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THERMODYNAMIC ANALYSIS OF THE GAS MEDIUM IN THE FORMATION OF DIFFUSION COATINGS USING COMPOSITE SATURATING CHARGES

Review of the main processes of formation of diffuse coatings doped with molybdenum, vanadium and tungsten. The basic features of the formation of diffusion layers during chemical-thermal treatment are considered.: When the SHS is tested, the container is heated to temperatures of 1173-1330 K. Within 1-2 hours, a diffusion coating is formed due to the saturation of the surface of structural materials with atoms of saturating elements - Cr, Al, V, Ti, B, W, Mo. As saturating elements, the defects of these elements and the chemical compounds of these elements were used, and to determine the possibility of using specific substances, chemical reactions were considered that can occur in the temperature range of diffusion saturation using SOS. It should be noted that the metallothermal Reduced oxide, which is used in the synthesis of powder media for CHT, is very fast. When obtaining diffuse layers using the composition of saturating the medium, a gas phase is formed, containing spolo-I, I_2, I_3, H, H_2, H_3, Cl_2, Cl_3 with chemical elements. With an increase in temperature, an increase in the amount of halides is observed. This confirms the possibility of transferring alloying elements for the formation of diffusion coatings. Also, the amount of products in the gaseous phase increases and condensed products are released. It is characteristic that in the temperature range of 700-1500 K, the decomposition of reaction products occurs during CHT, which is confirmed by the production of decomposition substances and a sharp increase in the number of gas moles.

Key words: diffusion, composite saturating media, thermo-dynamics, coatings, phase

Chemical heat treatment (CHT) of metals and alloys, consisting in saturation with various elements (metals or non-metals) from the external environment in order to change the chemical and phase composition, structure and properties of the surface layers of the product, is a high-temperature process that has a complex multistage nature [1]. It is based on such complex physicochemical phenomena as heterogeneous chemical reactions and phase transformations, heat transfer, micro- and macroscopic mass transfer, which occur in solid, liquid and gaseous media (both in a saturating medium and in a growing solid coating).

The formation of a diffusion layer during CHT has the following characteristic features:

1) the final product formed on the surface of the saturable product (solid solution with an increased content of the saturating element or refractory compounds - carbides, nitrides, intermetalides, silicides etc.) is in a solid state in a wide range of process temperatures;

2) the initial or intermediate substances can be in a solid, liquid and gaseous state and undergo phase transitions;

3) heat and mass transfer in different phases have a significant effect on the kinetics and mechanism of heterogeneous reactions;

4) joint heat and mass transfer and heterogeneous reactions directly affect the structure and composition of the resulting product and, ultimately, the properties of the surface layers of the product;

5) these phenomena are manifested in different ways in various specific systems and technological processes of CHT.

Classification of CHT processes according to saturation methods, the nature of the saturating element, etc. is given in the literature [2-5]. According to the modes of implementation, various methods of chemotherapy can be conditionally divided into two groups:

a) traditional slow-flowing (furnace) processes;

b) intensive (fast-flowing) processes based on the use of fast heating, for example, high-frequency currents (HFC) or SHS processes, which, along with fast heat release and high temperature, are characterized by a short completion time of chemical reactions and phase transformations in a saturating mixture.

For the processes of metallothermal processes [6,7] an important characteristic is the adiabatic combustion temperature T_{ad} and the equilibrium composition of the reacting system at T_{ad}. Usually thermodynamic calculation of the quantity T_{ad} is based on a simple assumption [8]: the reaction proceeds completely (with a conversion of 100%) under adiabatic conditions; heat of reaction at initial temperature T_0 ($T_0 \geq 298$ K) spent on warming up to T_{ad} and possible melting of products. The quantity T_{ad} is determined from the enthalpy balance condition $\Delta H_{T_0}(r) = \Delta H_{T_{ad}}(pr)$:

$$\Delta H_{T_0}(r) = \sum_{\mathrm{r}} \left[\Delta H^0_{298}(r) + \int_{298}^{T_0} c_p(r)\mathrm{d}T \right] = \Delta H_{T_{ad}}(pr) =$$
$$= \sum_{pr} [\Delta H^0_{298}(pr) + (1 - x_m) \int_{298}^{T_{ad}} c_p(pr_s)\mathrm{d}T + \qquad (1)$$
$$+ x_m (\int_{298}^{T_m} c_p(pr_m)\mathrm{d}T + \Delta H_m(pr_m) + \int_{T_m}^{T_{ad}} c_p(pr_m)\mathrm{d}T)],$$

where ΔH^0_{298} – the standard enthalpy of formation of a substance; ΔH_{m} and T_m – heat and melting temperature; c_p – heat capacity; x_m – molar fraction of the melt in the reaction products; r means reagents, and pr – reaction products; subscripts s and m refer to solids (solid) and melt (melt), respectively.

Formula (1) was used to calculate the value of Tad in a large number of metallothermal systems in the course of one reaction [8–10].

When vanadium using a composite saturating medium, a gas phase is formed, which contains compounds H, H_2, OH, Cl, Cl_2, Cl_3, Cl_6, $2Cl$ with chemical elements (Fig. 1).

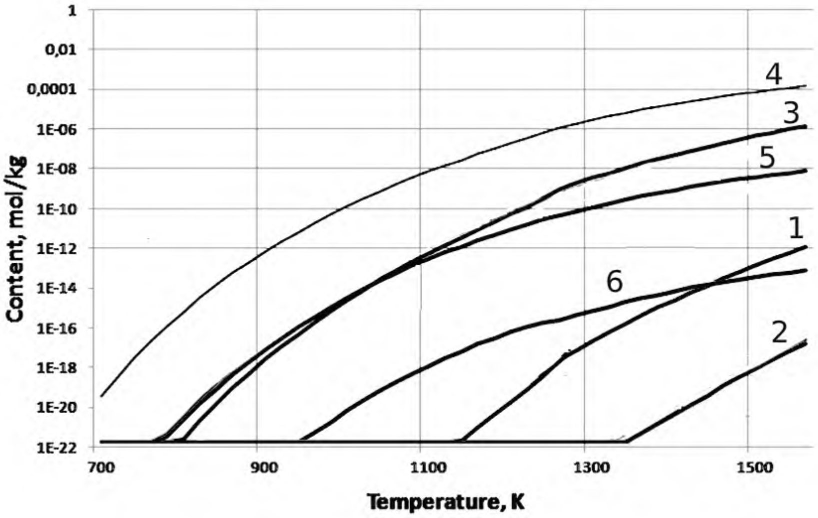

Figure 1 – The content of the gaseous vanadium compound in a container with a composite saturating medium for the system: 18% EC + 22% V + 55% Al_2O_3 + 3% NH_4Cl + 2% NH_4I:
1 - V, 2 - VO, 3 - VCl, 4 - VCl_2, 5 - VCl_3, 6 - VCl_4

Gaseous products interacting with elements of the powder system (V, Cr) и go into the gas phase (appear AlH, AlH_2, $AlOH$, $AlCl_2$, $AlCl_3$, Al_2Cl_6, $AlHCl$, AlH_2Cl, $AlOHCl_2$, CrO, CrH, $CrOH$, $CrCl$, $CrCl_2$, $CrCl_3$, $CrOCl$, $CrOCl_2$,VO, VCl, VCl_2, VCl_3, VCl_4).

When molybdenum is used with a composite saturating medium, a gas phase is formed that contains compounds H, H_2, H_3, Cl, Cl_2, Cl_3, Cl_6, I, I_2, I_3 with chemical elements (Fig. 2).

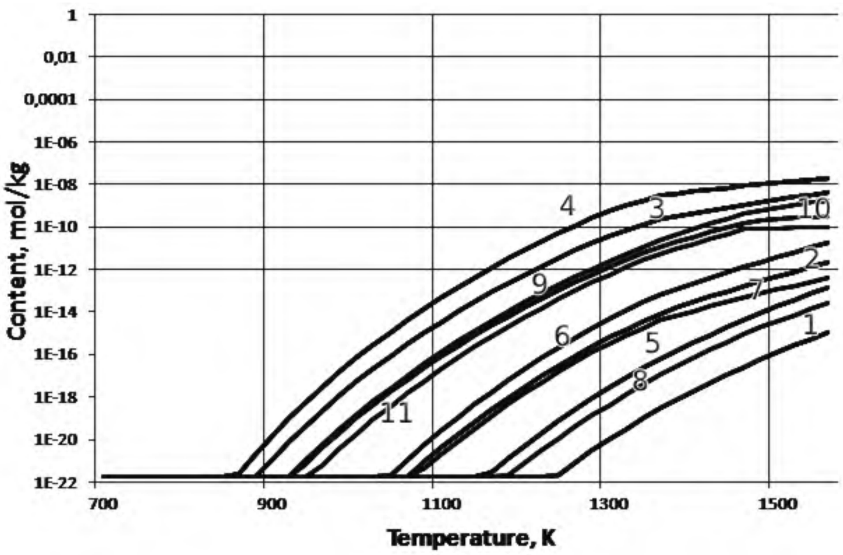

Figure 2 – Content of a gaseous molybdenum compound in a container with a composite saturating medium for the system:16% EC + 32% $FeMo$ + 46% Al_2O_3 + 2% I_2+ 4% NH_4Cl:
1 - $MoCl$, 2 - $MoCl_2$, 3 - $MoCl_3$, 4 - $MoCl_4$, 5 - $MoOCl$, 6 - $MoOCl_2$, 7 - $MoOCl_3$,
8 - MoI, 9 - MoI_2, 10 - MoI_3, 11 - MoI_4

Gaseous products interacting with elements of the powder system (Al, Mo, Cr) and transferred to the gas phase (appear CrH, $CrOH$, $CrCl$, $CrCl_2$, $CrCl_3$, $CrOH$, $CrOCl_2$, CrI, CrI_2, CrI_3, $MoCl$, $MoCl_2$, $MoCl_3$, $MoCl_4$, $MoOCl$, $MoOCl_2$, MoI, MoI_2, MoI_3, MoI_4).

When tungstening using a composite saturating medium, a gas phase is formed that contains compounds F, F_2, F_3, F_4, F_6, I, I_2, I_3, I_4 with chemical elements. With increasing temperature, an increase in the amount of halides is observed (Fig. 3).

Gaseous products interacting with elements of the powder system (Al, W, Cr) and transferred to the gas phase (appear AlF, AlF_2, AlF_3, Al_2F_6, $AlOF$, $AlOF_2$, AlI, AlI_2, AlI_3, CrF, CrF_2, CrF_3, CrF_4, $CrOF$, CrO_2F, $CrOF_2$, CrO_2F_2, CrI, CrI_2, CrI_3, WF_2, WF_3, WF_4, WOF, WO_2F, WOF_2, WOF_3, WI_2, WI_3, WI_4).

At temperatures of 700 K, part of the condensed phase practically does not change. This fact allows us to assume that in the temperature range of 700…1600 K, a reaction occurs with the release of a condensed phase, but without a change in the number of moles, which is typical for decomposition reactions, exchange of material, that is, in fact, chemical transport of elements takes place [11]. In the temperature range of 700…1600 K there are: condensed compounds: Al_2O_3(c), AlF_3(c), Cr_2O_3(c), W(c), WO_2(c), Al_2O_3(c), AlN(c), Fe(c), Cr(c), $CrCl_2$(c), CrI_2(c), Mo(c), Cr_2N(c), Al(c), Al_2O_3(c), AlN(c), V(c).

As a result of the thermodynamic calculation of the equilibrium composition of the reaction products, we can propose the following kinetic scheme of chemical transformations in the studied systems. The following are examples of the chemical reactions in vanadium:

1. Exothermic reaction (ER):

$$Cr_2O_3 + 2Al \Rightarrow 2Cr + Al_2O_3 \ . \tag{2}$$

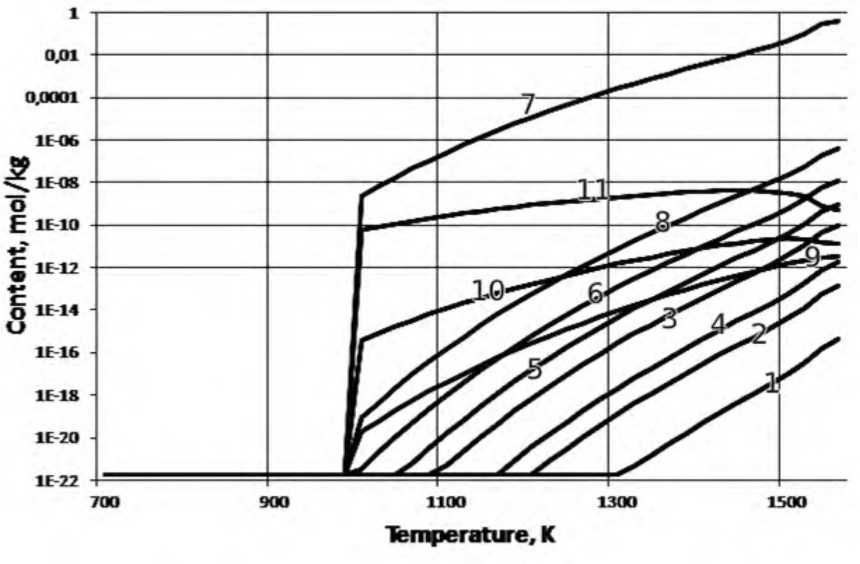

Figure 3 – The content of a gaseous tungsten compound in a container with a composite saturating medium for the system: 20% EC + 35% WO_3 + 39% Al_2O_3 + 2% I_2+ 4% AlF_3:

2. Decay reaction of a gas transport agent:

$$NH_4Cl \Rightarrow NH_3 + HCl\,; \tag{3}$$

$$2NH_3 \Rightarrow N_2 + 3H_2\ . \tag{4}$$

3. Chemical transport reaction:

$$Cr + J_2 \Rightarrow CrI_2(г)\ ; \tag{5}$$

$$Cr + Cl_2 \Rightarrow CrCl_2(г)\ ; \tag{6}$$

$$2Cr + 3Cl_2 = 2CrCl_3(г)\,; \tag{7}$$

$$2AlClO + 2H + N + 4HCl \Rightarrow 2AlCl_3 + N + H_2O\ ; \tag{8}$$

$$AlClO + 2H \Rightarrow AlCl_3 + H_2O\ ; \tag{9}$$

$$3AlClO \Rightarrow 2Al + AlCl_3\ ; \tag{10}$$

$$2AlCl_3 + 3H \Rightarrow Al + AlCl_3 + 3HCl\ ; \tag{11}$$

$$4Al + 2V_2O_5 + 3O_2 \Rightarrow Al_2O_3 + 2Al(VO_3)_3\ ; \tag{12}$$

$$2Al(VO_3)_3 \Rightarrow Al_2O_3 + 3V_2O_5\ ; \tag{13}$$

$$3V_2O_5 \Rightarrow V_6O_{14} + O\ ; \tag{14}$$

$$V_6O_{14} \Rightarrow 6VO_2 + 2O\ ; \tag{15}$$

$$V_2O_5 + 2Al \Rightarrow 2VO + Al_2O_3\ ; \tag{16}$$

$$V_2O_5 + Al_2O_3 \Rightarrow 2AlVO_4\ ; \tag{17}$$

$$V_2O_3 + AlO \Rightarrow AlV_2O_4\ ; \tag{18}$$

$$3Al + V \Rightarrow Al_3V\ ; \tag{19}$$

$$8Al + 5V \Rightarrow Al_8V_5 \;; \tag{20}$$

$$Al + H \Rightarrow AlH \;; \tag{21}$$

$$Al + 2H \Rightarrow AlH_2 \;; \tag{22}$$

$$Al + 3H \Rightarrow AlH_3 \;; \tag{23}$$

$$Al + Cl \Rightarrow AlCl \;; \tag{24}$$

$$Al + 2Cl \Rightarrow AlCl_2 \;. \tag{25}$$

4. Exchange reactions with structural material:

$$VCl_4 + 4/3Fe \Rightarrow V + 4/3FeCl_3 \;; \tag{26}$$

$$VCl_4 + 2Fe \Rightarrow V + 2FeCl_2 \;; \tag{27}$$

$$VCl_4 + 4/3Fe + C \Rightarrow VC + 4/3FeCl_3 \;; \tag{28}$$

$$VCl_4 + 2Fe + C \Rightarrow VC + 2FeCl_2 \;; \tag{29}$$

$$2VCl + 8/3Fe + C \Rightarrow V_2C + 8/3FeCl_3 \;; \tag{30}$$

$$2VCl_4 + 2Fe + C \Rightarrow V_2C + 4FeCl_2 \;; \tag{31}$$

$$VCl_4 + Fe_3C \Rightarrow VC + 4/3FeCl_2 + 5/3Fe \;; \tag{32}$$

$$VCl_4 + Fe_3C \Rightarrow VC + 2FeCl_2 + Fe \;; \tag{33}$$

$$VCl_4 + Fe_3C \Rightarrow V_2C + 8/3FeCl_3 + 1/3Fe \;; \tag{34}$$

$$2VCl_4 + Fe_3C + Fe \Rightarrow V_2C + 4FeCl_2 \;; \tag{35}$$

$$V_2O_5 + 2H_2 \Rightarrow V_2O_3 + 2H_2O \;; \tag{36}$$

$$2NH_4VO_3 + 2H_2 \Rightarrow V_2O_3 + 2H_2O \;; \tag{37}$$

$$2NH_4VO_3 \Rightarrow V_2O_3 + 2NH_3 + H_2O \;; \tag{38}$$

$$FeO \cdot V_2O_3 + 41/2\,CL_2 \Rightarrow 2VOCl_3 + FeCl_3 + O_2 \;; \tag{39}$$

$$Cr + 2C \Rightarrow CrC_2 \;; \tag{40}$$

$$7Cr + 3C \Rightarrow Cr_7C_{3_2} \;; \tag{41}$$

$$2V + 5/2O_2 \Rightarrow V_2O_5 \;. \tag{42}$$

Approbation and conclusions. Calculations are carried out and their analysis allows obtaining information about the mechanism of obtaining diffusion coatings using composite saturating media, and the use of software analysis - to perform an objective assessment of the composition of powder composite mixtures to regulate this process.

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