To the Question about the Source of Ozone in MAG Welding Using Carbon Dioxide

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Abstract

In this paper, we have considered the formation of ozone in arc welding in a protective atmosphere with carbon dioxide additives. It is a commonly shared view that ozone is formed in the air under the influence of ultraviolet radiation of the arc. But, at the MAG process, using carbon dioxide ozone is released intensively at the beginning of welding, and then the intensity of its release is significantly reduced. This indicates that in the case, another source of ozone is present and is located in the welding arc; to identify it, we calculated the mass composition of the products of thermal dissociation of carbon dioxide in the temperature range from 300 K to 20000 K. It was found that molecular oxygen is formed by decomposition of carbon dioxide in the temperature range from 1800 K to 4800 K. At temperature 3600 K, the concentration of molecular oxygen is about 17 wt.% in products of thermally dissociating carbon dioxide. As a result, the condition is created for the formation of ozone in the welding arc when the plasma temperature are building and reaches about 3600 K when the arc is ignited. The resulting ozone passes into the gaseous component of the welding aerosol. Along with the formation of ozone in the air, this process determines conditions of ozone emission into the environment when the arc is excited. This fact must be taken into account when designing ventilation of welding works when designs having a significant number of short welds are welded MAG process or pulsed gas metal arc welding using carbon dioxide is applied.

Keywords: Ozone, Thermal Dissociation of Carbon Dioxide, Carbon Dioxide, MMA, Arc Welding in Carbon Dioxide.

I. INTRODUCTION

Ozone is a poisonous gas, the toxicity of which is equated to the category of chemical warfare agents [1]. Ozone dissolves in water and liquids, including blood plasma ten times faster than oxygen [2]. Its occupational limit value is 0,2 mg/m³ [3]. At higher concentrations, ozone causes changes in the body. As a result, the following phenomena become possible [1]:

- the mucous membrane of the eyes is irritated;

- the functioning of the respiratory system is disrupted to the point where lung paralysis may occur;
- general fatigue of the body is observed and the possibility of allergic reactions occurs;
- headaches are coming;
- burning in the throat and nausea occur;
- a negative impact on the nervous system is.

Ozone toxicity is enhanced when combined with other gases, such as nitrogen oxides and carbon dioxide [1], which are part of the gaseous component of the aerosol during MAG welding [4].

As experimental data show, ozone is formed intensively only at the beginning of arc welding in a protective atmosphere with carbon dioxide additives. Further, the concentration of ozone in the environment is significantly reduced [4 - 6]. In the works [4 - 6] it is assumed that during arc welding in carbon dioxide ozone under the action of ultraviolet radiation of the arc is formed from air oxygen by reaction:

$$3O_2 \xrightarrow{Ultraviola} 2O_3.$$
 (1)

To explain that the ozone release is high at the beginning of arc welding in carbon dioxide, and then it is significantly reduced in the assumption is made that the ozone formed according to the reaction (1) in the air under the influence of ultraviolet radiation of the arc and then the ozone decomposes when interacting with the gas components of the air [4]. However, this statement contradicts the observed phenomena. Since in the vicinity of the welding site in relation to the gas components of the air, the beginning of the welding process is no different from its continuation, there is no visible reason for the increased concentration of ozone to occur at the beginning of welding.

Thus, at present a convincing explanation of the fact of a significant selection of ozone at the beginning of arc welding in carbon dioxide is missing. This determines the relevance of identifying the appropriate adequate physical and chemical mechanism. In this paper, the theoretical foundations of such a mechanism of ozone formation are considered.

II. RESEARCH METHODOLOGY, RESULTS AND DISCUSSION

To predict the composition of thermally dissociating carbon dioxide in the welding arc, we considered a number of chemical reactions occurring in a conditionally sequential mode:

$$CO_2 \rightarrow CO + \frac{1}{2}O_2;$$
 (2)

$$CO_2 \rightarrow CO_2^+ + \overline{e};$$
 (3)

$$CO_2^+ + \bar{e} \to C + 2O; \qquad (4)$$

$$CO \rightarrow C + O;$$
 (5)

$$CO \rightarrow CO^+ + \bar{e}$$
; (6)

$$CO^+ + \overline{e} \to C + O;$$
 (7)

$$O_2 \rightarrow 2O;$$
 (8)

$$O_2 \to O_2^+ + \overline{e} ; \qquad (9)$$

$$O_2^+ + \bar{e} \to 2O: \tag{10}$$

$$O \to O^+ + \bar{e} ; \qquad (11)$$

$$O^+ \to O^{2+} + \overline{e} ; \qquad (12)$$

$$C \to C^+ + \bar{e} ; \tag{13}$$

$$C^+ \to C^{2+} + \overline{e} \ . \tag{14}$$

The reaction equation (2) - (14) in general way can be written as an equation:

$$A + B \leftrightarrow nF + mD, \qquad (15)$$

where A and B are initial substances; and F and D are reaction products; and n, and m are stoichiometric coefficients.

The reaction equilibrium constant (15), expressed through partial pressures, is written as follows [7]:

$$K = P_F^n P_D^m / (P_A P_B).$$
⁽¹⁶⁾

As follows from Dalton's law, the partial pressure of i – th gas is calculated as the product of the pressure of the mixture P on the molar concentration of this gas X_i :

$$P_i = X_i P / 100 \,. \tag{17}$$

Given that to the welding in protective gases $P \approx 1$ atm., we are using equation (17) can equation (16) transform to the form:

$$K = 100^{2-n-m} \cdot \frac{X_F^n X_D^m}{X_A X_B}.$$
 (18)

Equilibrium constants of chemical reactions (2), (5), (8) presented in tabular form in the handbooks [7, 8] and we approximated them with a correlation coefficient of 0.995. In determining the equilibrium constants of ionization reactions

(3), (4), (6), (7), (9 - 14) together with equation (16) we used the Saha equation.

In general way, the Saha equation has the form [9]:

$$\frac{N_e N_{z+1}}{N_z} = \frac{2u_{z+1}}{u_z} \left(\frac{m_e kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} e^{-\frac{\chi_z}{kT}},$$
(19)

where N_e , N_{z+1} , and N_z are concentrations of electrons, ions and atoms respectively in unit/m³; u_{z+1} and u_z are statistical sums of ion and atom respectively; z and z + 1 are ionization stages (z = 1 for a neutral atom, z = 2 for a single ionized atom, etc.); m_e is electron mass; k and \hbar are Boltzmann and Planck constants respectively; χ_z is ionization energy.

Partial pressures are determined through N_e , N_{z+1} and N_z according to the following equations [10]:

$$P_{e} = \frac{N_{e}}{kT}, \ P_{z+1} = \frac{N_{z+1}}{kT}, \ P_{z} = \frac{N_{z}}{kT}.$$
 (20)

Substitution in equation (19) of numerical values of constants, coefficient for conversion of χ_z from electron-volts to joules, and equation (20) leads to the equation that, after logarithmization, is given by

$$lg\left(\frac{P_e P_{z+1}}{P_z}\right) = -6,47706 + \frac{5}{2}lgT - \frac{5040\chi_z}{T} + lg\left(\frac{2u_{z+1}}{u_z}\right).$$
(21)

From equations (16) and (21) we determined the equilibrium constants of the reactions (4), (6), (7), (9-14).

Finally, the equations for the equilibrium constants of reactions (2) - (14) have the form:

$$K_{\rm CO_2 \to CO_+ \frac{1}{2}O_2}(T) = 10^{4,22619 \cdot \frac{16068}{T^{1,01552}}};$$
 (22)

$$K_{\rm CO_2 \to CO_2^+ + \bar{e}}(T) = 10^{-5.875 - \frac{69502}{T} + \frac{5}{2} l_g T};$$
 (23)

$$K_{\rm CO_2^++\bar{e}\to C+2O}(T) = 10^{-42,605-\frac{14575}{T}+\frac{61,6132}{T^{0,016355}}}; \qquad (24)$$

$$K_{\rm CO\to C+O}(T) = 10^{7,58507 - \frac{54644}{T^{0.993665}}};$$
 (25)

$$K_{\rm CO\to CO^+ + \bar{e}}(T) = 10^{-5,875 - \frac{70631}{T} + \frac{5}{2}l_g T};$$
 (26)

$$K_{\rm CO^+ + \bar{e} \to C + O}(T) = 10^{97,3012 + \frac{143139}{T} - \frac{86,518}{T^{0,00901}}}; \qquad (27)$$

$$K_{\rm O_2 \to 2O}(T) = 10^{7,12985 \frac{24777}{T^{0,989124}}};$$
 (28)

$$K_{O_2 \to O_2^+ + \bar{e}}(T) = 10^{-6.05109 \pm \frac{60868}{T} + \frac{5}{2} l_g T};$$
(29)

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$$K_{O_{2}^{+}+\bar{e}\to 2O}(T) = 10^{2,619 \, \text{h} \frac{28208}{T^{0.95836}}};$$
(30)

$$K_{O \to O^{+} + \overline{e}}(T) = 10^{-6,52821 \cdot \frac{68635}{T} + \frac{5}{2} l_g T}; \qquad (31)$$

$$K_{O^{+} \to O^{2+} + \bar{e}}(T) = 10^{-5,82385 - \frac{107352}{T} + \frac{5}{2}lgT};$$
(32)

$$K_{C \to C^{+} + \overline{e}}(T) = 10^{-6,35212 - \frac{56851}{T} + \frac{5}{2}l_g T};$$
(33)

$$K_{C^{+} \to C^{2+} + \overline{e}}(T) = 10^{-6.95418 \cdot \frac{66039}{T} + \frac{5}{2}l_{g}T}.$$
 (34)

Following formula was used to convert molar concentrations into mass fractions [11]:

$$w_{\partial,i} = \frac{X_{\partial,i}M_i}{\sum \left(X_{\partial,i}M_i\right)},\tag{35}$$

where $X_{\partial,i}$ and $w_{\partial,i}$ are the molar fraction and the mass fraction of *i* - th component in thermally dissociating carbon dioxide respectively.

The solution of equations (18) - (35) is shown in Fig. 1.

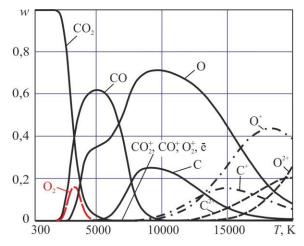


Fig. 1. Mass fractions of chemical reaction reagents (2) – (14) depending on temperature

Figure 2 illustrates the number of moles of reaction reagents (2) - (14) as a function of temperature.

As shown in Fig. 1, molecular oxygen is one of the products of thermal dissociation of carbon dioxide in the temperature range from 1800 K to 4800 K. This creates the conditions to ozone formation by reaction (1). At 3600 K the molecular oxygen content is maximum and is about the 17 wt.% in products of thermally dissociating carbon dioxide.

However, the temperature of the welding arc at gas metal arc welding is 13000 K – 15000 K in the central part of the arc and it is 7500 K in its periphery in a stationary or close to a stationary state [12, 13]. Under these temperature conditions, molecular oxygen is not present in the welding arc (see Fig.

1.) and the main source of ozone in welding is air oxygen according to the reaction (1). But when the arc is ignited (arc ignition time in process MAG welding is 0.009 - 0.015 s [14]), the temperature in it increases, and in parts of the arc atmosphere that have a temperature of about 3600 K the concentration of molecular oxygen significant becomes (see Fig. 1). As a result, reaction (1) takes place in an arc and ozone is formed intensively. In addition, when the arc is ignited, the formation of ozone in the air should also increase. This is because actinic ultraviolet radiation has a peak when the arc is ignited in the MAG process. In this case, the peak radiation exposure during arc ignition exceeds the intensity of ultraviolet radiation at a stationary arc discharge by almost 20% (for 70 A and 120 A of electric current in the arc) and about 4% (for 180 A) [14].

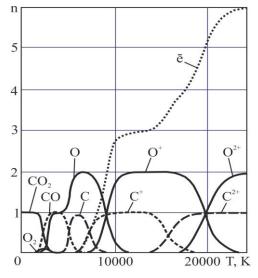


Fig. 2. The number of moles of the reactants of reactions (2) - (14) depending on the temperature

III. CONCLUSION

In this paper we showed that the beginning of the process of electric arc welding in carbon dioxide, conditions are created under which ozone is intensively formed in the welding arc and the formation of ozone in the air increases. The created in the welding arc ozone passes into the gaseous component of the welding aerosol. Intensive ozone release at the beginning of MAG welding, must be considered in the manufacture of structures with a significant number of short welds, as well as when the products are welded, pulsed arc welding in a protective atmosphere with carbon dioxide additives in the design of ventilation.

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