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HEAT AND MASS TRANSFER UNDER CONDITIONS OF HYDROGEN EVOLUTION IN REACTIONS OF AMORPHOUS-CRYSTALLINE ALLOYS WITH WATER

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We investigate the displacement of hydrogen from water by means of silicon-and-aluminum-based alloys obtained from the inorganic portion of coal. We present a variant of improvement of the process by a change in the structure of the alloys. Attention is mostly paid to external heat transfer between the alloys and aqueous solutions of alkali.

Production of hydrogen under autonomous conditions is based on reactions of interaction between alloys and water. By their intensity, the reactions under consideration occupy an intermediate position between the processes of combustion of metals on the one hand and corrosion of alloys on the other. While burning of metal particles takes fractions of a second and corrosion may take several years, reactions of alloys with aqueous solutions of alkalis proceed in a period of several minutes. In the latter case, a newly formed oxide film offers the main resistance to the transport of heat and mass of the substance. So, compared to a reaction of activated aluminum with water, slight damage to the layer of oxides on the surface of crystalline ferrosilicoaluminum (FSA) decreases the rate of hydrogen evolution by two orders of magnitude [1].

Preliminary hardening of an alloy during pouring into molds at 1600–1700°C ensures a considerable increase in the rate of the reaction [2]. The addition of sodium, potassium, calcium, copper, and boron into an alloy evidently favors the formation of numerous microgalvanopairs [3, 4] in it and also intensifies the process.

We investigated the effect of superfast hardening (spinning) on the reactivity of amorphous-crystalline alloys of the Fe–Si–Al system [5]. According to the technology of batching adopted, a jet of melted FSA was delivered onto a rotating copper disk. On coming in contact with the disk, the jet was cooled, and a solidified semiamorphous strip of thickness 18–45 μm and width 1–3 mm was released from the disk. The decrease in the temperature of the liquid alloy was within the limits of 10^6 K/sec [6].

For hardening we used FSA11 alloy obtained from wastes of coal preparation. Its composition (wt.%) was: 61.9 silicon; 11.13 aluminum; 18.15 iron, 4 calcium; 0.68 titanium; 0.15 magnesium; 0.059 phosphorus; 0.04 sulfur.

On the basis of FSA11 alloy we prepared compositions closely coinciding with the invariant points of the Fe-Si-Al system state diagram [7]. In this case, pure aluminum and iron were added to the initial alloy powder, and then the mixture was melted and subjected to spinning.

Basic investigations of the reactivity of the alloys were performed in a kinetic reactor according to the procedure described in [8]. The maximum intensity of the process is noted at the invariant point P_5 of the state diagram (composition, wt.%: 57 Al; 24.5 Fe; 16.8 Si). In this case the rate of hydrogen evolution amounts to $15 \cdot 10^{-5}$ $m^3/(m^2 \cdot sec)$. The mean rate of hydrogen evolution for the amorphous-crystalline FSA11 alloy is $12.5 \cdot 10^{-5}$ $m^3/(m^2 \cdot sec)$. Limitation of the reaction by heat transfer was studied on individual samples of the alloy by the procedure presented previously in [1].

We also investigated heat transfer at a medium temperature of 60–100°C in an open vessel and at 80–120°C in a closed reactor. The pressure in the reactor did not exceed 1.1 MPa.

The experiments showed that the temperature of the outer surface of the hydroxide layer in places of gas formation was 0.6–2.4°C higher than the temperature of the liquid circulating near the sample. The temperature of the sample center was 2.4–6.2°C higher than that of the medium. When the reaction front approached the

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thermocouple at the sample center, we observed an abrupt increase in the temperature by 5–9°C in the open vessel and by 37–50°C in the closed reactor. Upon passage of the jump, the thermocouple showed the temperature of the medium. The temperature jump took 15–50 sec.

The inertia of the system was estimated in the following way. We immersed a thermocouple with a junction temperature of 20°C in an open vessel with boiling water and began time reckoning. The device recorded an increase in the temperature to 95°C in 5 sec; after 2–4 min a temperature of 99°C was established. When the thermocouple was immersed in a vessel with oil heated to 180°C, the device recorded a temperature of 115°C in 5 sec. After 3 min a temperature of 180°C was established.

The thermal heads measured make it possible to determine the coefficients of heat transfer under conditions of natural circulation. Knowing the rate of gas evolution, it is not difficult to calculate the specific heat flux equivalent to this rate.

Under the investigated conditions, for crystalline FSA11 alloy (fraction 0.1–0.4 mm) at a mean reaction temperature of 97°C and a concentration of alkali of 20% the maximum specific heat flux was $q = 305$ W/m^2. The coefficient of external heat transfer was $\alpha_e = 127$ W/(m$^2 \cdot$K).

For amorphous-crystalline FSA11 alloy (fraction 0.01–0.5 mm) at an alkali concentration of 20% and a mean reaction temperature of 84–112°C we obtained the values $q = 430–1223$ W/m^2 and $\alpha_e = 180–510$ W/(m$^2 \cdot$K).

The maximum specific heat flux was recorded for the FSA composition corresponding to the point P_5 and it was equal to $q = 1600$ W/m^2. In that case $\alpha_e = 667$ W/(m$^2 \cdot$K).

In its intensity, the heat transfer approaches that observed in evaporators with a falling film [8]. The removed heat flux is very small and can be increased by increasing the temperature difference. From this it follows that the external heat transfer does not impose restrictions on the rate of the reaction. Judging from the thermal heads measured, the friable portion of the oxide layer also does not present any appreciable resistance. The earlier conclusion is confirmed that the resistance of a dense oxide layer near a reaction surface is dominant for an amorphous-crystalline alloy too.

As is known, the amorphous (vitreous) state of a portion of the alloy subjected to spinning is characterized by the absence of translational symmetry in the arrangement of the atoms. In the case of superfast cooling of the alloy, the free energy has no time to reach the minimum. The thermodynamic instability is manifested in the formation of stresses in the structure of the randomly arranged atoms. The increase in the temperature during the reaction allows the atoms nearest the reaction zone to occupy their traditional place in the ordered crystal lattice, and then they come into contact with molecules of water. This sequence of translations of the atoms accompanied by rearrangement of their electronic shells favors free separation of the solid reaction products at the moment of formation of hydrogen.

Thus, amorphous-crystalline alloys satisfy two basic requirements imposed on reagents under conditions of autonomous production of hydrogen: not to be oxidized in storage and to exhibit high activity upon increase in temperature. It should be noted that spinning is the simplest and least expensive method of alloy activation.

A procedure for calculating the process of heat transfer in gas formation was developed. The hydrodynamic situation developing in the wall layer can be represented as circulation of a liquid in a multitude of cells near the reaction surface of particles drifting in a flow [9].

For an isobaric-isothermal process the rate of heat and mass transfer in the laminar sublayer within the zone of nucleation is proportional to the change in the chemical potential, and in the turbulent part of the wall layer it is proportional to the decrease in the enthalpy of the expanding flow. In the intervals between events of vapor and gas formation the process is calculated as for ordinary convective heat and mass transfer.

Calculation by the procedure presented gives satisfactory agreement with experimental data.

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