PHYSICOCHEMICAL INTERACTION OF GAS AND LIQUID PHASES
IN PLASMA WELDING

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It is shown that during plasma fusion of the filler wire particle recombination kinetics affect gas composition at the interphase surface, and the content of thermally dissociated particles, both atoms and ions.

When a metal is melted by a plasma arc physicochemical interactions at the metal-gas interphase boundary are intensified. Oxidation of alloying elements intensifies [1], and the gas concentration in the liquid metal increases [2]. Calculations show that the thermodynamic probability of physicochemical interaction on the interphase boundary depends on the composition of the gas phase. Thus, saturation of the metal by gas encourages dissociation and ionization [3].

The goal of the present study is to investigate the kinetics of the change in gas composition on such an interphase boundary.

The degree of gas dissociation and ionization is determined by its temperature and pressure. At temperatures characteristic of the welding arc (11,000-14,000 K) nitrogen is completely dissociated and ionized to a significant degree (Table 1). When metal is melted by the arc (primarily the filler rod) the gas temperature at the interphase boundary decreases significantly due to the intense heat exchange. However, because of inertia of recombination processes, the high velocity of the gas flow, and the small dimensions of the interphase boundary, it can be expected that the gas composition at the metal surface will not be in equilibrium. In a number of cases Damkeller's criterion has been used to estimate transient processes at the interphase boundary, although the results obtained have been contradictory. While [5] indicates that the gas composition corresponds to the temperature of the interphase surface, the data of [6] indicate that the gas phase composition at the surface does not reach equilibrium.

Using the molecular kinetics equations [7] we can evaluate the inertia of the gas recombination processes upon temperature decrease at the interphase surface. We will consider the kinetics of atomic recombination using the example of nitrogen:

$$N^+ + e \rightleftarrows N,$$

$$N + N \rightleftarrows N_2.$$
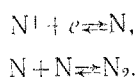
The rate of the recombination reaction can be expressed by a second-order kinetic equation

$$dc/dt = -kc_0^2.$$

TABLE 1. Degree of Dissociation and Ionization of Nitrogen vs Temperature for $P = 1.013 \cdot 10^5$ Pa [4]

T, K	2000	4000	6000	8000
α'	0	0,04	0,84	1,0
T, K	5000	8000	11000	14000
α''	0	0	0,09	0,51

Considering that $c_0 = n_0/N_A$, we obtain

$$\tau_r = \frac{(\alpha_L - \alpha_f)N_A}{kn_r(1 - \alpha_L)(1 - \alpha_f)}.$$

Here dc/dt is the molecular or atomic recombination rate, mole/sec; k is the rate constant of the recombination reaction, $m^3/(mole \cdot sec)$; c_0 and c are the initial and current concentrations of interacting particles in the gas phase, mole/m^3; τ_r is the recombination time, at which the degree of ionization or dissociation has changed from α_l to α_f, sec; N_A is Avogadro's number, 1/mole; n_r is the concentration of particles which interact upon recombination; $k = k_0 P$, where k_0 is a constant dependent on temperature and gas properties, $m^3/(mole \cdot sec)$; P is the probability of active collision of particles (upon which recombination occurs); $k_0 = NN_A/n^2$, where N is the specific particle collision rate, $1/(m^3 \cdot sec)$; n is the total concentration of all particles, $1/m^3$.

For recombination of atoms and equal concentrations of ions and electrons

$$N = 2f_s Q_{e-i} n_e^2 \sqrt{\frac{2KT}{\pi m_e}}.$$

For recombination of identical atoms into molecules

$$N = 2f_s Q_{a-a} n_a^2 \sqrt{\frac{KT}{\pi m_a}},$$

where f_s is a steric coefficient which considers spatial orientation of the particles (for spherical particles $f_s = 1$); Q_{e-i} and Q_{a-a} are electron—ion and atom—atom collision sections, m^2; K is Boltzmann's constant, J/K; m_e and m_a are the mass of the electron and an atom, kg; n_e and n_a are the electron and atom concentrations, $1/m^3$.

If we do not consider multiple ionization, then $n_e = n_i$. Then the electron and nitrogen atom concentrations are determined by the degree of dissociation α' and ionization α'':

$$n_e = \frac{2\alpha'\alpha'' N_L P'}{(1 + \alpha' + 2\alpha'\alpha'')T}; \quad n_a = \frac{2\alpha'(1 - \alpha'')N_L P'}{(1 + \alpha' + 2\alpha'\alpha'')T'},$$

where N_L is Loschmidt's number, $1/m^3$; n_i is the ion concentration, $1/m^3$,

$$P' = P/P_0; \quad T' = T/T_0,$$

where $P_0 = 1.013 \cdot 110^5$ Pa, $T_0 = 273.15$ K.

In calculating the rate constant for molecule recombination the particle collision section used is the gas kinetic section [8]. In calculating the rate constant for atom recombination to determine the electron—ion attachment section, dependent on temperature and type of gas, the expression of [4] was used:

$$Q_{e-i} = \frac{0.567 z^2 e^4 c^4 \mu_0^2}{16\pi^2 \gamma_E (KT)^2}; \quad \ln\frac{4\pi KT}{ze^2 c^2 \mu_0 n_i^{1/2}}; \quad \gamma_E = 3\gamma_T/\alpha; \quad \alpha = \left(\frac{\partial \ln D}{\partial \ln T}\right)_p,$$

where z is the effective charge of the ion; e is the charge of the electron, C; c is the speed of light, m/sec; μ_0 is the magnetic constant, $(kg \cdot m)/(A^2 \cdot sec^2)$; γ_E and γ_T are dimensionless coefficients characterizing the thermodiffusion properties of the plasma; D is the charged particle mutual diffusion coefficient, m^2/sec.

The following values were used for the constants in the calculations: $N_A = 6.022 \cdot 10^{23}$ 1/mole, $K = 1.381 \cdot 10^{-23}$ J/K, $N_L = 2.687 \cdot 10^{25}$ $1/m^3$, $e = 1.602 \cdot 10^{-19}$ C, $\mu_0 = 4\pi \cdot 10^{-7}$ $(kg \cdot m)/(A^2 \cdot sec^2)$.

The quantities z and γ_E for a nitrogen plasma were calculated as functions of temperature in [4]. For atomic recombination electron attachment to the ion occurs if $E_k \leq E_i$, where E_k is the kinetic energy of the moving electron, J; E_i is the atomic ionization energy, J.

For nitrogen $E_i = 2.33 \cdot 10^{-18}$ J, and the mean electron kinetic energy $E_{k.m}$ for the temperature range 5000-15,000 K comprises $(0.07-0.21) \cdot 10^{-18}$ J. Since $E_i \gg E_{k.m}$, the probability of atomic recombination upon collision of an ion and electron is close to unity. Therefore, the calculations assumed $k = k_0$.

TABLE 2. Initial Data and Results of Nitrogen Atom Recombination Rate Calculations

T, K	$Q_{i-e} \cdot 10^{18}$, m²	$n_e \cdot 10^{-23}$, 1/m³	$n \cdot 10^{-23}$, 1/m³	α'	α''	N, $\frac{1}{\text{m}^3 \cdot \text{sec}}$	k, m³/mol·sec	τ, sec
14000—13000	0,379—0,456	169—130	5,24—5,64	1,0	0,48—0,3	$6,8 \cdot 10^{35}$	$1,38 \cdot 10^{12}$	$3,68 \cdot 10^{-12}$
13000—12000	0,456—0,629	130—80	5,64—6,12	1,0	0,3—0,15	$4,13 \cdot 10^{35}$	$7,19 \cdot 10^{11}$	$2,66 \cdot 10^{-11}$
12000—11000	0,629—0,953	80—40	6,12—6,65	1,0	0,15—0,063	$1,89 \cdot 10^{35}$	$2,79 \cdot 10^{11}$	$3,31 \cdot 10^{-10}$
11000—10000	0,953—1,82	40—8,5	6,65—7,32	1,0	0,063—0,124	$5,21 \cdot 10^{34}$	$6,42 \cdot 10^{10}$	$9,96 \cdot 10^{-9}$
10000—9000	1,82—2,86	8,5—3,14	7,32—8,07	1,0—0,95	0,024—0,004	$4,8 \cdot 10^{33}$	$4,88 \cdot 10^{9}$	$4,4 \cdot 10^{-6}$
9000—8000	2,86—4,12	3,14—0,42	8,07—9,16	0,95—0,83	0,004—0,0005	$6,3 \cdot 10^{32}$	$5,2 \cdot 10^{8}$	$1,15 \cdot 10^{-3}$

TABLE 3. Initial Data and Results of Nitrogen Molecule Recombination Rate Calculations ($Q_{a-a} = 3.9 \cdot 10^{-20}$ m²)

T, K	$n_a \cdot 10^{-23}$, 1/m³	$n \cdot 10^{-23}$, 1/m³	α'	α''	N, $\frac{1}{\text{m}^3 \cdot \text{sec}}$	k, $\frac{\text{m}^3}{\text{mol·sec}}$	τ, sec
9000—8000	7,81—8,33	8,07—9,18	0,95—0,83	0,004—0,0005	$9,12 \cdot 10^{31}$	$7,38 \cdot 10^{7}$	$1,55 \cdot 10^{-9}$
8000—7000	8,33—6,1	9,18—10,49	0,83—0,41	0	$6,84 \cdot 10^{31}$	$4,27 \cdot 10^{7}$	$2,41 \cdot 10^{-8}$
7000—6000	6,1—1,96	10,49—12,24	0,41—0,087	0	$1,98 \cdot 10^{31}$	$9,22 \cdot 10^{6}$	$1,47 \cdot 10^{-6}$
6000—5000	1,96—0,52	12,24—14,62	0,087—0,018	0	$1,73 \cdot 10^{30}$	$5,76 \cdot 10^{5}$	$3,71 \cdot 10^{-4}$
5000—4000	0,52—0,14	14,62—18,28	0,018—0,004	0	$1,1 \cdot 10^{29}$	$2,46 \cdot 10^{4}$	$1,44 \cdot 10^{-1}$

According to the data of [9], the process of nitrogen molecule recombination has no barrier ($E_{act} = 0$), i.e., for each atomic collision a molecule is formed ($P = 1 \rightarrow k = k_0$).

Calculations were then performed of the duration of the process of nitrogen atom and molecule recombination at the interphase surface, produced by the decrease in gas temperature. The calculations did not consider inertia of the gas temperature change; it was assumed that the temperature of the gas in contact with the metal surface instantaneously changed from 14,000 to 4000 K (with the gas density changing in a similar inertia-free manner). The reaction rate depends on temperature, so to increase accuracy the temperature interval under consideration was divided into individual intervals of 1000 K. In each temperature interval a unique recombination rate constant was used, calculated for mean temperature and particle concentration values.

The calculation results showed that recombination of nitrogen atoms occurs significantly more rapidly than molecule recombination (see Tables 2, 3). This is related to the fact that for nitrogen the electron—ion attachment section is 3-4 orders of magnitude greater than the gas kinetic section of the atom.

The results of the calculations performed agree well with data in the literature. Experimental values of nitrogen molecule recombination rate constants were presented in [9] for a reaction occurring within a shock wave.

Thus, in the temperature interval 8000-9000 K the experimental value of the constant k_{exp} comprised $3.51 \cdot 10^7$-$63.56 \cdot 10^7$ m^3/(mole·sec). It was determined experimentally in [19] that the time for residual ionization of the arc column comprised $3 \cdot 10^{-4}$ sec. According to the calculations performed, over such a time period the degree of nitrogen ionization decreases by almost three orders of magnitude ($\alpha'' \leq 0.001$).

In analyzing the physicochemical processes, to consider the nonequilibrium composition of the gas at the interphase boundary a correction ΔT was used, assuming that the gas composition corresponded not to the surface temperature T, but to a higher value $T + \Delta T$. Then with increase in the gas flow velocity and decrease in the dimensions of the interphase boundary the lack of equilibrium in gas composition and thus, the value of the correction ΔT will increase. It was established from an estimate of the chemical activity of the gas phase performed in [11] that for arc welding in carbon dioxide gas with a melting electrode the value of ΔT comprises 300-800 K. For plasma welding the value of ΔT may be significantly higher. In this case due to nonequilibrium of the gas phase at the liquid metal surface the intensity of physicochemical processes increases significantly. In fact, ejection of air by the plasma flow in the arc upon disruption of gas shielding of the weld zone leads to a significant increase in nitrogen concentration in the joint metal: for high-quality protection and a long arc, $c_N = 0.032 \pm 0.005\%$, for low-grade protection and a short arc, $0.055 \pm 0.014\%$, for low-grade protection and a long arc, $0.058 \pm 0.029\%$.*

The material welded in the experiments was 08Kh18N10T steel 20 mm thick, with the filler wire being Sv-08Kh19N10G2B wire 2 mm in diameter. The specimens were welded by a plasma arc in argon with reverse polarity and axial feed of the current-carrying filler wire [12]. Welding parameters were: plasma arc current, 220 A; feed wire current, 280 A; weld rate, 12 m/h; plasma supply flow, 5 liters/min; forming flow, 12 liters/min; protective flow, 30 liters/min.

This welding regime insured "jet" transport of the fused filler metal, with a liquid metal cone $(1.0-1.2) \cdot 10^{-2}$ m high being formed on the end of the filler wire. Considering that in the compressed arc the axial gas flow is greater than in the free state [13-15], and taking that value equal to $(2.5-3.0) \cdot 10^2$ m/sec, we find that the duration of the contact between gas and liquid phases comprises $(3.3-4.8) \cdot 10^{-5}$ sec. This is 5-6 orders of magnitude less than the time for achievement of equilibrium concentration upon saturation of the liquid metal by molecular nitrogen under arcless heating conditions [16]. It can be proposed that the high intensity of filler metal saturation by nitrogen under plasma welding condi-

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*The arc length in the experiments was regulated by adjusting the filler wire voltage (short arc, $U_W = 30$ V, long, $U_W = 35$ V). For high quality protection thermostable fiberglass blinds were installed around the nozzle to prevent admission of air to the weld zone; for the low quality shielding the blinds were removed and drafts within the laboratory introduced nitrogen into the weld zone.
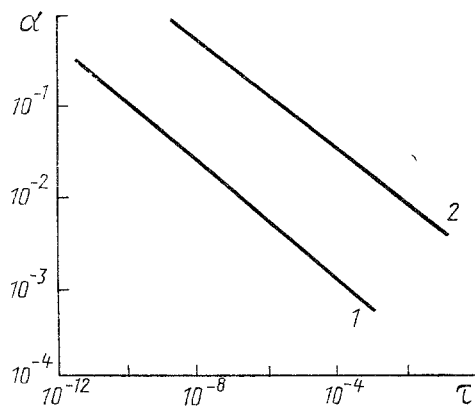
Fig. 1. Kinetics of nitrogen atom (1) and molecule (2) recombination upon gas temperature decrease: $P = 1.013 \cdot 10^5$ Pa; τ, sec.

tions is caused by a significant concentration of nitrogen atoms at the interphase surface. According to [17], the saturation rate of liquid iron by atomic nitrogen is $6.57 \cdot 10^7$ times higher than the molecular rate. In fact, analysis of the data obtained herein (Fig. 1) shows that over the time of $(3.3\text{-}4.8) \cdot 10^{-5}$ sec upon decrease in temperature of the gas phase the degree of ionization of the nitrogen at the liquid metal surface decreases to $(1.51\text{-}1.74) \cdot 10^{-3}$, with the degree of dissociation decreasing to $(3.89\text{-}4.27) \cdot 10^{-2}$. Thus, even at the end of the physicochemical interaction of the gas and liquid phases the nitrogen atom concentration at the interphase boundary remains high.

Conclusions. In analyzing the physicochemical processes which occur upon fusion of a filler metal by a plasma arc, it is necessary to consider nonequilibrium of gas composition at the interphase boundary. The presence at the surface of the drop of dissociated particles significantly intensifies the process of metal saturation by the gas.

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