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Effect of Hydrogen on Conductivity of Metals

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Abstract. The work considers the application of a magnetic spectrometer (MS) for analyzing the hydrogenation of metals (particularly, titanium and copper). Therefore, for the sake of increasing the sensitivity of the magnetic spectrometer, the following ratios are introduced: $(\Delta U/U)/(\Delta d/d)$ (where $\Delta U/U$ is the relative change of the MS signal and $\Delta d/d$ is the relative change in the thickness of a sample), $(\Delta U/U)/(\Delta \delta/\delta)$ (where $\Delta \delta/\delta$ is the relative change in the depth of eddy current penetration into metal) and $(\Delta U/U)/(\Delta S/S)$ (where $\Delta S/S$ is the relative change in the area of sample). These parameters allow to eliminate or reduce the error in determining the conductivity value. Parameter β that is equal to the product of the sample area and the inverse value of eddy current penetration depth into metal corresponds to the effectiveness of the current penetration into metal. The authors derived a formula that ties the electric conductivity of metal to the number of implanted hydrogen atoms, which allows determining the composition of titanium hydride at different depth of metal.

Introduction

During operation by hydrogenation complex structural changes are frequently observed in the surface layer and generally in metal. Saturated layers, characterized by the presence of hydrogen implementation phases and changes of the parameters of the crystal lattice at different depths of the metal, are formed. As a result, there are structural defects [1]. Despite the diffusion effects, which are characteristic of titanium, hydride formation, reducing the mobility of hydrogen, there is hydrogen distribution in the depth of the titanium sheet. The analysis of copper is of great importance. In particular, in the manufacture of electro-vacuum devices, OFC with oxygen of not more than 0.0005% is used. When oxygen in copper is excessive the "hydrogen disease", caused by the presence of hydrogen in copper, occurs.

The quality of copper is determined by measuring the number of bends of copper strips, pre - annealed in a hydrogen atmosphere. This process is not technological. Thus, the analysis proves the relevance of finding alternative non-destructive methods for determining the concentration of hydrogen in metals. Eddy current transducers are used for a variety of measurements of properties and for detail and material control. However, in this case there is a following problem. If the controlled samples are sufficiently thin, the signal measured with an eddy-current transducer is dependent not only on the material properties of the sample, but also on its thickness. Due to the fact that the conductivity is a function of hydrogen concentration in metals, the eddy-current method can be used to measure the hydrogen content in metals [2, 3]. However, in all cases, the topical problem is the accuracy and sensitivity of the measurements.

The purpose of this paper is to study the sensitivity of eddy current measurement of electrical conductivity of non-ferrous metals by the example of copper and titanium for the further application of the method for the metal diagnosis.

Principles

As it is known, penetration depth δ of the eddy current into metal is a function of the electrical conductivity of metal σ, the frequency of the eddy current ω and magnetic permeability of metal μ.

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$$\delta = \frac{1}{\sqrt{\omega\mu\mu_0\sigma/2}} \tag{1}$$

In general, the conductivity of metals is a complex function of its structure. For example, the conductivity tensor of metal is :

$$\sigma_{xx} = \sigma_0 - \frac{e^2\tau^2(K_F)L_s}{2\pi\hbar^3\Omega}(\frac{2}{3}\varepsilon_F A)^2 \int d^2 p p_x^2 p_y^2 p^{-5} \times \Theta(2K_F - p) \sum_{i,j} \exp(i\vec{p}\cdot\vec{r}_{i,j}) \tag{2}$$

$$\sigma_{yy} = \sigma_0 - \frac{e^2\tau^2(K_F)L_s}{2\pi\hbar^3\Omega}(\frac{2}{3}\varepsilon_F A)^2 \int d^2 p \frac{p_y^4}{p^5} \times \Theta(2K_F - p) \sum_{i,j} \exp(i\vec{p}\cdot\vec{r}_{i,j}) \tag{3}$$

$$\sigma_{zz} = \sigma_0 = \frac{e^2\tau^2(K_F)}{m} \tag{4}$$

In the formula, the following notations are used: τ - free path of the electron, $\sum_{i,j}\exp(i\vec{p}\cdot\vec{r}_{i,j})$ – lattice structure factor; k_F - the wave vector on the Fermi surface; $k_F = (3\pi^2 n_S/\Omega)^{1/3}$; n_S – concentration of effective charge carriers in the metal; L_s – length of dislocation, ε_F – Fermi energy; $\varepsilon_F = h^2 k_F^2/2m_e$ $A = -b(1-2\nu)/2\pi(1-\nu)$ – lattice parameter, b - Burgers vector, ν - Poisson's ratio , Ω - atomic volume, N - number of dislocations , P_x and P_y - lattice parameters. Calculation of integrals in the small-angle approximation scattering of charge carriers leads to the following formulas [4, 5]:

$$\sigma_{xx} = \sigma_0 - \frac{e^2\tau^2(K_F)L_s}{2\pi\hbar^3\Omega}(\frac{2}{3}\varepsilon_F A)^2 I_x \tag{5}$$

$$I_x \approx \int d^2 p p_x^2 p_y^2 p^{-5} \times \Theta(2K_F - p) \sum_{i,j} \exp(i\vec{p}\cdot\vec{r}_{i,j}) = \frac{1}{2}\pi N k_F \tag{6}$$

$$\sigma_{yy} = \sigma_0 - \frac{e^2\tau^2(K_F)L_s}{2\pi\hbar^3\Omega}(\frac{2}{3}\varepsilon_F A)^2 I_y \tag{7}$$

$$I_y \approx \int d^2 p p_y^4 p^{-5} \times \Theta(2K_F - p) \sum_{i,j} \exp(i\vec{p}\cdot\vec{r}_{i,j}) = \frac{3}{2}\pi N k_F \tag{6}$$

As can be seen from (4) - (7) in the case of small-angle scattering of electrons by dislocations, the formulas are significantly simplified [4, 5]. It can be expected that at different depths of the sample the active and reactive components of the eddy current will depend on the angular position of a sensor magnetic spectrometer. Since the parameters I_x and I_y are three times different, the sensor readings can vary greatly. However, if the electron scattering by defects is small, the sensitivity determination of the magnetic spectrometer is of great importance.

Material and research methods

To carry out research, samples of copper and titanium 0.5 mm - 50 mm in size and with the area of 5 - 2500 mm^2 were polished. The samples were annealed in vacuum (0.1PA) at 650 °C. As an eddy-current instrument the 3MA magnetic spectrometer, made in Germany, was used. The following parameters of magnetic spectrometer were investigated. The ratio ϒ = (ΔU/U)/(Δd/d), where ΔU/U is relative increment (change) of the magnetic spectrometer signal (MS), arising from the change Δδ / δ of the penetration depth δ of the eddy current in metal, Δd/d is a relative change in the thickness of the samples subjected to the measurement, the parameter β=d/S and $\chi = S.\delta^{-1}$ (see the table).

Results and discussion

As it can be seen from formula (1), it is necessary to simultaneously determine the penetration depth of the eddy current in metal and electrical conductivity σ. In this case σ is a function of the penetration depth of the eddy current in metal. Best results can be obtained if the thickness of the

sample is less than or equal to the depth of current penetration into metal. However, at different depths σ is a complex function of metal parameters (formula (4) - (7). Therefore, for the application of a layered model for the determination of the defects concentration, caused by hydrogen, it is important to know the sensitivity of the spectrometer. Test results are tabulated and shown in Figure 1.The signal measured with a magnetic spectrometer depends on the size of the sample, on which the sensor magnetic spectrometer is set up (Fig. 1). Therefore, the sensitivity of the spectrometer on the area as the ratio Y = (ΔU / U) / (ΔS / S), where ΔS / S - the relative change in the sample. results of measurements of active and reactive component of eddy currents for annealed copper are shown in Fig. 1. follows from the figure that the value of active and reactive component of the eddy current is linear and synchronous depends on the area of the sample up to S = 100 mm2 . further increase in the area of the sample being measured does not change the eddy current sensor readings within the measurement error [5]. These tables allow you to assess the effectiveness of determining the concentration of hydrogen in a magnetic spectrometer depending on the frequency, the depth of the layer selected and the sample size. The more derivative values β (f), χ (f) and Y (f), the higher the sensitivity of MS.

Table. Dependence of the sensitivity of the spectrometer parameters on frequency of the eddy current (copper)

Frequency f, kHz	U, mV	β=d/S	$\chi = S.\delta^{-1}$	$\Upsilon = (\Delta U/U)/(\Delta d/d)$
10	0.145	1.735	4.230	0.645
20	0.134	2.454	5.982	0.646
30	0.109	3.006	7.327	0.574
40	0.093	3.471	8.460	0.523
50	0.081	3.881	9.459	0.487
60	0.073	4.251	10.362	0.455
70	0.066	4.592	11.192	0.421
110	0.037	5.756	14.030	0.271
150	0.036	6.721	16.383	0.301

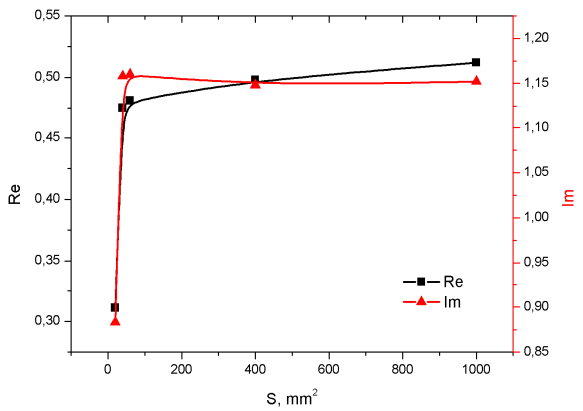

Fig. 1. Dependence of active and reactive component of the eddy current (mA) on the area of the copper sample (frequency 400 kHz)

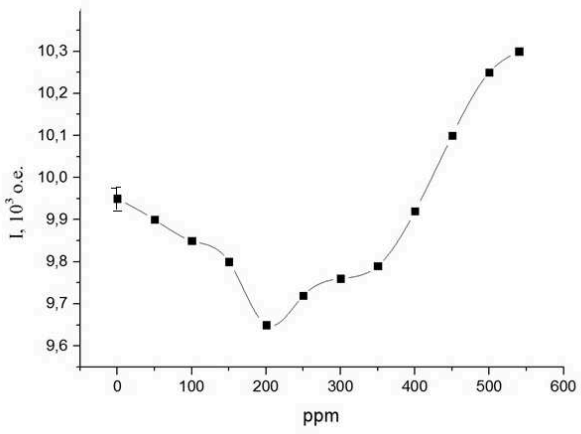

Fig. 2. Dependence of active component of the eddy current on the concentration of hydrogen in the titanium (500 kHz)

It is known that any hydrogenation changes integral conductivity of metal. The dependence of titanium conductivity on the hydrogen content in the metal according to [4] (X - ratio of the number of hydrogen atoms per an atom of titanium) can be expressed in the following regression equation:

$$\sigma = -6620X + 20731 \quad (8)$$

Substituting this expression for the electrical conductivity of metal σ in the formula for the penetration depth of the eddy current in metal δ(Formula 2) , we get the following expression :

$$\delta = \frac{1}{\sqrt{\omega\mu\mu_0(20731 - 6620X)/2}} \quad (9)$$

The resulting formula helps to clarify the distribution of hydrogen concentration at a depth of titanium sample by the stratified subtraction method [2]. Equation (9) links the measured conductivity to the hydrogen content of titanium, which makes it possible to use the method for research of the hydrogen diffusion in metal [5].

Hydrogenation was carried out as described in [6]. Microstructural studies of the side face of the VT1- 0 samples subjected to hydrogenation indicated that the increased to 200 ppm hydrogen content does not result in the formation of the hydride phase. By increasing the hydrogen concentration above 500 ppm, lamellar titanium hydride release is observed in the volume of samples. Indeed, when the concentration of lamellar titanium hydride is increased, an increase in the eddy-current sensor signal is observed (Fig. 2).The dependence of the reactive component has a similar shape. At the same time an increase of the hydrogen content to 200 ppm is characterized by a decrease in eddy current signal. Apparently, this can be explained by different structure of the of titanium hydride at different depths of the titanium sample. This result indicates the effect of layered distribution in metal hydride and the sensitivity of the eddy current method.

Conclusion

Thus, the developed method for determination of the measurement sensitivity of the electrical conductivity in metals, improves the effectiveness of the eddy current method for determination of the hydrogen content in nonmagnetic metals. Maximum accuracy can be obtained at a frequency which corresponds to the current penetration depth equal to the thickness of the sample used. Otherwise, the model of the layered distribution of current in sample must be used. The area of efficient distribution of the current in metal is also a function of its penetration depth into metal. This follows from the law of the function variation $\beta = d/S$, $\chi = S.\delta^{-1}$, $\Upsilon = (\Delta U/U)/(\Delta d/d)$ depending on the current frequency .The method for the study of non-uniform distribution of hydrogen in metal by face location of magnetic spectrometer sensor against the sample is suggested.

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