

Activation of Metallic Aluminum by Tin and Gallium Chlorides in Oxidation with Water

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Abstract—We have studied the effect of gallium chloride and tin chloride solutions on the water oxidation of aluminum at SnCl₂ concentrations of 0.68 and 6.32 wt %, GaCl₃ concentrations of 0.56 and 2.67 wt %, and MCl_n: Al (M = Sn, Ga; n = 2, 3) molar ratios from 0.017 to 0.3. The results indicate that, when aluminum is oxidized in the presence of these salts, the reaction rate and hydrogen yield increase with reaction temperature and salt concentration and reach the highest levels when a mixture of gallium and tin chlorides is used. The reaction products are identified and the likely mechanism of the processes involved in the oxidation of aluminum is discussed.

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INTRODUCTION

The activation of aluminum that makes it reactive with water involves the rupture of the dense oxide film on its surface and can be achieved in a variety of ways, which can be classified according to the underlying reaction type: nominally catalytic reactions, including amalgamation [1, 2] and treatment of metallic aluminum with gallium-based liquid alloys [3–6], and stoichiometric metal oxidation reactions at high temperatures [7] or in alkaline and acidic solutions [8]. To a first approximation, the last reaction type can be thought to include aluminum oxidation by solid crystalline hydrous salts, in which the water molecules acquire acidic properties when coordinated to the central atom [9]. Some salts, e.g., copper and tin chlorides, are reduced to the metals when reacting with aluminum [9, 10], which suggests the formation of an electrochemical pair. Since aqueous solutions of a number of salts also promote aluminum oxidation, a more complicated mechanism of the process is possible: reaction of the metal with their hydrolysis products.

In this context, it is of interest to investigate the effect of solutions of salts that possess the above possibilities, that is, to run the aluminum oxidation process in catalytic, electrochemical, and stoichiometric modes at salt contents within 10–15 mol % relative to aluminum. These requirements are met, e.g., by gallium(III) and tin(II) chlorides, whose behavior is the subject of this study.

EXPERIMENTAL

Starting reagents. In our preparations, we used ASD-4 aluminum metal (Purity Standard TU 48-5-226-8, 99+% purity), commercially available pure-grade SnCl₂ · 2H₂O, gallium and indium metals of 99.9+% purity, and other chemicals of reagent or analytical grade. Tin chloride solutions were prepared by dissolving SnCl₂ · 2H₂O in water. The tin dioxide that was present in the as-purchased tin chloride and the basic tin chloride that resulted from hydrolysis were filtered off. The resultant solutions were analyzed for Sn and Cl by standard techniques and then diluted with distilled water to desired concentrations. Next, the solution pH was measured. The pH of the tin chloride solutions was 2–3, and that of the gallium chloride solutions was 4–4.5. In the course of aluminum oxidation, the solution pH increased to 6, probably because of the surface oxide film dissolution and aluminum hydroxide formation. An aqueous gallium chloride solution was prepared by dissolving an excess of metallic gallium in moderately heated 10% hydrochloric acid, followed by decantation of the solution containing the residual metal. Indium chloride was prepared in a similar way. The gallium and indium chloride solutions were analyzed argentometrically for chlorine. Gallium and indium were determined by atomic absorption in an acetylene–air flame, using the 287.4- and 303.9-nm resonance lines and a deuterium background corrector. The concentrations used to activate solutions are listed in Table 1.

Experimental procedure and analytical techniques. To a glass reaction vessel having a charging port and a

Table 1. Water oxidation of aluminum in the presence of tin, gallium, and indium salt solutions

Run no.	t , °C	wt % salt in solution (solution volume, ml)	Salt : Al molar ratio	Induction period, min	50% oxidation time, h	H ₂ yield in 3.5 h, %	Total oxidation time, h	H ₂ yield, %	Maximum rate of the process, ml/(g min)
SnCl ₂									
1	20	0.68 (10)	0.111	330	100	6.7	150	100	0.540
2	20	0.68 (10)	0.018	210	96	8.7	96	46	0.277
3	20	6.32 (10)	0.311	300	30	19	72	95	0.375
4	41.5	0.68 (10)	0.017	25		15.5	3.5	16	1.53
5	41.5	0.68 (10)	0.043	4	7.5	40	10	64	3.55
6	41.5	6.32 (10)	0.072	3	3.5	60	13	100	14.2
7	60	0.68 (10)	0.016	2		39	4.5	40	7.0
8	60	0.68 (10)	0.080	1	1.5	80	6.5	100	10.6
9	60	6.32 (10)	0.154	1	1.3	86	3.5	86	16.4
10*	20	0.68 (10)	0.037	270		3.3	150	18	0.283
11	20	0.68 (10)	0.014 plate	4		1.1	144	2.2	0.060
GaCl ₃									
12	20	0.56 (11)	0.015				6	0	
13	40	0.61 (11)	0.015	120		5.2	3.5	5.2	0.427
14	50	0.56 (11)	0.017	40		11.9	3.5	12	1.167
15	60	0.58 (10.9)	0.017	4		14	3.5	14	1.75
16	20	2.65 (10.5)	0.082	313		7.1	24	20	0.875
17	40	2.67 (10)	0.080	30		16	4.5	19	7.41
18	60	2.67 (10)	0.084	3		29.6	4.5	35	7.60
SnCl ₂ + GaCl ₃									
19	20	0.66 + 0.25 (10.2)	0.026(Sn) 0.010(Ga)	210		10.5	25	21	0.311
20	20	4.6 + 0.60 (10.5)	0.127(Sn) 0.019(Ga)	150	49	10.8	69	51	0.73
21	20	2.8 + 1.2 (11.5)	0.077(Sn) 0.035(Ga)	140		9.1	24	26	0.53
GaCl ₃ + InCl ₃									
22	60	2.67 + 1.33 (10)	0.084(Ga) 0.019(In)	4		30.5	4	30.8	8.5
23	20	HCl solution pH 2.0 (10)		330			22	1.3	0.40

* Al + SnCl₂ · 2H₂O (s).

side arm connected to a water-filled gas burette was added 10–12 ml of an activator solution of particular concentration. The scale division of the measuring burette was 0.2 ml (0.2% at a total volume of 100 ml). The vessel was placed in a preheated thermostat, whose temperature was maintained with an accuracy of 0.5°C. Next, a weighed amount of aluminum was added to the reactor, and the vessel was hermetically sealed. In our experiments, we measured the amount of released hydrogen as a function of time. For com-

parison, we examined water oxidation of aluminum powder ground with crystalline SnCl₂ · 2H₂O (7 wt % based on Sn) (Table 1, run 10) and dilute (0.01 N) hydrochloric acid (pH 2) (run 23).

At moderate hydrogen release rates, the oxidation of aluminum was terminated at low degrees of conversion.

After the oxidation process, the resultant dark gray precipitate was filtered off, dried at room temperature,

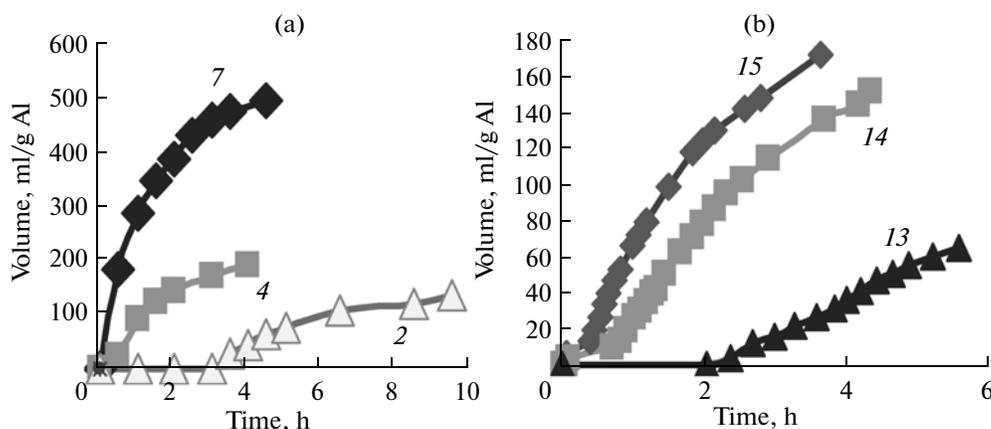


Fig. 1. Temperature effect on the water oxidation of aluminum in the presence of (a) tin chloride and (b) gallium chloride: (2) 20, (4) 41.5, (7, 15) 60, (13) 40, and (14) 50°C (the numbers of the curves correspond with the numbers of the runs in Table 1).

and examined by X-ray diffraction (XRD) on an ADP-2 diffractometer ($\text{CuK}\alpha$ radiation). The products of the oxidation of aluminum activated with tin and gallium chloride solutions were also characterized by energy dispersive X-ray analysis on a SUPRA 25 scanning electron microscope equipped with an INCA x-sight X-ray spectrometer.

RESULTS AND DISCUSSION

Qualitative experiments aimed at studying reactions of tin and gallium chloride solutions with an aluminum plate showed that, when the reactants were brought into contact, a three-dimensional metallic tin sponge or a dark gray deposit containing small liquid gallium droplets was formed on the surface of the plate. This was accompanied by active hydrogen release, which, however, slowed down rather rapidly and stopped in 1.5 to 2 days. The amount of released hydrogen was 2–4 wt % of that expected for the dissolution of the entire aluminum plate. No reduction of indium from indium chloride was detected.

To quantitatively assess the effect of activator additions, quantified by the rate of hydrogen release and the weight of the hydrogen reduced from water in the presence of the salts in different concentrations, we used ASD-4 aluminum powder, with a predominant particle size of 4 μm and specific surface area $S = 0.36 \text{ m}^2/\text{g}$. The results are presented in Table 1 and Figs. 1 and 2.

It can be seen from these data that the oxidation of aluminum has an induction period, whose duration depends primarily on the oxidation temperature and the nature of the activator, and to a lesser extent on the initial salt concentration in solution. All other factors being the same, the total oxidation time of equal amounts of aluminum powder activated with different chloride solutions ranges very widely: from 150 h to 60 min.

The time dependences of the hydrogen volume evolved have a sigmoidal shape, typical of topochemical reactions involving the formation and growth of nuclei of solid reaction products. Raising the temperature, initial activator concentration in solution, or salt : Al ratio increases the rate and extent of hydrogen release. The reaction rate depends only slightly on the activator, decreasing in the order $\{\text{SnCl}_2 + \text{GaCl}_3\} > \text{SnCl}_2 > \text{GaCl}_3 \approx \{\text{GaCl}_3 + \text{InCl}_3\}$ (Figs. 1, 2).

Reaction products. XRD examination showed that the precipitates obtained at various stages of incomplete aluminum oxidation in the presence of tin chloride contained aluminum, tin, and semiamorphous aluminum hydroxide (probably, in the form of gibbsite). The complete oxidation products contained the aluminum hydroxychloride $\text{Al}_{11}(\text{OH})_{30}\text{Cl}_3$. In the products of aluminum oxidation in the presence of gallium chloride, no gallium was detected, presumably because gallium was present in the form of liquid or a thin film on the aluminum surface.

Microstructural characterization. Figures 3–5 show regions where the elemental composition of phases on the aluminum surface was determined after aluminum had been reacted with aqueous solutions of gallium chloride and tin chloride for a limited period of time, insufficient for complete oxidation of the metal. The percentages of the elements detected on its surface are listed in Tables 2–4.

The data in Tables 1–4 and Figs. 1–5 lead us to the following conclusions: After the induction period, the activator metal reduced from its chloride appears on the aluminum surface. In the case of the activation with gallium chloride, the surface layer contained, in addition to gallium, a large amount of chlorine, whereas when tin chloride or a mixture of tin chloride and gallium chloride was used, no chlorine was detected in this stage of the process. It seems likely that the presence of chlorine in the former case may be due to the formation of poorly soluble complexes compris-

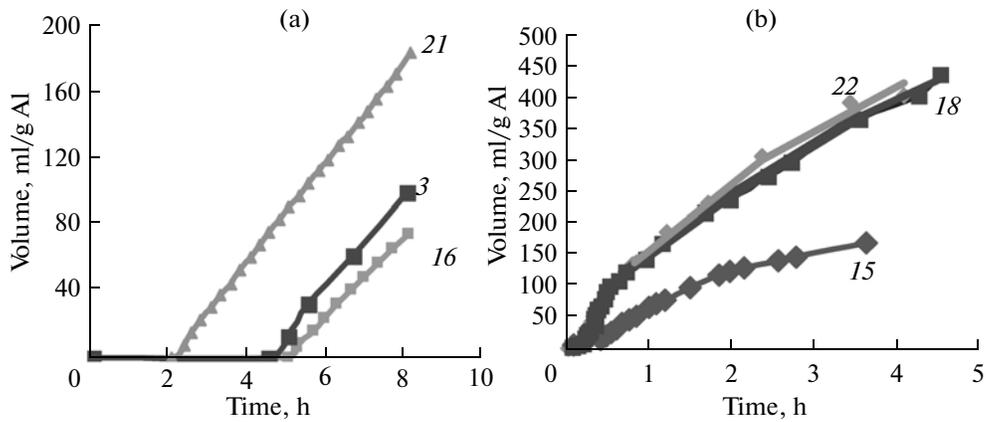


Fig. 2. Effect of the nature of the activator on the water oxidation of aluminum at (a) 20 and (b) 60°C in the presence of (3) tin chloride, (15, 16, 18) gallium chloride, (21) a $\text{SnCl}_2 + \text{GaCl}_3$ mixture, and (22) a $\text{GaCl}_3 + \text{InCl}_3$ mixture (the numbers of the curves correspond with the numbers of the runs in Table 1).

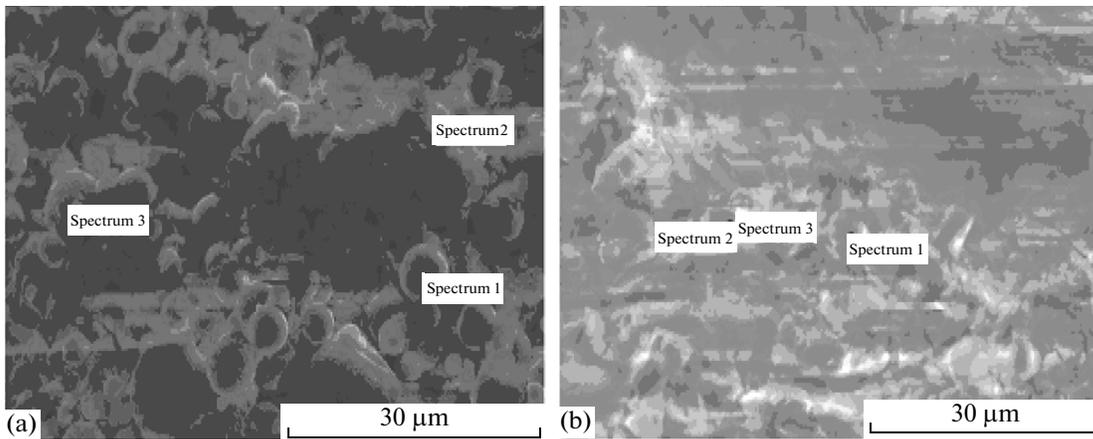


Fig. 3. SEM micrographs of the products of aluminum powder oxidation in the presence of a gallium chloride solution ($\text{Ga} : \text{Al} = 0.013$) (a) after an induction period (2.5 h) and (b) after 69 h of reaction (51% conversion). The micrographs indicate the regions analyzed.

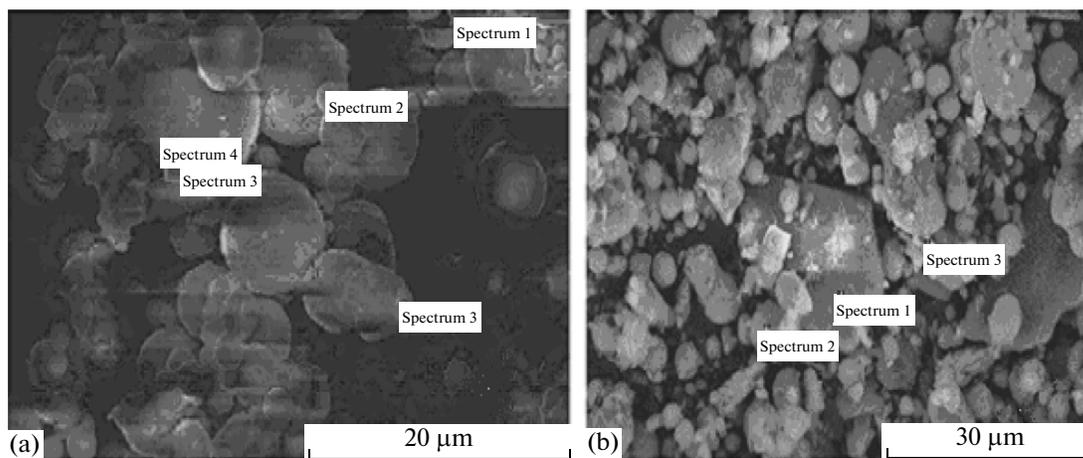


Fig. 4. SEM micrographs of the products of aluminum powder oxidation in the presence of a tin chloride solution ($\text{Sn} : \text{Al} = 0.075$) (a) after an induction period (3.5 h) and (b) after 96 h of reaction (95% conversion).

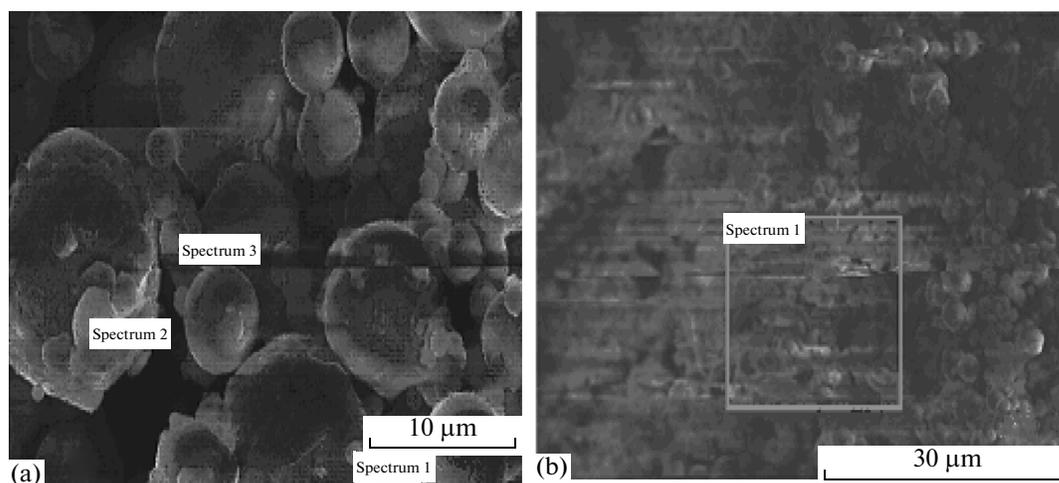


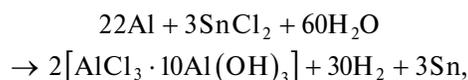
Fig. 5. SEM micrographs of the products of aluminum powder oxidation in the presence of a mixture of tin chloride and gallium chloride solutions (Sn : Al = 0.016, Ga : Al = 0.0168) (a) after an induction period (5 min) and (b) after 3.5 h of reaction at $t = 50^{\circ}\text{C}$ ($\approx 20\%$ conversion).

ing all three elements. The rather low oxygen content in both cases indicates that, in this stage of oxidation, only a small amount of aluminum hydroxide forms.

As would be expected, deeper oxidation products contain more oxygen and, accordingly, less aluminum and other components. In addition, the solid oxidation products contain chlorine. The chlorine : oxygen and chlorine : aluminum ratios are considerably smaller than those in crystalline $\text{AlCl}_3 \cdot 10\text{Al}(\text{OH})_3$, which was identified by XRD when aluminum was

activated with tin chloride and which has Cl : O and Cl : Al weight ratios of 1 : 4.5 and 1 : 2.8, respectively.

Thus, the activation and oxidation of aluminum in tin(II) chloride and gallium(III) chloride solutions follow different mechanisms and give different final products but seem to have identical initial stages: dissolution of the aluminum oxide film in the hydrogen chloride present in the salt solution as a result of a hydrolysis reaction, followed by the reduction of cations to a metallic state, e.g., according to the reaction scheme



which leads, in addition, to the formation of aluminum hydroxychlorides. Given the low pH of tin chloride solutions, comparable to that of 0.01 N hydrochloric acid, the dissolution of the oxide film (the first step of the process) in the presence of tin chloride should have a higher rate in comparison with gallium chloride.

Subsequently, the reactions take different paths. In the case of SnCl_2 , the tin metal remains on the surface and forms an electrochemical pair with the aluminum, leading to an effective electrochemical corrosion of the matrix in the presence of electrolyte.

In the case of activation with GaCl_3 solutions, only part of the gallium is reduced to the metallic state, and the rest forms poorly soluble heterocomplexes containing gallium in lower oxidation states. By virtue of the Rebinder effect, metallic gallium breaks down intergranular contacts in compact aluminum, increasing the density of unoxidized zones that react with water to release hydrogen. At the same time, Kozin and Samurzina [3] reported that, at a gallium content in aluminum under 5 wt %, the rate of aluminum oxi-

Table 2. Element distribution on the surface of aluminum powder activated with a gallium chloride solution

Spec-trum	Ele-ment	wt %	at %	Ele-ment	wt %	at %
1	Al	92	87.9	Al	52.8	42.0
	Ga	0.3	0.1	Ga	5.1	1.6
	O	7.2	11.7	O	42.1	56.4
	Cl	0.4	0.3	Cl	—	—
2	Al	54.2	43.0	Al	34.1	35.7
	Ga	2.0	0.6	Ga	4.1	1.2
	O	41.0	54.7	O	53.9	68.5
	Cl	2.8	1.7	Cl	7.9	4.6
3	Al	78.4	70.0	Al	26.8	19.3
	Ga	0.9	0.3	Ga	6.9	1.9
	O	18.8	28.4	O	63.6	77.3
	Cl	1.9	1.3	Cl	2.7	1.5

Table 3. Element distribution on the surface of tin-chloride-activated aluminum powder and oxidation products

Spec-trum	Ele-ment	wt %	at %	Ele-ment	wt %	at %
1	Al	91.4	86.7	Al	50.8	38.4
	Sn	0.41	0.09	Sn	0.91	0.16
	Cl	—	—	Cl	—	—
	O	8.24	13.19	O	48.3	61.5
2	Al	95.4	94.1	Al	91.2	87.3
	Sn	1.22	0.27	Sn	1.14	0.25
	Cl	—	—	Cl	—	—
	O	3.4	5.63	O	1.70	12.44
3	Al	96.3	94.0	Al	23.6	21.3
	Sn	0.03	0.01	Sn	26.4	5.40
	Cl	—	—	Cl	3.10	2.10
	O	3.66	6.02	O	46.9	71.2
4	Al	100	100			
	Sn	0.03	0.01			
	Cl	—	—			
	O	—	—			
5	Al	100	100			
	Sn	—	—			
	Cl	—	—			
	O	—	—			

Table 4. Element distribution on the surface of tin-chloride- and gallium-chloride-activated aluminum powder and partial oxidation products

Spec-trum	Ele-ment	wt %	at %	Ele-ment	wt %	at %
1	Al	91.4	86.7	Al	62.7	61.3
	Sn	0.41	0.09	Sn	11.77	2.62
	Ga	—	—	Ga	4.00	1.51
	O	8.24	13.19	O	20.50	33.80
	Cl	—	—	Cl	1.03	0.76
2	Al	95.4	94.1			
	Sn	1.22	0.27			
	Ga	—	—			
	O	3.39	5.63			
	Cl	—	—			
3	Al	96.6	94.6			
	Sn	—	—			
	Ga	0.16	0.06			
	O	3.24	5.36			
	Cl	—	—			

dation with water and hydrogen yield were rather low, on the whole comparable to those in this study. According to Parmuzina et al. [6], they can be increased many times by using alloys of gallium with indium and/or tin. Since the present results demonstrate that indium cannot be reduced by aluminum from indium chloride, it becomes clear why the hydrogen generation rate and hydrogen volume evolved are independent on whether solutions of individual gallium chloride or a mixture of gallium chloride and indium chloride (run 22) are used, whereas a combined effect of gallium and tin chlorides increases the rate of aluminum oxidation because tin is considerably easier to reduce to the metallic state in contact with aluminum.

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