The dependence of the direction of stratification on the grain size of the metal being saturated can be explained on the basis of data concerning the saturation of monocrystalline molybdenum [1], where it was found that with small thicknesses of the carbide layer the preferred arrangement of the basal plane is parallel to the surface of saturation. With increasing thickness of the layer the orientation of the carbide lattice changes. With saturation of monocrystalline molybdenum to a depth larger than the average size of the grains the growth of carbide phase in each grain can be considered approximately independent, occurring in the same manner as in monocrystalline molybdenum.

Saturation of molybdenum with large grains leads to orientations of the carbide lattice that are determined by the grain size in the direction of the diffusional flow of carbon. In fine-grained molybdenum the development of such orientations is prevented by the small grain size in the direction of the flow of carbon. Because of this, when the orientation of grains in molybdenum corresponds to texture of the (100) type then because of the small grain size the carbide layer will retain the primary orientation in which the basal planes are parallel to the surface of saturation. In this case the perfection of the orientation obtained depends directly on the grain size of the metal being saturated.

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DYNAMICS OF THE PROCESS OF CHANGE IN THE DEGREE
OF DISSOCIATION OF AMMONIA IN NITRIDING FURNACES

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The dissociation of ammonia in nitriding furnaces occurs in two stages — heating of ammonia and dissociation by the chemical reaction

$$100\,NH_3 \rightarrow a\,N + 3a\,H + (100 - a)\,NH_3.$$

(1)

Both stages occur with intensive mixing of the gas.

The extent of dissociation α by reaction (1) depends mainly on the temperature of the process and the ammonia input. Since the temperature depends on the properties of the metal being nitrided, the dissociation of ammonia is controlled in practice by the input [1, 2]. The character of the change in the dissociation of ammonia with time is of interest in this case, i.e., the dynamic characteristic of the furnace. This work was undertaken to determine this characteristic.

Dynamics of Heat Transfer. To determine the heating rate of ammonia one can use the heat balance equation [3], which for a furnace as an ideal mixer [4, 5] in time period dt takes the form

$$h_1 Q_1\,\theta_1\,dt + AF\,(\theta_f - \theta_2)\,dt - h_2 Q_2\,\theta_2\,dt = h_2 Vd\,\theta_2,$$

(2)

where h_1, h_2, Q_1, and Q_2 are the specific heats and the ammonia input and the products of its partial dissociation; θ_1 and θ_2 are the initial and final temperatures of the ammonia and its dissociation products; θ_f is the furnace temperature; V is the volume of the furnace; A is the coefficient of heat transfer from the walls of the retort (muffle) and the surface of the load to the gas; F is the total contact surface of the load and the walls of the retort.

If in first approximation we neglect the change in the volume of the gas due to its dissociation, i.e., $Q_1 = Q_2 = Q$, and take $h_1 = h_2 = h$ for simplicity, we obtain

$$\frac{hV}{hV+AF}\frac{d\theta_2}{dt}+\theta_2=\frac{AF}{hQ+AF}\theta_f+\frac{h\theta_1}{hQ+AF}Q.$$ (3)

Here

$$\frac{hV}{hQ+AF}=T_1$$

is the constant time of the heating of the gas entering the furnace;

$$\frac{AF}{hQ+AF}=k_1$$

is the intermediary coefficient of heating in terms of furnace temperature;

$$\frac{h\theta_1}{hQ+AF}=k_2$$

is the intermediary coefficient in terms of the ammonia input.

Using these notations, we have

$$T_1\frac{d\theta_2}{dt}+\theta_2=k_1\theta_f+k_2Q.$$ (3a)

The coefficient of heat transfer

$$A=A_k+A_r,$$ (4)

where A_k is the convection term; A_r is the coefficient of heat transfer by radiation.

For nitriding at 520°C, $A_k \approx 7$ kcal/$m^2 \cdot$ h $\cdot$ deg C.

At the same time, the ammonia−nitrogen−hydrogen mixture is fairly black [6], the blackness reaching a value of $\varepsilon = 0.5$ during nitriding. As the result, the total value of A is 33.5 kcal/$m^2 \cdot$ h $\cdot$ deg C.

Calculations with these values of A for a furnace of the Ts−75 type gives $T_1 = 2.68$ sec.

With an average time that the gas remains in the furnace $t_{av} = V/Q = 600$ sec the process of heating the gas can be regarded as practically inertialess.

Dynamics of Dissociation. Taking the furnace as an ideal mixer [3−5] and using the notations given above, we obtain the following equation for the material balance of ammonia in the furnace:

$$C_1Q_1dt-\left(C_2Q_2\,dt-VdC_2^*\right)=VdC_2,$$ (5)

where C_1 and C_2 are the concentrations of ammonia in the incoming and outgoing gases expressed in volume percent ($C_1 = 1$ for nitriding with undiluted ammonia); dC_2^* is the change in the concentration of ammonia due to partial chemical dissociation by reaction (1); dC_2 is the total change in the concentration of ammonia as the result of partial chemical dissociation and mechanical carryout from the exhaust gases.

According to the law of mass action

$$\frac{dC_2^*}{dt}=-KC_2,$$ (6)

where K is the constant of the rate of the chemical reaction.

Then Eq. (5) takes the form

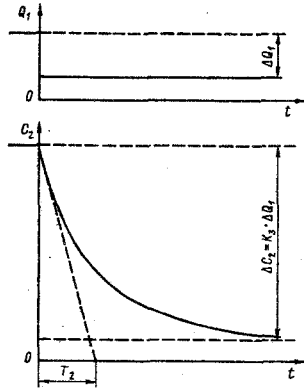$$C_1Q_1dt-(C_2Q_2dt+KVC_2dt)=VdC_2.$$

Fig. 1. Schematic variation of the ammonia concentration in the outgoing gas in relation to its input at different temperatures.

Hence

$$V \frac{dC_2}{dt} + (Q_2 + kV) C_2 = C_1 Q_1,$$

or

$$\frac{V}{Q_2 + KV} \frac{dC_2}{dt} + C_2 = \frac{C_1}{Q_2 + KV} Q_1. \tag{7}$$

Relationships were established previously [2] by which

$$Q_2 = Q_1 (1 + x), \tag{8}$$

$$C_2 = \frac{1 - x}{1 + x}, \tag{9}$$

where $x = \alpha/100$.

Thus, Eq. (7) transforms to

$$\frac{V}{\dfrac{2Q_1}{1 + C_2} + KV} \frac{dC_2}{dt} + C_2 = \frac{C_1}{\dfrac{2Q_1}{1 + C_2} + KV} Q_1. \tag{10}$$

In this case

$$\frac{V}{\dfrac{2Q_1}{1 + C_2} + KV} = T_2$$

is the constant time of the process of dissociation of ammonia;

$$\frac{C_1}{\dfrac{2Q_1}{1 + C_2} + KV} = K_3$$

is the intermediary coefficient of the dissociation process in terms of the gas input.

In these notations we have (see Fig. 1)

$$T_2 \frac{dC_2}{dt} + C_2 = K_3 Q_1. \tag{10a}$$

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Furnace type	Temp., °C	Parts nitrided	V, m³	Q_1, m³/h	C_2	K, 1/h	T_2, min
PA-32	530	Plunger sleeve of a force pump	0,16	1,5	0,79	1,39	5,1 (5,4)
	560		0,16	1,5	0,65	3,06	4,15 (3,5)
TS-75	500	Valves of internal combustion engine	0,43	4,89	0,92	0,52	4,8 (5,0)
	528		0,43	•	0,86	0,99	4,6 (5,0)
	750		0,43	•	0,085	112	0,46 (Not det.)

Note. 1) Experimental data given in parentheses. 2) $C_1 = 1$, K and T_2 are given for corresponding values of Q_1.

It should be noted that differential equations (10), (10a) are nonlinear, since T_2 and K_3 vary with the quantity of nitriding gas entering the furnace (Q_1) and the concentration of ammonia in the exhaust gas (C_2). The principal complication is to determine K of the chemical reaction of the dissociation of ammonia at a given temperature, since the surface of the load of parts in the furnace has a strong catalytic effect on the rate of reaction (1).

The values of K can be determined from experimental static characteristics expressed as the variation of the steady degree of dissociation of ammonia with the ammonia input $x = f(Q_1)$. These characteristics are well known from nitriding practice for any conditions of the process. For steady conditions we have from Eq. (10):

$$C_2 = \frac{C_1 Q_1}{\dfrac{2Q_1}{1 + C_2} + KV}$$

(10b)

or

$$K = \frac{Q_1}{V}(1 + x)\left(\frac{C_1}{1 - x} - 1\right).$$

(10c)

With known values of C_1, Q_1, V, and x it is easy to determine the value of K and from this value calculate the constant time T_2. Experimental verification showed satisfactory agreement between the calculated and experimental data (see Table 1).

The slight difference between the calculated values of T_2 and the experimental values can be explained by the experimental error and also the deviation of the process from the model of ideal mixing.

CONCLUSIONS

1. The process of heating ammonia in the furnace for nitriding is practically inertialess.

2. Analytical expressions for the dynamic characteristic of the dissociation of ammonia during nitriding were obtained in relation to its input in the form of a nonlinear differential equation of the first kind.

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