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LETTERS TO THE EDITOR

Synergetic Improvement of Aluminum Reactivity in the Presence on the Surface of Quaternary Ammonium Compounds

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Chemical sorption of various donor-acceptor modifiers is a means of altering metals reactivity, water-repellent and tribochemical properties [1–3]. In the case of solid-state hydride synthesis of metals, hydride reducing reagents (NH_3, CH_4, SiH_4, etc) are used as modifiers [1, 2]. For adsorption modification of nickel, copper, iron, and aluminum surface quaternary ammonium compounds are promising, like triamon and alkamon [3, 4].

In this work, the synergetic acceleration of high-temperature metal oxidation (1173 K) by at least 45% was observed after the treatment of dispersed aluminum in vapor of triamon and alkamon.

Aluminum powder (PAP-2, according to State Standard of the Soviet Union GOST 5494–71, specific surface of 2.6 $m^2\,g^{-1}$) was treated in the triamon and/or alkamon vapor as described in [3, 5]. Triamon and alkamon are liquid cationic surfactants $[R^1R^2R^3R^4N]X$, R^i are organic groups bound to nitrogen atom in the hydrophobic surfactant cation, X is anion [6]. The molecular mass of triamon $[(HOC_2H_4)_3N^+CH_3]\cdot[CH_3SO_3^-]$ is lower than that of alkamon. Alkamon contains methylsulfate anion as well, and the alkyl chains in the surfactant cation are 10–12 carbon atoms long. According to X-ray fluorescence analysis and EDX spectroscopy, the initial Al powder did not contain nitrogen and sulfur. After treating with alkamon vapor, the modified Al sample contained 0.13 mol % of N and 0.12 mol % of S. After treating with triamon vapor, the modified Al sample contained 0.21 mol % of N and 0.22 mol % of S. The successive treatment of Al powder in vapors of triamon and alkamon led to the increase in the N and S content to 0.55 mol % and 0.43 mol %, respectively (as determined by EDX in the surface-sensitive mode, 6 kV). The carbon content in the modified metal samples did not exceed 2.7 mol %. The specific surface of all samples was practically the same, 2.7±0.1 $m^2\,g^{-1}$. The modified metals were heated in a muffle furnace (1173 K, 300 s) in air (101±1 kPa), and the relative increase of the samples mass ($\Delta m/m$) upon oxidation was determined by gravimetry [3, 7]. The heterogeneous oxidation rate V_{ox} was calculated using the usual method as $V_{ox} = \Delta m/(mS_{sp}t)$ [8], with S_{sp} being the sample specific surface ($m^2\,g^{-1}$), t being time. The oxidation rate was dependent on the sample, and equaled 0.013 $g\,m^{-2}\,min^{-1}$ in the case of Al/alkamon, 0.012 $g\,m^{-2}\,min^{-1}$, in the case of Al/triamon, 0.019 $g\,m^{-2}\,min^{-1}$ in the case of Al/triamon/alkamon, and 0.014 $g\,m^{-2}\,min^{-1}$ in the case of initial Al powder. The highest oxidation conversion in the case of Al/triamon/alkamon sample was also confirmed by precision instrumental analysis of the obtained Al-based powders. The effect of two components modifying the surface Al layer was significantly (no less than by 45%) higher than that of both modifiers taken individually. Thus, the synergetic effect of oxidation reactivity enhancement (as reflected by V_{ox}) was evident in the case of subsequent treatment of aluminum with two ammonium compounds containing alkyl groups of different size: triamon (C_1–C_2) and alkamon (C_{10}–C_{18}).

According to EDX spectroscopy (6 kV) results, the surface layer after oxidation in the above-mentioned conditions was of the following composition: Al

82.1 mol %, O 15.6 mol % (before oxidation: O 7.1 mol %), C 1.6 mol %, N 0.39 mol % in the case of Al/triamon/alkamon; Al 88.2 mol %, O 10.1 mol % (before oxidation: O 6.6 mol %), N 0.18 mol % in the case of Al/triamon; Al 87.3 mol %, O 10.7 mol % (before oxidation: O 6.7 mol %), C 1.5 mol %, N 0.08 mol % in the case of Al/ alkamon. According to X-ray phase analysis, weak single peaks of aluminum oxide were observed in the solid products of Al/triamon/alkamon and initial PAP-2 Al samples.

The rate of Al/triamon/alkamon sample oxidation was noticeably higher than that of the Al/(alkamon + triamon), obtained via treatment with the surfactants mixture [V_{ox} 0.015 г/(м^2·мин)], and that of initial Al powder. The relative error of V_{ox} determination was no more than ±3%. The reactivity of PAP-2 in oxidation and burning reactions was considered comparable to that of aluminum nanopowder [7]. It was assumed that the highest oxidation rate in the case of Al/triamon/alkamon sample was due to the stabilization of bilayer nanofilm of triamon/alkamon with triamon sublayer at the metal M surface via the formation of heteroatomic M–N bonds. The probability of such interaction was confirmed by about 2 eV increase of N1s layer energy according to X-ray photoelectron spectroscopy [9]. We assumed that this was favored by better steric accessibility of the nitrogen atom in triamon towards direct electronic interaction with metal, and by structural conformity of triamon and alkamon [3, 5, 9]. As a result of the interaction between nitrogen and metal, the latter turned more electron-saturated and more active in oxidation with air.

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