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Acceleration of aluminum oxidation in the presence of quaternary ammonium compounds on its surface

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ABSTRACT

The influence of alcamon and triamon treatment on the oxidation rate of aluminum surface is reported. Gravimetric and surface analysis measurements were applied to characterize the effect which was discussed in terms of the interaction of metal with nitrogen in the presence of quaternary ammonia compounds. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Quaternary ammonium compounds;
Tribology;
Metals treatment;
Adsorption modifying substrate;
Surface modification.

INTRODUCTION

Earlier it was shown that as a result of a chemical sorption of different modifiers, possessing donor and acceptor properties, tribological properties of different metals can be significantly varied by solid-state reactions of metal reducing^[1,2,3] or electrochemically^[1]. Except tribological properties, the water repellent properties and surface activity for participation in a specific chemical reactions can be greatly varied as well. The next following hydride-based surface modifiers as reducing agents were mainly used for surface treatment: NH_3 , CH_4 , SiH_4 ^[1, 2]. When Ni, Cu, Fe or Al surface was chosen as an adsorption-modifying substrate, best results for surface modification were obtained when substances on the basis of quaternary ammonia compounds (QAC): triamon and alcamon, were used for modification^[3, 5].

Here it is reported the step-wise process of treatment of a dispersed Al in triamon (TR) and alcamon (ALC) vapors, which results in a synergistic acceleration of metal oxidation in the process of its thermal treatment (1173 K) at a factor of not less than 45%.

EXPERIMENT

Al-powder PAP-2 (GOST 5494-71) with a unit surface area $2.6 \text{ m}^2/\text{g}$ was treated by vapors of TR and/or ALC at room temperature following methodic described elsewhere^[3, 6].

Compounds TR and ALC belong to liquid cationic surfactant of a generalized structure $[\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}]\text{X}$, where R_i – organic group directly bonded to nitrogen atom in hydrophobic cation belonging to surfactant, X – inorganic anion^[7]. The structural formula of TR, which possess lower molecular weight than ALC, is $[(\text{HOC}_2\text{H}_4)_3\text{N}^+\text{CH}_3][\text{CH}_3\text{SO}_4^-]$.

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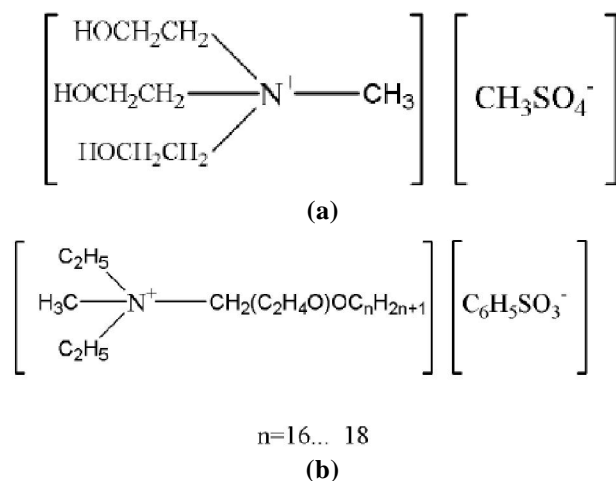


Figure 1 : a) Triamon, b) Alcamon

ALC possess methyl benzylsulfite polar group and alkyl radicals belonging to the structure of a cation, with a number of units $n=16-18$, (Figure 1).

APPARATUS

X-ray fluorescent analysis (RFA) was carried on "Bruker S4 Explorer" X-rays fluorescent spectrometer. Measurements were taken without filter at 10 kV voltage and 100 s exposure time.

Element dispersion X-rays analysis (EDX) was taken by EDAS/TSL attachment of Nanolab electron scanning microscope. Surface sensitive mode with applied potential 6 kV was used for EDX measurements.

RESULTS AND DISCUSSION

RFA analysis has shown that after the treatment in ALC vapors, Al/ALC sample contained 0.13 at.% N and 0.12 at.% S. Al/TR sample after TR vapors treatment contained 0.21 at.% N and 0.22 at.% S. Step-wise Al powder treatment by TR and ALC va-

por, sequentially, resulted in an increased N and S contents in Al/TR/ALC samples up to 0.55 and 0.43 at.%, respectively. According to X-ray fluorescent data and EDX-spectroscopy data, initial Al powder did not contain any noticeable amounts of nitrogen either sulfur, TABLE 1.

Carbon contents in modified metallic samples did not exceed 2.7 at.%. Surface unit area of all the samples was approximately equal – 2.7 ± 0.1 m²/g (BET). Obtained metallic samples with modified surface were simultaneously heated in muffle furnace (1173 K, 300 s) in air under (101±1 kPa) pressure. Gravimetric measurements were taken to determine relative mass increase ($\Delta m/m$) during oxidation^[3,8] Figure 2.

Calculation of the rate of heterogeneous oxidation of samples V_{ox} was taken at a standard procedure^[3]:

$$V_{ox} = \Delta m / (m \cdot S_{un} \cdot t)$$

where: S_{un} – surface unit area (m²/g), t – time.

It was shown that surface modified metal oxidation rate depends on the kind of modification applied in this process and for samples Al/ALC bears the value 0.013 g/(m²·min), Al/TR – 0.012 g/(m²·min), Al/TR/ALC – 0.019 g/(m²·min), and for the initial Al-powder – 0.014 g/(m²·min). The highest Al/TR/ALC samples oxidation rate is confirmed by a precision instrumental analysis methods (EDX, XRD) on aluminum-based powders. Action of two-component (OR/ALC) layer on Al surface, significantly, (not less than by 1.45 times) exceeds an action of each of this component taken separately.

Therefore, a synergistic effect of an increased oxidation rate was observed. This synergistic effect was clearly visualized as an increased V_{ox} on Al step-wise developed by QCA with the different size of organic radicals belonging to nitrogen atom (Figure

TABLE 1 : Content of elements adsorbed on Al-powder surface

Sample	Elements content			Molar ratio N/S
	N (EDX), at. %	S (EDX), at. %	S (RFA), mass %	
Al	-	-	-	-
Al/ALC	0,13	0,12	-	1,08
Al/TR	0,21	0,22	-	0,95
Al/TR/ALC	0,55	0,43	0,81	1,27
Al/(ALC+TR)	0,32	0,59	1,10	0,54

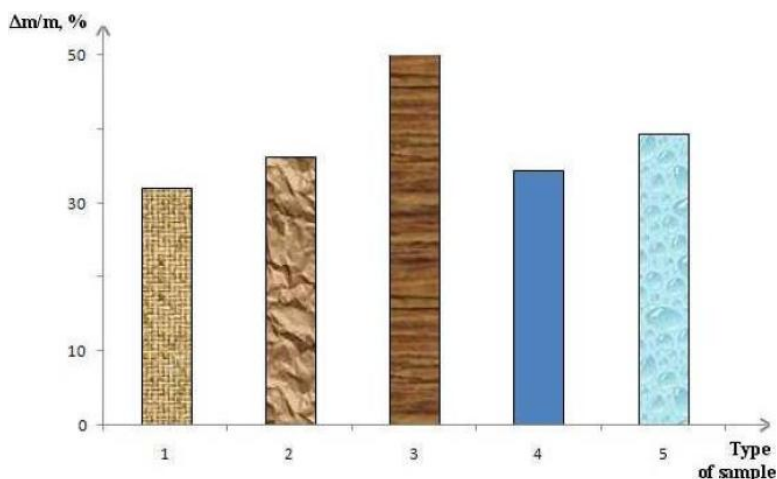


Figure 2 : The influence of the composition of a treating layer on relative mass increase during oxidation (1773 K, 300 s) for Al-powder samples: 1-Al/TR, 2-Al/(ALC+TR), 3-Al/TR/ALC, 4-Al/ALC, 5-Al

1): triamon (C_1-C_2), and alcamon ($C_{16}-C_{18}$).

According to data obtained by EDX, samples surface composition after heating under conditions specified above may be characterized as:

- Al/TR/ALC: Al – 82.1 at.%, O – 15.6 at.% (before oxidation: O – 7.1 at.%), \tilde{N} – 1.6 at.%, N – 0.39 at.%;

- Al/TR: Al – 88.2 at.%, O – 10.1 at.% (before oxidation O – 6.6 at.%), N – 0.18 at.%;

- Al/ALC: Al – 87.3 at.%, O – 10.7 at.% (before oxidation: O – 6.7 at.%), \tilde{N} – 1.5 at.%, N – 0.08 at.%.

It is interesting that, according to XRD data, weak discrete peaks of aluminum oxide were observed only from solid Al/TR/ALC sample and from an initial Al powder.

Al/TR/ALC sample oxidation rate ($V_{ox} = 0.019$ g/(m²·min), was noticeably higher than that of Al/(ALC+TR) sample obtained by treating of a mixture, as well as for an initial aluminum powder. Accuracy of the results is within 3% of calculated V_{ox} value. Al powder chemical activity at oxidation and burning is considered to be compatible with the activity of other types of Al nanopowders^[7]. It is assumed that the highest burning rate of Al/TR/ALC sample is related to a stabilization of bi-layered O/ALC nanofilm and triamon underlayer at metal (M) surface due to formation of heteroatomic bonds M←N.

The possibility of mentioned metal-nitrogen interaction can be confirmed by increasing approxi-

mately by 2-3 eV N1s binding energy, according to XPS data^[6,7]. According to our understanding, this is due to steric availability of nitrogen atom in triamon for electronic interaction with metal and structural co-planarity of QASs in triamon and alcamon mixtures^[3,5,9]. As a result of nitrogen and metal surface interaction, the latter, obviously, becomes more electronically saturated system, and more actively behaves as reducing agent under conditions of oxidation in air.

CONCLUSIONS

Quaternary ammonium compounds possess pronounced oxidation rate of Al surface. By selecting proper combination of QACs, synergistic effect can be achieved with a pronounced influence of surface chemical activity, such as oxidation rate. Attractive properties of QACs treatment find variety of practical applications in decreasing of surface friction, modifying surfaces for application as protective coatings, and corrosion protection.

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