УДК 620.186.1: 669.017.3: 548.01: 548.4

THERMOMAGNETIC ANALYSIS OF SURFACE DIFFUSION LAYERS IN IRON-BASED ALLOYS AFTER NITRIDING, CARBURIZING AND CARBONITRIDING

PhD, Ass. Prof. L.D. Demchenko[1], PhD, Senior Researcher A.M. Titenko[2], PhD, Prof. T.-Zh. Ren[3]

[1] *National Technical University of Ukraine "Igor Sikorsky Kiev Polytechnic Institute", Kiev, Ukraine*
[2] *Institute of Magnetism, National Academy of Sciences and Ministry of Education and Science of Ukraine, Kyiv, Ukraine*
[3] *Hebei University of Technology, School of Chemical Engineering, TianJin, China*
E-mail: lesyademch@gmail.com

The technique of differential thermomagnetic analysis allowing to determine interstitials (N and C) concentration in surface layers is proposed. The concentration distributions of carbon and nitrogen in surface diffusion layers were investigated. The relative error of elements concentration is 5÷20 %.
Key words: thermomagnetic analysis, diffusion layers, nitrogen and carbon concentration

1 Introduction

The diffusion saturation of iron-based alloys with carbon and nitrogen is now widely used in industry for significant increasing strength, hardness, wear and corrosion resistance of surface layers of steel products. The study of chemical and phase composition of surface diffusion layers in iron alloys is an important task for the majority of investigations of chemical-thermal treatment such as nitriding, carburizing and carbonitriding [1].

To determine elements concentration and their distribution on diffusion layer depth, the chemical, spectral, X-ray, radiometric and other methods of analysis are widely used. Unfortunately, these methods are usually laborious and enough expensive.

Elements concentration on layer depth can be determined relatively quickly by means of differential thermomagnetic analysis provided that the analyzed diffusion elements form with basic metal the ferromagnetic phases with a constant composition and a Curie point at temperatures below 873 K.

The principal calculation procedures of differential thermomagnetic analysis are given in the work [2]. The detailed calculations of interstitials (carbon, nitrogen) concentration using this technique are presented for cold-deformed steels in [3] and for tempered ones in [4].

2 Experimental

The aim of this work is to investigate concentration distributions of interstitial elements (such as carbon and nitrogen) in iron on surface diffusion layer depth using differential thermomagnetic analysis. Then, using nitrogen and carbon concentration distributions, one can establish the diffusion mechanism (whether it is reactive or atomic) of these elements in iron.

The surface diffusion layers were obtained in iron after thermal saturation by carbon and nitrogen (carbonitriding) at 1323 K during 90, 420, 600, 720 s. Obtained layers were investigated by means of magnetic analysis with a differential dipole magnetometer using a permanent magnet and a magnetic field strength in a pole pieces gap at the level of 470-480 kA/m, and by means of X-ray diffraction analysis with the iron anode radiation as well.

As a result of carbon and nitrogen diffusion in iron, the carbide, nitride and carbonitride phases are formed in surface diffusion layers. It's believed that after high-temperature tempering (at 873 K) of Fe-C-N alloys, all carbon (or/and nitrogen) with the exception of the insignificant amount in ferrite is in the θ (Fe$_3$C) - cementite in case of carburizing (or/and γ' (Fe$_4$N) – phase in case of nitriding).

The quantity of cementite (or/and γ'-phase) can be determined by differential magnetic analysis [2-4]. The typical differential thermomagnetic curve for Fe-based alloy after carbonitriding is presented on Fig. 1. The magnitude of magnetic effect in Curie point of cementite (or/and γ'-phase) at cooling is proportional to a quantity of cementite (or/and γ' - phase) and the latter is proportional to a carbon (or/and nitrogen) content in these ferromagnetic phases. The mass of cementite (Fe$_3$C) is larger than the mass of a carbon atom by 15. Thus, it takes place the correlation between a magnitude of magnetic effect in Curie point of cementite (Δ_θ) or γ'-phase (Δ_γ) at cooling of an etalon specimen and a carbon (or nitrogen) content in it:

$$\Delta_\theta = \sigma_\theta^{300K} \cdot m_\theta \tag{1}$$

$$\Delta_\theta = \sigma_\theta^{300K} \cdot 15 \cdot C_e \cdot 10^{-2} \cdot m_e \tag{2}$$

for γ'-phase:

$$\Delta_{\gamma'} = \sigma_{\gamma'}^{300K} \cdot m_{\gamma'} \tag{3}$$

$$\Delta_{\gamma'} = \sigma_{\gamma'}^{300K} \cdot 17 \cdot N_e \cdot 10^{-2} \cdot m_e \tag{4}$$

where Δ_θ, Δ_γ is the magnitude of magnetic effect in Curie point of cementite (or γ'-phase) at cooling of etalon specimen; $\sigma_\theta^{300 K}$, $\sigma_\gamma^{300 K}$ is the specific magnetisation of cementite and γ'-phase at 300 K accordingly; m_e, m_x is the mass of an etalon and a studied specimen, accordingly; C_e, N_e is the carbon and nitrogen content in etalon specimen.
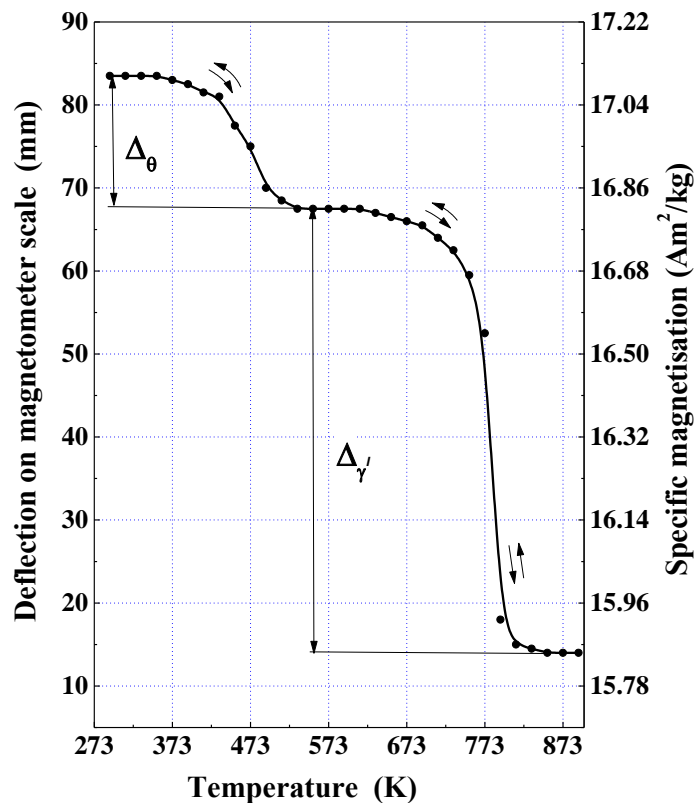

Fig. 1. The differential thermomagnetic curve of Fe-based alloy after carbonitriding (in a gas mixture of 90 % of ammonia and 10 % of propane-butane) at 853 K for 4 hrs

The magnitude of magnetic effect Δ_x in Curie point of cementite (or γ'-phase) at cooling of a studied specimen with an unknown content of carbon C_x or nitrogen N_e in it:

$$\Delta_x = \sigma_\theta^{300K} \cdot 15 \cdot C_x \cdot 10^{-2} m_x \qquad (5)$$

for γ′ (Fe₄N) – phase:

$$\Delta_x = \sigma_{\gamma'}^{300K} \cdot 17 \cdot N_x \cdot 10^{-2} m_x \qquad (6)$$

Therefore, the carbon C_x (or nitrogen N_x) content in studied specimens can be determined according to the following correlation:

$$\qquad (7)$$

$$C_x = \frac{\Delta_x}{\Delta_\theta} \cdot \frac{m_e}{m_x} \cdot C_e$$

$$\qquad (8)$$

$$N_x = \frac{\Delta_x}{\Delta_{\gamma'}} \cdot \frac{m_e}{m_x} \cdot N_e$$

Removing a layer of certain thickness (up to 0.1 mm) from the specimen surface, and then, defining the magnitude of magnetic effect in Curie point of cementite (or/and γ′-phase) at cooling one can calculate a carbon (or/and nitrogen) concentration (C_{layer} or/and N_{layer}) in the layer:

$$\qquad (9)$$

$$C_{layer} = \frac{C_x - C_x'}{m_{layer}}$$

$$\qquad (10)$$

$$N_{layer} = \frac{N_x - N_x'}{m_{layer}}$$

where C_x' and N_x' is the carbon and nitrogen content in a specimen with removed layer which can be calculated using the formulas (7) and (8), accordingly; m_{layer} is the mass of removed layer.

The carbon (or/and nitrogen) concentration distribution in layer depth can be determined by finding the average of obtained concentrations in layer thickness.

3 Results and discussion

The carbon concentration in surface diffusion layer depth was determined by this technique and the results presents on Fig. 2 (a). They show that the carbon distribution in diffusion layer is typical for an *atomic* mechanism of diffusion.

According to Fig. 2 (a), after the saturation for 90 s, the carbon concentration decreases from 0.45 % in specimen surface to 0.15 % in depth of 0.3 mm. The saturation duration at a constant temperature affects the carbon distribution character. So, the iron saturation by nitrogen and carbon for 420 s results in the formation of a diffusion layer containing 1 % of carbon in specimen surface and 0.3 % in the depth of 0.35 mm. After the saturation for 600÷720 s, the carbon concentration in the surface is about 0.90÷0.95 %, that is lower, than in the depth of 0.2 mm from a surface where concentration is 1.0÷1.2 %.

We gave the description of carbon concentration distribution within diffusion layer. Unfortunately, it is difficult to explain a carbon and nitrogen diffusion mechanism without taking into account the character of nitrogen concentration distribution.

To solve this task, the following technique was used. The duplicate line (112) - (211) of the martensite, containing carbon and nitrogen, was obtained using X-ray diffraction analysis. By the interduplicate distance value, the martensite tetragonality ratio c/a was calculated. Considering with a quite degree of conventionality [4] that all carbon in martensite is in normal interstitial positions,

one can calculate the ratio of martensite tetragonality related to a quantity of carbon atoms in martensite [5]. We assume that the carbon and nitrogen influence on c/a is additive. In this case, one can determine c/a part caused by the presence of nitrogen in martensite.
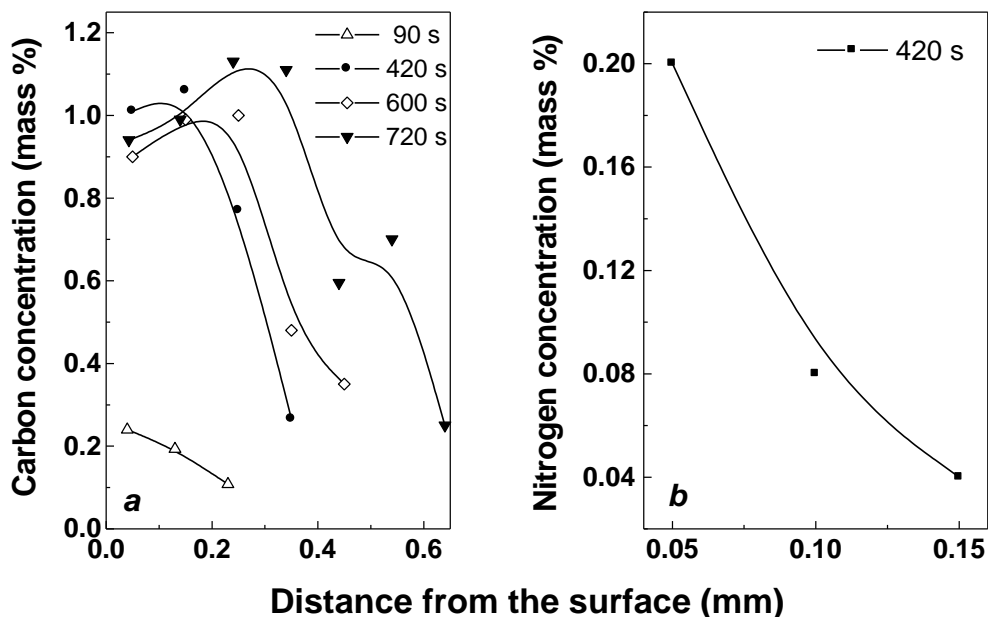

Fig. 2. The carbon (a) and nitrogen (b) concentration distribution on surface diffusion layer depth in iron after the saturation by nitrogen and carbon at 1323 K [6]

.   Application of this technique allows to establish the nitrogen existence in an analyzed layer and to estimate its content. According to Fig. 2 (b), the nitrogen concentration in the diffusion layer surface after the saturation by nitrogen and carbon at 1323 K for 420 s is about 0.2 %, and after the saturation for 600÷720 s is 0.2÷0.3 %.

CONCLUSION

The technique of differential thermal magnetic analysis was proposed for determination of carbon and nitrogen concentration distribution on diffusion layer depth in iron after nitriding, carbonization or carbonitriding, etc. The relative error of element concentration determination in layer depth is in the margin of 5 to 20 % depending on a quantity of ferromagnetic phase presented in a layer. Using this technique the character of concentration distribution of nitrogen and carbon in iron was analyzed and their atomic diffusion mechanism was established.

REFERENCES

[1] L. Demchenko, S. Sidorenko: Defect and Diffusion Forum Vols. 309-310 (2011) pp 155-160
[2] M.V. Belous, V.T. Cherepin and M.A. Vasiljev: *Phase Transformations during Steel Tempering*. Metallurgy, Moscow, 1973 (in Russian).
[3] M.V. Belous, G.M. Molchanovskaya, V.B. Novozhilov and V.T. Cherepin: *Metal Physics and advanced technology*, Vol. 16, N 2 (1994) p. 52 (in Russian).
[4] M.V. Belous, V.B. Novozhilov, L.A. Shatalova and Yu.P. Sheiko: *Physics of metals and metal science*. Vol. 79, N 4 (1995) p. 128 (in Russian).
[5] G.V. Kurdyumov, L.M. Utevsky and R.I. Entin: *Transformations within iron and steel.* Science, Moscow, 1977 (in Russian).
[6] S. Sidorenko, V. Tinyayev, L. Demchenko, Yu. Shejko: Izvestiya Visshikh Uchebnykh *Zavedenii. Chernaya Metallurgiya,* 1996, 11, pp.59-60 (in Russian).