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DETERMINATION OF ACTIVE METAL IN ULTRADISPERSED IRON POWDERS AND TG STUDY OF THEIR OXIDATION

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Abstract

Two oxidation stages of electrolytic ultradispersed iron powder at the temperature range of 90-450°C have been stated. The contribution of increasing mass and evolving heat at the first oxidation stage due to changing Fe^0 into Fe_2O_3 in the total oxidation effect is predominant. The thermal method of active metal determination in electrolytic iron powders has been developed. The coarse-grained reduced iron powder was not oxidized completely just to 900°C because of local sintering of big iron particles as a result of evolving heat at oxidation of high-dispersed iron particles.

Keywords: active metal, high-dispersed iron powder, oxidation, thermogravimetry

Introduction

Ultra-dispersed metals in iron powders have high reactivity. For this reason the development of new effective methods of their protection from corrosion is very important but difficult because there are no sufficient data on kinetics and mechanism of such powders oxidation.

Experimental

Objects under study were high-dispersed iron powders produced in two-layer bath [1] with dendritic particles (anisotropy coefficient of 1:5–1:7), big axis length of 0.5-0.8 μm and BET specific surface area of 35–40 $m^2 g^{-1}$. Oleic acid (OA) and its mixture with epoxyde oligomer ED-20 (EO) were used as stabilizers for producing powders. The obtained specimens were marked as Fe-OA and Fe-OAEO accordingly.

Besides, powders of reduced iron Fe_{red} with uniform particles size of 50–500 μm (basic fraction) have been studied. Before investigation, Fe_{red} was dispersed in a planet mill for 1 and 4 h. The obtained powders had contained 40.0 and 70.8% of 40 μm fraction accordingly.

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The thermogravimetric study of iron powders was performed using Q-1000 derivatograph in air medium at the temperature range of 20–1000°C.

The analysis of TG curves of iron powders shows that their oxidation process occurred in two stages [2] (Table 1).

Table 1 The influence of heating rate on the thermal properties of high-dispersed iron powders

V_{heat}/ °C min^{-1}	First oxidation stage			Second oxidation stage	
	T_0^1–T_1/°C	DOX/%	V_{ox}/mg min^{-1}	T_0^2–T_1/°C	V_{ox}/mg min^{-1}
2.5	100–250	84.1	0.32	250–400	0.12
5.0	110–220	89.2	2.90	220–420	0.15
10.0	110–200	92.6	4.20	200–390	0.17
20.0	110–200	95.8	4.70	200–360	0.16

Results and discussion

The increase of the heating rate V_{heat} leads to the shift of the starting temperature of oxidation T_0 to higher temperatures and to narrow oxidation temperature range T_0–T. Simultaneously, oxidation degree DOX and rate V_{ox} raise, especially for the second feature. It must be noted that almost all the increasing powder mass and heating took place at the first oxidation stage.

The TG curves of iron powders stabilized by the mixture of oleic acid and epoxyde oligomer [3] indicate the shift of T_0 and heat maximum temperature T_{max} by 10–30°C towards high temperature in comparison with the powder Fe–OA (Table 2).

Table 2 The thermal properties of modified high-dispersed iron powders

Type of powder	First oxidation stage					Second oxidation stage		
	T_0^1/°C	T_{max}/ °C	$\Delta m/m$/ %	V_{ox}/ mg min^{-1}	E_{act}/ kJ mol^{-1}	T_0^2/°C	T_{max}^2/ °C	$\Delta m/m_0$/ %
Fe–OA	100	170	22.5	3.6	25	190	300	1.6
	110	145	24.0	0.8	40			
Fe–OAEO	120	180	21.3	2.8	45	200	330	1.6
	120	170	23.0	0.4	130			

Fraction denominators are data obtained at limited contain oxygen media (closed crucible)

Furthermore, powders Fe–OAEO have smaller V_{ox} and higher oxidation activation energy E_{act}. The obtained results show that at the lower partial oxygen pressure essential fall of V_{ox} and raise of the iron powder E_{act} took place especially in the case of Fe–OAEO. The comparison of iron powder E_{act} with one for a block iron (160–180 kJ mol^{-1}) [4] confirms that oxide crystalline boundary layers were formed in this case and provided good oxygen resistance. The calculation of ratio of specimens with increasing mass to metal contain shows that in the initial iron powder the oxide phase contents corresponds to the mixture of Fe_2O_3 and FeO in molar ratio of 1:1.

The investigation of the oxidation process of coarse-grained powders Fe_{red} enables to reveal significant shifting their T_0 into the high-temperature area, essential increasing powder mass during the second oxidation stage and the process of oxidation retardation at high-temperatures (Table 3).

The higher the content of small size particles in the powder is, the lower temperature of slowing down the oxidation process T_{slow} and the temperature of mass powder stabilization T_{stab} were observed. In spite of the relatively small content of fine particles in the powder (5–10%) its contribution in total exothermic oxidation effect was 30–60%.

Table 3 The thermogravimetric properties of reduced iron powders

Feature	Dispersing duration/h		
	0	1	4
T_0/°C	200.0	190.0	190.0
I oxidation stage $\Delta m/m$/%	2.3	7.9	13.3
II oxidation stage $\Delta m/m$/%	31.0	40.7	68.1
V_{ox}/mg min^{-1}	4.3	12.1	11.2
T_{low}/°C	740.0	700.0	650.0
T_{stab}/°C	820.0	780.0	720.0

The observed phenomenon can be explained by local sintering of coarse-grained iron particles due to considerable amount of heat evolving at high-dispersed particles oxidation.

Summarizing the investigation of high-dispersed iron powders oxidation the conditions for obtaining TG-curves with well defined 5 parts corresponding to various states of oxidized iron powder have been stated (Fig. 1).

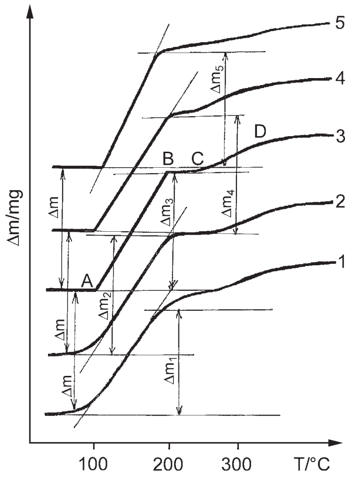

Fig. 1 The influence of heating rate on a mass of electrolytic iron powder: 1 – 5.0; 2 – 7.5; 3 – 10.0; 4 – 12.5; 5 – 15.0°C min^{-1}

It was found that the second part becomes strictly linear transitiving into the next one parallel to the temperature axis at only narrow range of heating rates (7.5–12.5°C min^{-1}). This effect became a base to calculate an active metal content in electrolytic iron powders by using Q-1000 derivatograph [6].

The thermal analysis of electrolytic iron powders and investigations of other authors concerning oxidation of a block iron [4] and high-dispersed iron powders [7] show that an active metal Fe^0 in these objects transformed into Fe_2O_3 in the temperature range of 90–200°C. The active metal amount can be calculated according to the following expression:

$$[Fe^0]=2.33\times\Delta m/m\times100$$

where m – the powder mass, mg; Δm – the increasing mass of the powder on the AB part of a TG-curve, mg; 2.33 – the coefficient corresponding mass ratio Fe/O in Fe_2O_3.

The comparison of active metal content measurements in electrolytic iron powders by thermal method with other chemical methods evidences for its high accuracy, reliability and effectiveness (Table 4).

Table 4 The results of electrolytic iron powders analysis by various methods

Analysis method	C^*/%				Analysis duration/min
	Fe^0	Fe^{2+}	Fe^{3+}	Fe_{tot}	
Chloriron	47.1	11.6	23.2	82.9	80–90
Chloriron[**]	48.5	12.1	22.6	83.5	65–75
Hydrogen	48.3	12.0	22.8	83.2	40–45
Thermal	48.7	11.9	22.7	83.4	25–30

[*] Fe^{2+} and Fe^{3+} content are determined by the method [8]
[**] a powder is wetted with methylethyl ketone preliminary to analysis

The peculiarities of iron powders oxidation are defined by their particles size and conditions of oxidation process. In the case of powders modified with organic comounds chemisorbed on the powder particles surface they also depend upon the nature of modifying substance and its thermal oxidative destruction.

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