Effect of V_2O_5 on the Oxidation Mechanism of ASD-4 Powder

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Abstract: Thermokinetic data on the oxidation of ASD-4 powder modified by impregnation with V_2O_5 gel were obtained by thermogravimetry and differential scanning calorimetry under heating in air to 1250°C at a rate of 10 deg/min. The phase formation process directly during oxidation of the modified ASD-4 was studied by powder x-ray diffraction method using a synchrotron radiation source. A mechanism for the effect of V_2O_5 on the oxidation of ASD-4 is proposed on the basis of literature data and analysis of the results of the studies performed.

Keywords: powdered aluminum, vanadium-containing hydrogels, activation of oxidation, completeness of oxidation, in-situ study of structural conversion.

INTRODUCTION

Based on energy parameters, cost, and availability, aluminum is one of the most promising metal fuels for energetic condensed systems for various applications. However, the high barrier properties of the oxide film on the aluminum surface and the low melting point of the metal do not allow its potential to be fully realized. This has motivated the development of methods for the modification of particulate aluminum to activate its oxidation [1].The most common are the following methods: preparation of fine powders, including nano-sized ones [2–5]; protection and activation of particulate aluminum using organic modifiers, including teflonization [4, 6–9]; activation by aluminum alloying with active metals or using mixtures of metals [6, 10–16]; encapsulation of aluminum powder particles with d metals to reduce agglomeration [17, 18]; addition of oxidants (WO_3, MoO_3, V_2O_5, Ta_2O_5, In_2O_5, Cr_2O_3, Fe_2O_3, Bi_2O_3, and CuO), which are strong oxidizers that provide thermite reaction on the surface [9, 13, 19–27]; addition of low-melting alkali metal polyvanadates and vanadium oxide bronze $Na_2V_{12}O_{30}$, which are considered as efficient transporters of oxygen through the barrier oxide layer and catalysts of Al oxidation [28].

A method of activating ASD type powder by impregnating the oxide layer on its surface by V_2O_5 hydrogel has been proposed to increase the energy efficiency of aluminum [29]. This method shifts the beginning of active interaction to lower temperatures and increases the rate and completeness of the oxidation of microsized aluminum particles during interaction with atmospheric oxygen.

In this paper, we study the thermokinetic features of oxidation of modified ASD-4 powder and the mechanisms of the effect of vanadium oxide (V) on its oxidation kinetics.

EXPERIMENTAL

In the experiment, we used ASD-4 aluminum powder obtained by spraying molten metal with nitrogen. The specific surface of the powder was 0.4 ±0.04 m²/g, the active metal was 98.7 ±0.5%, and the particle shape was almost spherical. The activator was applied to the

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particle surface by impregnating the metal powder with V_2O_5 hydrogel. The concentration of vanadium was varied by evaporation of the hydrogel, and the vanadium content in the powder was controlled by repeating the impregnation procedure. In single impregnation, samples containing 0.5–0.8% vanadium were obtained. The procedure of preparing the gel of the nominal composition $V_2O_5 \cdot nH_2O$ and applying coating is described in detail in [29].

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on a NETZSCH STA 409 PC/PE thermal analyzer. Samples of the same initial mass of 15 mg were placed in thin-walled plate-type corundum crucibles and heated in air at $10°C/min$. XRD analysis was carried out on a STADI P (STOE, Germany) x-ray powder autodiffractometer using $CuK_{\alpha 1}$ radiation and the RFS-2 x-ray structural database (Release 2009). IR spectra were recorded with a Tensor 27 FTIR spectrometer in the frequency range of $4000–400$ cm^{-1} for powder pellets with KBr. A JSM-6390LA (JEOL, USA) instrument was used to determine the shape and size of powder particles by scanning electron microscopy, and the vanadium content in the samples (by the atomic emission method on a JY-48 spectrum analyzer with an inductively coupled plasma and locally by IDX). Specific surface area was estimated by low-temperature nitrogen adsorption using the BET method on a TriStar 3000 (Micromeritics, US) automatic analyzer.

The oxidation reaction in air of the initial aluminum powder and the powder modified with hydrogel $V_2O_5 \cdot nH_2O$ were studied using x-ray diffraction with synchrotron radiation from a VEhPP-3 storage at the station of the 4th SI channel [30]. Monochromatic radiation ($\lambda = 0.368$ Å) passed through a thin layer of the sample, and the diffraction pattern was recorded with a flat two-dimensional detector consisting of a set of mboxMar345 Marreseach image plates. Powder sample inserted into the alumina holder was heated at a rate of $10°C/min$ to a temperature of $1100°C$.

RESULTS AND DISCUSSION

According to the elemental analysis data, the vanadium content in the sample prepared by impregnation of ASD-4 powder with a vanadium-containing hydrogel followed by drying is 0.78 ± 0.08 wt.%. The diffraction pattern contains lines belonging exclusively to metallic aluminum, which is consistent with the x-ray amorphous state of the xerogel formed due to partial dehydration of the hydrogel at the drying stage [31]. The presence of vanadium in the form of the xerogel is supported by the fact that the IR spectrum of the
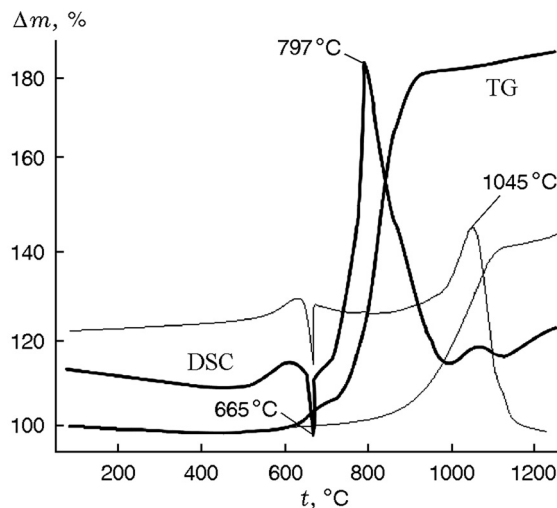

Fig. 1. TG and DSC curves of the initial aluminum powder (thin line) and the powder modified with V_2O_5 hydrogel (thick line).

sample contains bands with absorption maxima in the ranges $1010–1005$, $770–750$, and $510–505$ cm^{-1}, which correspond to the vibrational frequencies of the V—O bonds in the structure of the polymer phase of the $V_2O_5 \cdot nH_2O$ xerogel [31, 32]. The presence of water is also indicated by a slight decrease in sample weight at a temperature below $400°C$ (Fig. 1). From this it is clear that the resulting sample is a system in which the xerogel formed after drying is fixed on the real surface of aluminum particles coated with an oxide layer. It is known that $V_2O_5 \cdot nH_2O$ xerogels obtained by dehydration of the corresponding gels have a quasi-dimensional layered structure, making it possible to intercalate water, various organic compounds, and metal cations in the interlayer space [32–34], effectively impregnate highly dispersed materials, including metals, and produce stable films on their surface. Due to the layered structure of the xerogel, the specific surface of the modified aluminum powder is more than two times larger (0.873 ± 0.009 m^2/g) and its flow ability is much higher than those of the initial material.

According to the data of thermogravimetric analysis and DSC (see Fig. 1), the region of active oxidation of the initial ASD-4 powder under heating in air corresponds to the peak of the exothermic effect at a temperature of $1045°C$; the degree of conversion at $1250°C$ is 45.9%. The powder modified by impregnation with the vanadium-containing hydrogel begins to markedly react with air oxygen at a temperature of about $500°C$, i.e., below the melting points of Al ($660°C$) and V_2O_5 ($678°C$, obtained from the DSC

curve of $V_2O_5 \cdot nH_2O$). Generally, the process is shifted to lower temperatures: the temperature of the maximum heat release rate (DSC) of the modified ASD-4 powder is 797°C, which is almost 250°Clower than that of the initial powder (1045°C), the degree of conversion of the modified powder at a temperature of 1250°C exceeds 90%, and the degree of conversion of the initial sample at the same temperature reaches only 45.9%.
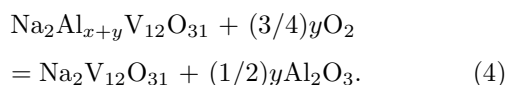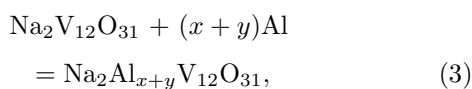
Analysis of the thermoanalytical data the shows that the impregnation of the ASD-4 micro-sized powder by the vanadium-containing gel has a positive effect on its oxidation in air under heating. At a temperature above the melting point of aluminum, there is a strong exothermic effect with a maximum at 797°C, and the degree of conversion in this process reaches 80%, which is significantly higher than that for the initial aluminum powder ($\approx$5%), as shown in Fig. 1. The effect of the addition of V_2O_5 and polyvanadate of alkaline elements on the oxidation of aluminum by air oxygen has been described previously [19, 28]. It is known that V_2O_5 can be used as a component of thermite mixtures [15, 23, 35]. However, in the literature, there are no reliable information and consensus on the mechanism of the activating effect of addition of vanadium compounds.

Thus, Romodanova et al. [19] believe that, due to capillary forces, molten V_2O_5 in contact with aluminum particles can penetrate directly to the metal–oxide interface, where the following reactions occur that provide continuity of its participation in the oxidation process:

$$4Al + 3V_2O_5 + 3O_2 \rightarrow Al_2O_3 + 2Al(VO_3)_3, \quad (1)$$

$$2Al(VO_3)_3 \rightarrow Al_2O_3 + 3V_2O_5. \quad (2)$$
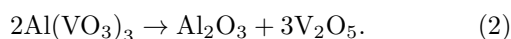
Vanadium oxide (V), regenerated by reaction (2), re-enters the interaction with aluminum. It should be noted that reactions (1) and (2) are speculative because in [19] their experimental confirmation for the real conditions of the activated processes is absent. In addition, in the Al_2O_3–V_2O_5 system, a single $AlVO_4$ compound is formed, which melts incongruently at 740°C according to the peritectic reaction $AlVO_4 \leftrightarrow Al_2O_3 + L$ (L is melt enriched with vanadium) [36].
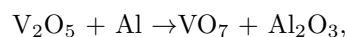
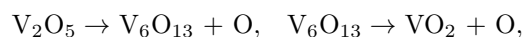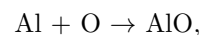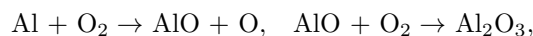It has been suggested [28] that the reaction between the components of mixtures of $Al + V_2O_5$ and $Al + Na_2V_{12}O_{31}$ most likely produces vanadium oxide bronzes $Al_xV_2O_5$ and $Na_2Al_7V_{17}O_{30}$. For the $Al + Na_2V_{12}O_{31}$ system, the following reactions are assumed to proceed at the interface:

$$Na_2V_{12}O_{31} + (x+y)Al$$
$$= Na_2Al_{x+y}V_{12}O_{31}, \quad (3)$$
$$Na_2Al_{x+y}V_{12}O_{31} + (3/4)yO_2$$
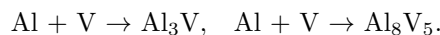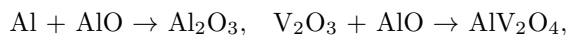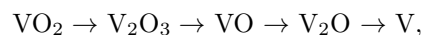$$= Na_2V_{12}O_{31} + (1/2)yAl_2O_3. \quad (4)$$

The accelerating effect of alkali metal polyvanadates on the kinetics of aluminum oxidation is considered to involve a catalytic mechanism resulting in the formation of an unstable liquid intermediate $Na_2Al_{x+y}V_{12}O_{31}$ complex, in which the chemical nature of aluminum is not clear.

Details of the mechanism of interaction between the components of a thermite mixture of 33% Al + 67% V_2O_5 in argon and air were investigated in [37]. Based on these data, the combustion of aluminum powder in contact with vanadium oxide (V) is a two-wave process:
the first wave involves the reactions

$$Al + O_2 \rightarrow AlO + O, \quad AlO + O_2 \rightarrow Al_2O_3,$$
$$Al + O \rightarrow AlO,$$
$$V_2O_5 \rightarrow V_6O_{13} + O, \quad V_6O_{13} \rightarrow VO_2 + O,$$
$$V_2O_5 + Al \rightarrow VO_7 + Al_2O_3,$$

and the second wave,

$$VO_2 \rightarrow V_2O_3 \rightarrow VO \rightarrow V_2O \rightarrow V,$$
$$Al + AlO \rightarrow Al_2O_3, \quad V_2O_3 + AlO \rightarrow AlV_2O_4,$$
$$Al + V \rightarrow Al_3V, \quad Al + V \rightarrow Al_8V_5.$$

As can be seen, each combustion wave is a complex multistep process involving the formation of a large number of compounds, including Al_3V and Al_8V_5 intermetallides. However, the basis of this mechanism in all cases is, in our opinion, the ability of vanadium to change the degree of oxidation, i.e., be an effective carrier of oxygen. A simplified model of the oxygen transfer from the medium to the metal can be represented by the following hypothetical reactions:

$$10Al + 3V_2O_5 \rightarrow 5Al_2O_3 + 6V, \quad (5)$$
$$2V + (5/2)O_2 \rightarrow V_2O_5. \quad (6)$$
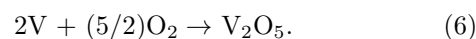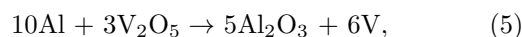
Reaction (5) is the basis of the well-known thermite process using vanadium oxide (V) as oxidizer [15, 23, 35]. In our view, the low-temperature activation of oxidation Al caused by addition of vanadium-containing gels is associated with the destruction of the oxide film covering the metal grains, for example, according to the reaction

$$V_2O_5 + Al_2O_3 \rightarrow 2AlVO_4. \quad (7)$$

The results of cynchrotron radiation diffraction studies of the modified ASD-4 powder heated to 650°C show that in the initial stage of the oxidation process, the phase composition is represented by Al, Al_2O_3, and V_2O_5 (Fig. 2a). Above this temperature, i.e., after
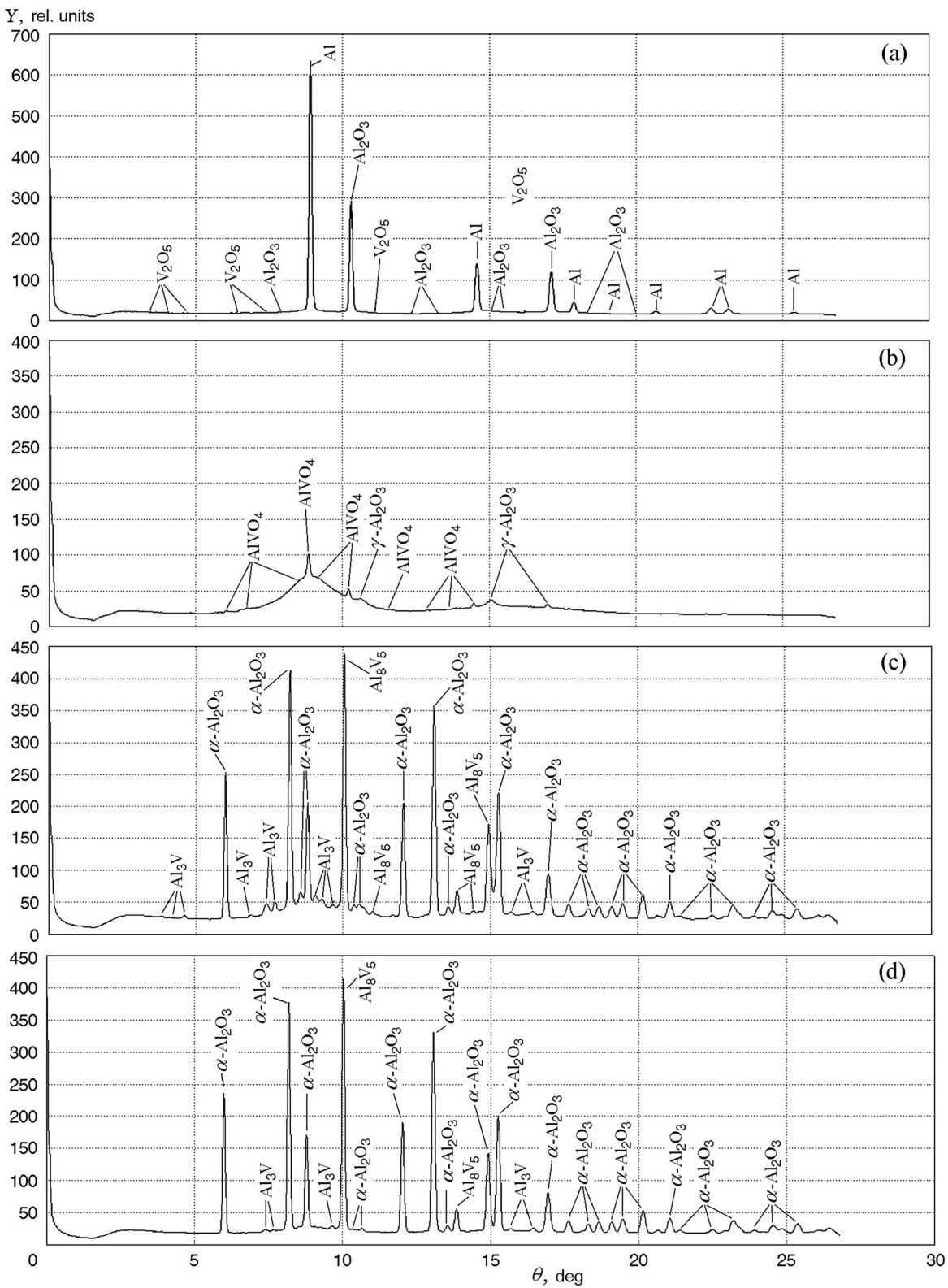
Fig. 2. Diffraction patterns of aluminum modified with the V$_2$O$_5$ by hydrogel at a temperature of 500 (a), 650 (b), 900 (c), and 1100°C (d).

the transition of aluminum and the V_2O_5 modifier to the liquid state (Fig. 2b), $AlVO_4$ lines appear in the diffraction spectra while the lines corresponding to all crystalline forms of metal oxides (Al_2O_3 and V_2O_5) disappear. Further increase in temperature leads to the appearance of intense diffraction peaks corresponding to alumina (α-Al_2O_3) and weak reflections caused by the formation of Al_3V and Al_8V_5 intermetallic compounds (Fig. 2c) present in the phase diagram of the Al–V system [38]. In the diffraction patterns of the samples taken at 1100°C, which is the maximum possible temperature under the conditions of the experiment, the intensity of the lines belonging to the metallic phases is markedly reduced and the halo from the liquid phase disappeared (Fig. 2d). These results are consistent with the above data [37] on the interaction in the thermite system based on metallic aluminum and V_2O_5.

The experimental and literature data allow the mechanism of the effect of V_2O_5 additives on the oxidation of ASD-4 powder to be represented as follows. During melting, liquid aluminum breaks the oxide film and comes in contact with V_2O_5, which at a temperature of $\approx$680°C also becomes liquid and interacts with alumina by reaction (7) to form $AlVO_4$. The simultaneously occurring intense oxidation of aluminum, accompanied by an increase in the sample temperature, leads to melting of $AlVO_4$ [36]. The variety of almost simultaneous processes in the volume and on the sample surface related to the multivalent nature of vanadium promotes the efficient transfer of oxygen to the reaction zone, resulting in intense self-heating of the system.

CONCLUSIONS

The oxidation of ASD-4 powder with the surface modified with V_2O_5 gel under programmed heating in air at a rate of 10°C/min to 1200°C was first studied.

It has been found experimentally that the impregnation of the powder surface with the gel leads to a shift of the active regions of interaction to lower temperatures and to significant activation of the oxidation process in the region above the Al melting point.

Information on the phase-formation process during heating in air was obtained by x-ray diffraction using synchrotron radiation under conditions similar to the conditions of thermoanalytical studies.

A mechanism for the effect of V_2O_5 on the oxidation of ASD-4 is proposed based on the polyvalent nature of vanadium, providing efficient transfer of oxygen to the reaction zone, and based on the ability of its melt to form $AlVO_4$ upon interaction with the surface layer of Al_2O_3.

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