ANNALS OF FACULTY ENGINEERING HUNEDOARA
– INTERNATIONAL JOURNAL OF ENGINEERING
Tome X (Year 2012) – FASCICULE 2 (ISSN 1584 – 2665)

[1.] Angel ZUMBILEV

ABOUT THE MECHANISM OF CARBONITRIDING IN LOW TEMPERATURE PLASMA

[1.] TECHNICAL UNIVERSITY SOFIA – PLOVDIV BRANCH, DEPARTMENT OF MATERIAL SCIENCE AND TECHNOLOGY, PLOVDIV, BULGARIA

ABSTRACT: *The paper suggest a probable mechanism of carbonitriding in glow discharge in a medium of ammonia, argon and carbon dioxide, according to which the diffusion capable nitrogen and carbon atoms are formed directly on the surface of the treated articles without preliminary forming of iron nitrides.*
KEYWORDS: *carbonitriding, low temperature plasma, mechanism*

INTRODUCTION

Treatment of materials in glow discharge (nitriding, carbonitriding) is characterized by their active participation in the discharge as they play the role of a cathode. The impact on the cathode by ions and atoms leads to increasing the temperature of the cathode, as well as to active emission of electrons. Except for emission of electrons, the ion impact also results in detaching atoms from the material of the cathode. The detached particles are neutral atoms and molecules, obtained due to the pulverization of composite substances. Another peculiarity of the low temperature plasma is the influence of the glow discharge over the saturating medium, containing ammonia, argon, carbon dioxide etc., which leads to dissociation and ionization of the employed gases [2,10,13,14,15].

Many chemical processes in glow discharge plasma proceed with the participation of atoms and radicals. In order to form a free atom it is necessary to introduce into the system a bigger amount of energy than it is required for a unit of molecular dissociation. It is worth noting that the energy required for forming an atom always exceeds the energy for breaking the corresponding molecular bond, as, alongside with the dissociation of the molecules, a great amount of other processes go in the system, in particular excitation of the vibration and electronic states of the molecules. Great part of the initially introduced into the employed gas energy is consumed by these processes. Thus the energy required for forming an atom is also characterized by increasing the temperature of the gases in the saturating medium. This circumstance is extremely important in the cases when the process goes under low temperatures [2, 3, 9].

Despite the numerous investigations, conducted with the use of ammonia, nitrogen or a mixture of nitrogen and hydrogen as saturating media, there is no an integrated model yet, representing the mechanism of nitriding and carbonitriding in glow discharge. There are two principle methods concerning the question of forming diffusion capable nitrogen and carbon atoms on the surface of the treated articles.

According to the first method, iron nitrides are formed initially, which then dissociate into lower substances and release nitrogen, in its turn diffusing into the threated material. According to the model, developed by Kölbel, it is assumed that, as a result from the pulverization of iron in the glow discharge, iron nitrides rich of nitrogen are formed and they deposit on the surface of the treated articles. The deposited nitrides decompose and release nitrogen, which diffuses into the interior of the material [16]. The availability of ions could increase the number of the centers of chemisorption. In nitrogen and hydrogen containing atmospheres the process goes with the participation of NH-radicals, which, after taking hydrogen, turn into the very active radical NH_2. In result from the interaction between the iron and the neutral nitrogen atoms or radicals on the surface of the substrate iron nitrides are formed, which release diffusion capable nitrogen [17].

According to the second method, diffusion capable nitrogen is directly formed on the surface of the treated articles, i.e., without the preliminary forming of iron nitrides [18]. Materials, having cathode, anode or floating potential, have been treated by the comparatively new method of nitriding in two-step vacuum-arc discharge under low pressure. The fact, that the samples with a positive potential can be nitrided renounces the idea of forming iron nitrides in the gas medium, as a surface, subject to

electron impact does not pulverize [19]. The high activity of the saturating medium in this case is due to the neutral nitrogen atoms. The process depends only on the concentration of atomic nitrogen and the temperature of the article, while the electron/ion impact plays the role of a convenient tool for ensuring the temperature needed for the process. By investigating the area of the dark cathode space of a direct current glow discharge in the presence of hydrogen the work for electron detachment from the iron is reduced and thus the absorption of the nitrogen atoms is facilitated [20]. Ultimately, during the process of glow discharge nitriding, atomic nitrogen is formed on the surface of the articles, which, depending on their temperature, diffuses into their interior.

DISSOCIATION AND IONIZATION OF CARBON DIOXIDE AND AMMONIA

It is necessary to note that two areas could be distinguished in the structure of the glow discharge: the zone of the discharge, where the processes of dissociation of the employed gases (CO_2, NH_3, Ar) occur, and the zone of the discharge, where reactions of recombination proceed.

Carbon dioxide dissociation has been investigated by a great number of authors both theoretically and experimentally by using various sources of plasma such as a microwave discharge, a plasma reactive burner or radio frequency arc discharge. Despite the numerous works the kinetic mechanism of CO_2 dissociation has not been studied very well yet [1,5]. Actually the mechanism of CO_2 dissociation is determined mainly by the parameters of the glow discharge (average energy of the electrons in the plasma) and the properties of the plasma gas (pressure, velocity of flow, energy) [2,14].

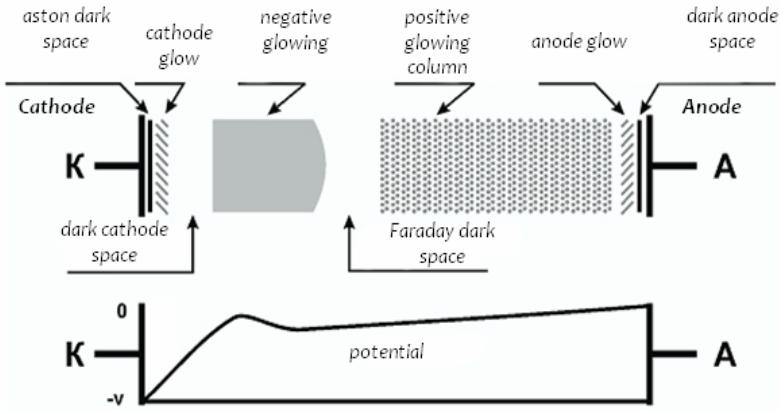

Figure 1. Glow discharge structure

In the cathode space of the glow discharge (Figure 1) the ordered motion of electrons and the position of the positively charged ions is the predominant event, while in the anode section the chaotic motion of the electrically charged particles prevails. Electrons are detached from the cathode and they are accelerated in the direction towards the anode, acquiring energy, sufficient for dissociation and ionization of the atoms and molecules. The obtained positive ions are directed toward the cathode (C) and, colliding with its surface, they cause an emission of new electrons, while the secondary electrons, formed during the ionization, are accelerated by the field toward the anode (A).The cathode dark space in the structure of the glow discharge (Figure 1) includes the whole area of the cathode up to the next section of the negative glowing. This area is related to a big part of the voltage, called cathode fall of the potential. In this area the gas glowing is weak, as the energy of the electrons is higher than the maximum for excitation. This energy is sufficient for causing dissociation and ionization of the employed gases. The electrons, originated from the ionization of the atoms, are accelerated by the field and move toward the area of the negative glowing. The gases in this area are in ionized state (plasma). The plasma results from the accelerated electrons, coming from the cathode dark space. At the moment the accelerated electrons impact the CO_2 molecule, it decomposes in result from the bond breakage, which leads to forming CO, C and O, expressed by the following reactions [1, 9]:

a) dissociation at direct electron impact:

$$CO_2 + e^- \rightarrow CO_2^* + e^- \rightarrow CO + O - 532\ kJ/mol\ (energy\ of\ dissociation\ -\ 7.3\ eV) \quad (1)$$

$$CO \leftrightarrow C + O - 1076\ kJ/mol\ (energy\ of\ dissociation\ -\ 11.1\ eV) \quad (2)$$

$$CO_2 \leftrightarrow CO + 1/2O_2 - 281\ kJ/mol\ (energy\ of\ dissociation - 2.9\ eV) \quad (3)$$

$$O_2 \leftrightarrow 2O - 497\ kJ/mol\ (energy\ of\ dissociation - 5.12\ eV) \quad (4)$$

*The symbol * corresponds to the state of high excitation. The addition of inert gases (He, Ar) into the CO_2, medium leads to increasing the average energy of the electron in the discharge. At sufficient concentration of CO_2, considerable reduction in the energy used for dissociation of one molecule is achieved [8, 12].*

It can be noted that with the increase in the vibration temperature the energy consumption for forming an atom reduces significantly since in these cases the decomposition of molecules is facilitated.

However, the energy consumption for forming a carbon atom many times exceeds the energy for molecular dissociation. This is the case with CO [1,3]. It can be explained first of all by the higher energy of dissociation of CO so that it considerably exceeds the average energy of the electron and the process of dissociation becomes a multiple-stage one.

b) dissociation bonding

$$CO_2 + e^- \rightarrow (CO_2^-)^* \rightarrow CO + O^- \quad (5)$$
$$\rightarrow C^- + 2O \rightarrow CO^- + O$$

During the reaction the negative ions from CO_2 are minority [1]. The last reaction could lead to forming vibration excited CO_2 molecules by recombination of CO^- and O, causing dissociation in CO + O after that.

c) ionization at electron collision

$$CO_2 + e^- \rightarrow CO_2^+ + e^- + e^- \text{ (energy of ionization – 13.8 eV)`} \quad (6)$$

For the initial process of ionization many different types of positive ions are obtained (CO^+, O^+, O_2^+), but the most important is CO_2^+, the others are usually neglected [5]. Recently the following reactions have been identified [1,5]:

$$CO_2^+ + e^- \rightarrow CO_2\,,\ CO_2^+ + e^- \rightarrow C + O_2\,,\ CO_2^+ + e^- \rightarrow CO^- + O \quad (7)$$

It can be noted that CO_2^+ molecules can be formed in two excited states and forming a stable CO_2^+ dominates. CO_2 dissociation is mainly due to vibration excitation caused by electron collisions. It is clear in this case that by heating the employed gases in imbalanced conditions higher efficiency of dissociation can be achieved, since then the introduced energy is not used in all degrees of freedom [3]. As the molecular dissociation goes due to vibration excitation, the effective dissociation could occur at imbalanced conditions, in which the increase in the vibration excited states is higher than it is at balanced conditions. Therefore it is assumed that molecular dissociation occurs in imbalanced plasma with high vibration temperature [1, 3, 7, 9]. With the imbalanced gas the efficiency of the dissociation increases for two reasons. The first reason is the comparatively smaller energy, used for excitation of translational and rotational degrees of freedom. The second reason is the inharmoniousness of the molecules, leading to an increase of the relative number of vibration excited molecules. Due to it the same extent of dissociation of the molecules is obtained at lower temperature of vibration, than the temperature at the lack of inharmoniousness. It can be noted that in the zone of the negative glowing of the glow discharge both processes of dissociation and ammonia ionization occur, leading to obtaining nitrogen and hydrogen by the following probable reactions [3,13,14]:

$$NH_3 \rightarrow HN_3^+ + e^- \text{ – 164,65kJ/mol (energy of ionization - 1.69 eV)} \quad (8)$$
$$NH_3^+ \rightarrow N^+ + 3H \text{ – 2298,29kJ/mol (energy of ionization and dissociation-23.67 eV)} \quad (9)$$
$$NH_3^+ = N + 2H + H^+ \text{ – 2216,96 kJ/mol (energy of ionization and dissociation - 22.83 eV)} \quad (10)$$
$$NH_3 = NH_2 + H^+ + e^- \text{ – 1656,08 kJ/mol (energy of ionization and dissociation - 17.05eV)} \quad (11)$$
$$NH_2 = NH + H^+ + e^- \text{ – 1582,16 kJ/ mol (energy of ionization and dissociation – 16.29 eV)} \quad (12)$$
$$NH = NH^+ + e^- \text{ – 1242,47 kJ/ mol (energy of ionization and dissociation – 12.79eV)} \quad (13)$$
$$NH^+ = N + H^+ \text{ – 334,67 kJ/ mol (energy of ionization and dissociation – 3.44 eV)} \quad (14)$$
$$N = N^+ + e^- \text{ – 1381,51 kJ/ mol (energy of ionization and dissociation – 14.22 eV)} \quad (15)$$
$$H_2 \leftrightarrow 2H \text{ – 434,95 kJ/ mol (energy of dissociation – 4.48 eV)} \quad (16)$$
$$N_2 \leftrightarrow 2N \text{ – 948,54 kJ/ mol (energy of dissociation – 9.77 eV)} \quad (17)$$

On the basis of the above exposed data the following probable mechanism of carbonitriding in a saturating medium of ammonia and corgon could be suggested:

As the energy of dissociation and ionization of ammonia and carbon dioxide is higher, in the area of the cathode fall of the glow discharge probably atomic carbon should form initially by the reaction $CO_2^+ + e^- \rightarrow C + O_2$ and atomic nitrogen by the reaction $NH_3^+ = N + 3H$.

The dissociation of the ammonia molecule and the breakage of the carbon-oxygen bonds go close to the cathode in the zone of the negative glowing. Consequently, processes of ionization of the carbon (reaction $CO_2 + e^- \rightarrow CO_2^+ \rightarrow C^+ + 2O$) and nitrogen (reaction $NH_3^+ = N^+ + 3H$) atoms occur, these atoms impact the surface and diffuse at a certain distance into the material – Figure 2. The process of saturation of the metal surface depends only on the concentration of the atomic carbon and nitrogen in the plasma, as well as on the temperature of the article, while the electron or ion impact plays role for ensuring the necessary temperature of the details [20].

The availability of argon in the saturating medium in combination with CO_2, leads to increasing the average energy in the discharge, which, at sufficient concentration of CO_2, results in considerable reduction of the energy spent on the dissociation of a molecule.

In the process of carbonitriding part of the nitrogen atoms are replaced by the bigger carbon atoms, which causes forming the ε-phase in the carbonitrided layer. It is possible for two reasons: approximately the same ion radius of the nitrogen [r_{ion} = 13(5+1)pm, r_{ion} = 16(3+1)pm] and the carbon [r_{ion} = 16(4+1)pm]; the possibility for the carbon atoms to take up the vacant junctions.

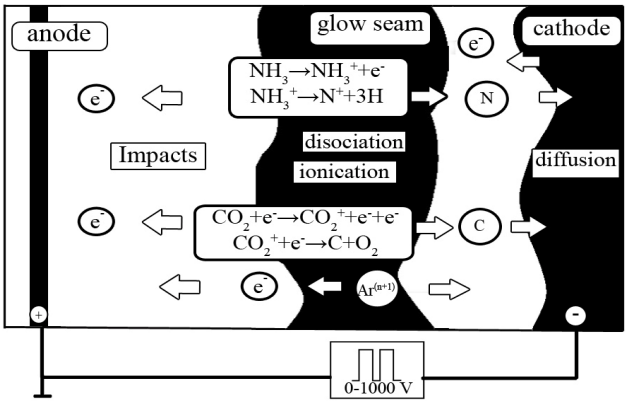

Figure 2. Reactions, going in close proximity of the cathode space in a medium of ammonia, carbon dioxide and argon

CONCLUSIONS

A probable mechanism of glow discharge carbonintriding in a medium of ammonia, carbon dioxide and argon is suggested. As a consequence of the dissociation and ionization of the ammonia molecules and the carbon dioxide molecules, close to the cathode in the zone of the negative glowing diffusion capable nitrogen and carbon are obtained, which impact the surface and diffuse at a certain distance into the material. The process of saturation of the metal surface depends only on the concentration of the atomic carbon and nitrogen in the plasma and the temperature of the article, while the electron/ion impact plays role for ensuring the necessary temperature of the details.

REFERENCES

[1.] Rond C., A. Bultel, P. Boubert, B. G. Cheron, Spectroscopic Measurements of Nonequilibrium CO_2 Plasma in RF Torch, Chemical Physics, 354, 2008, pp.16-26.
[2.] Kobayashi A., K. Osaki, C. Yamabe, Treatment of CO_2 Gas by High-energy Type Plasma, Vacuum 65, 2002, pp.475-479.
[3.] Eletskii A., B.Smirnov, Dissociation of Molecules in Plasma and Gas: The Energy. Pure & Appl. Chem., Vol. 57, No. 9, pp.1235-1244, 1985.
[4.] Pietro F., R.Thissen, J. Zabka, J. Roithova, Z.Herman, Odile Dutuit, Internal Energy Effects in the Reactivity of CO_2^{2+} Doubly Charged Molecular Ions With CO_2 and CO, International Journal of Mass Spectrometry 228, 2003, pp.507-516.
[5.] King Simon, J. Stephen, D. Price, Electron Ionization of CO_2, International Journal of Mass Spectrometry 272, 2008, pp. 154-164.
[6.] Rond C., P. Boubert, J. Felio, A. Chikhauoi, Nonequilibrium Radiation Behind a Strong Shock Wave in CO_2-N_2, Chemical Physics, 340, 2007, pp. 93-104.
[7.] Indarto Antonius, D. Ryook Yang, J. Choi, H. Lee, H. Song, Gliding Arc Plasma Processing of CO_2 Conversion, Journal of Hazardous Materials, 146, 2007, pp.309-315.
[8.] Abdullah M., Y. Tanaka, Y. Uesugi, Observation of Non-chemical Equilibrium Effect on Ar- CO_2-H_2 Thermal Plasma Model by Changing Pressure, Thin Solid Films 518, 2009, pp.943-951.
[9.] Andreev S., V. Zakharov, V. Ochkin, S. Savinov, Plasma-Chemical CO_2 Decomposition in a Non-self-sustained Discharge With a Controlled Electronic Component of Plasma, Spectrochimica Acta Part A, 60, 2004, pp. 3361-3369.
[10.] Yasuda H., Plasma Polymerization, Academic Press, Inc.(Harcourt Brace Jovanovich, Publishers) Orlando, San Diego, New York, London, Toronto, Montreal, Sydney, Tokyo, 1985.
[11.] Григоръянц А., Основы лазерной обработки материалов, М., Машиностроение, 1989.
[12.] Арутюнян Р., Воздействие лазерного излучения на материалов, М., Наука, 1989.
[13.] Toshkov V., Nitriding in Low-temperature Plasma, King, Sofia, 2004, p.242
[14.] Toshkov V., Theoretical and Practical Aspects of Nitriding of Iron and Iron-carbon Alloys in Low-temperature Plasma, (Ph.D. thesis, Sofia Technical University), 1997.
[15.] Русев Р., Особености, механизъм на образуване и морфология на карбонитридни слоеве, получени в среда от амоняк и въглероден двуокис, Дисертация, 1979.
[16.] Kölbel, H., Die Nitridschichtbildung bei der Glimmentladung. Forschungsberichte des Landes Nordreihn-Westfalen, Nr. 1555, Westdeutscher Verlag Opladen, 1965
[17.] Michalski J., D.C glow discharge in a gas under lowered pressure in ion nitriding of Armco iron. J. Mat. Sci. Lett., 19. 2000, pp.1411-1414
[18.] Tibbetts, G., Role of nitrogen atoms in "ion nitriding". J. Appl. Phys., 45, 11, 1974, pp.5072-5073
[19.] Андреев, А., В. Шулаев, Л.Саблев, Азотирование сталей в газовом дуговом разряде низкого давления. Физическая инженерия поверхности, 4, 3-4, 2006, 191-197
[20.] Suraj K., P.Bharathi,,V. Prahlad., S.Mukherjee , Near cathode optical emission spectroscopy in N_2-H_2 glow discharge plasma. Surf. Coat. Technol., 202, 2007, pp.301-309