ± 52
AISI 1020	6.9 ± 1.7	16.3 ± 5.8	23.5 ± 2.7	32.0 ± 1.2	828 ± 31
AISI 1060	6.8 ± 1.3	16.3 ± 8.4	27.7 ± 2.2	35.0 ± 2.5	910 ± 60

Table 4 Thickness (µm) of carbonitride case treated at 700 °C for different operating times

Time, min	AISI 1020			AISI 1060		
	ζ phase	ε phase	$\gamma + \alpha''$ layer	ζ phase	ε phase	$\gamma + \alpha''$ layer
60	16.3 ± 5.8	23.5 ± 2.7	32.0 ± 1.2	16.3 ± 8.4	21.7 ± 2.2	35.0 ± 2.5
90	0	12.2 ± 1.9	36.8 ± 1.0	0	0	156.9 ± 8.3
120	0	0	51.2 ± 1.5	0	0	48.6 ± 7.7

Table 5 Fluctuation of the products of decomposition from triazine polymers in a closed volume at 700 °C

Time, min	CO_2, %	C_nH_m, %	O_2, %	CO, ppm	(%)
0	0	0	20.90	0	79.10
15	0.49	1.5	19.60	130	78.41
30	1.07	0.86	19.00	158	79.07
45	1.80	0.60	18.40	214	79.20
60	1.11	0.30	19.40	190	79.20

Table 6 Effect of pre-oxidation on the thickness of the carbonitride case produced by coat-nitrocarburizing at 700 °C for 1.5 h

Material	Pre-oxidized film, µm	Coat-nitrocarburized case, µm	
		ε-phase	$\gamma + \alpha'''$- phase
AISI 1020	0	22.2 ± 1.9	26.8 ± 1.0
	3.9	19.1 ± 3.8	29.9 ± 1.5

The microstructure of the carbonitride case obtained at 565 and 700 °C for 1 h are shown in Fig. 2. The near-surface hardness profiles for the specimens are shown in Fig. 3. It is clear that coat-nitrocarburizing at 700 °C for 1 h followed by oil quenching makes it possible for pure iron and plain-carbon steels to obtain a 0.2 to 0.4 mm deep high-quality diffusion case. This case consists of a 16 to 17 µm thick layer of the ζ-phase (Fe_2N) with a low hardness value, a 22 to 29 µm thick layer of the ε-phase ($Fe_{2\text{-}3}[N,C]$) with a hardness of 600 to 800 HV, a 32 to 35 µm thick austenite-martensite layer with a hardness of 600 to 1000 HV, and a zone of solid solution of nitrogen in α-iron. Optical and electron microscopy reveal the ε-phase to be a columnar structure and indicate the presence of porosity in the ζ- and ε-phases. In comparison with the ε- and γ′-phases, the austenite-martensite layer still possesses a much higher hardness. Consequently, this high-temperature coat-nitrocarburizing will provide better wear resistance than the low-temperature process.

The presence of oxygen during the coat-nitrocarburizing has a significant effect on the process (see Eq 4, 5, and 6). Some existing experimental data demonstrated that a pre-oxidation treatment[21] or the presence of oxygen to a level of ≤1% O_2 or ≤3% CO_2[6,9] contributes to an increased impregnation speed. In contrast, the traditional nitrocarburizing practice emphasizes the importance of having a reducing atmosphere above the specimen, otherwise the traditional nitrocarburizing process will not work. This new coat-nitrocarburizing method involves a closed volume filled with air. The oxygen content during the coat-nitrocarburizing process is maintained around 20% (see Table 5), and the atmosphere is practically oxidizing. The specimen surfaces are covered by a thick oxide skin that is apt to flake.

To investigate the effect of pre-oxidation on coat-nitrocarburizing, a pre-oxidation treatment was carried out for AISI 1020 and 1060 steel by heating the specimens in air to 700 °C and holding for 2 h without any nitrocarburizing reagent. Then, the specimens were loaded together with the normal surface-polished specimens and nitrocarburized at 700 °C for 1.5 h. The results are shown in Table 6. The carbonitride case of pre-oxidized specimen is thicker than that of the normal specimen. It seems that the pre-oxidation treatment contributes to the speed of the impregnation process.

5. Summary

There are some essential distinctions between the coat-nitrocarburizing process described here and the traditional gaseous nitrocarburizing. First, the coat is not only the source of active nitrogen and carbon, but also forms a protective barrier to prevent further oxidation and denitridation. Second, the presence of oxygen in a closed volume leads to the acceleration of the catalytic decomposition of the coat-triazine polymers, namely oxygen activates the impregnation agents and reinforces the impregnating process.

6. Conclusion

Coat-nitrocarburizing is a very simple, easily controlled, economic, and nonpolluting process. Nitrogen and carbon can be added simultaneously to steel from triazine polymers by using coat-nitrocarburizing. The carbonitride case can be generated by means of this process in a fraction of the time required to generate comparable case depths by conventional gaseous or liquid nitrocarburizing. The presence of oxygen in the coat-nitrocarburizing volume accelerates the impregnating process.

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