JOURNAL OF MATERIALS SCIENCE 29 (1994) 129–135

Coloration of molten aluminium surface in various atmospheres

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Various kinds of coloration were observed on a surface of metallic aluminium heated above its melting temperature under seven different atmospheres with different p_{O_2}. Similar distributions of the coloration on a diagram of temperature (600–1400 °C) and time (1–90 min) were found among these atmospheres. Yellowish colours (beige, gold, yellow, blonde, camel and sand) appeared over a fairly wide range of the diagram. From estimated thicknesses determined by weight increases and the order of appearance of the colours, it was concluded that the colour is caused by interference by the oxidized thin film produced on the smooth surface of the molten aluminium.

1. Introduction

Aluminium, as a lighter material than iron, is currently increasing in importance for strengthening, by alloying of lithium or titanium and by introduction of fibres or whiskers for composites. In the employment of such materials, surface oxidation of the aluminium metal has been continuously investigated for many years. The protective property of this oxidized layer against subsequent oxidation is excellent at room temperature or higher temperatures. In an oxidation study of aluminium in air in this laboratory, yellow spots have been observed in a white oxidized layer formed after heating at 1400 °C and the mechanism of the coloration has been traced in more detail. The oxidation of aluminium above its melting point is reported here.

Czochralskii [1] reported in 1922 that molten aluminium absorbed 0 vol % oxygen at 900 °C, 2.5 vol % at 1200 °C and 12 vol % at 1500 °C, accompanied by a small formation of chemical compounds. Withey and Millar [2] reported in 1926 only a small oxidation on the surface even at 1150 °C. Many kinetic studies of the oxidation of molten aluminium in oxygen, air or vacuum, have been reported [3–14] in temperature range of melting point to 1700 °C. A parabolic weight increase is described. Products on the surface are amorphous and γ-Al_2O_3, followed by α-Al_2O_3 above 1000 °C. However, no report of coloration at high temperatures has been found in the literature. Only one report [15] described a blue coloration in the oxidation of a single-crystal surface Al (1 1 1) heated at 850 K (below melting point) in vacuum.

In the present study, oxidation experiments of aluminium specimens (pellets from powders, plate, foil and vapour-deposited thin film) in the temperature range from the melting point to 1400 °C, have been conducted in several kinds of gaseous flow with different oxygen partial pressures.

2. Experimental procedure

Pellet-type specimens (13.5 mm diameter and 2 mm thick) were prepared from commercial aluminium powders (Kanto Chemical Co. Inc., particle size 2–10 μm) by compaction in a mould under 1 t cm^{-2}. Other specimens were aluminium plate (0.5 mm thick), foil (0.02 mm thick) and vacuum-deposited film. Both sides of the foil were used (lustrous and dull faces) in the same run of heat treatment. The thin film was deposited in vacuum on a silica glass plate from fused aluminium. These specimens had sizes of about 10 mm × 15 mm.

Heat treatments were conducted in a furnace with SiC heaters in a temperature range 600–1400 °C and for up to 90 min. The specimen was placed in a mullite boat and inserted in a mullite tube (20 mm inner diameter) held at a constant temperature. Seven kinds of gases (oxygen, air, N_2/O_2 (= 9), nitrogen, argon, NH_3/N_2 (= 0.8) and hydrogen) were used. The gas, dried by silica gel, was passed through the mullite tube at a flow rate of 200 ml min^{-1}, corresponding to 1.1 cm s^{-1} linear velocity. The specimen after the treatment in the gaseous flow was pulled out to a cold

TABLE I Colour numbers used in the tables and figures

1	Red	14	Gold	27	White
2	Baby pink	15	Yellow ochre	28	Pearl grey
3	Cork	16	Glass green	29	Silver
4	Camel	17	Pastel green	30	Silver grey
5	Buff	18	Green	31	Grey
6	Blonde	19	Opal green	32	Silver pink
7	Beige	20	Celadon	33	Rose grey
8	Flax	21	Ice green	34	Smoke blue
9	Golden yellow	22	Cerulean blue	35	Ash grey
10	King's yellow	23	Lavender	36	Mouse grey
11	Bamboo	24	Crocus	37	Lead grey
12	Sand	25	Lilac	38	Shark
13	Old gold	26	Orchid		

0022–2461

region in the flowing gas and subjected to colour determinations, X-ray diffraction (XRD) and scanning electron microscopy (SEM). In the colour determination, colour names were taken from "Colour Guide International" [16], and they may be easily understood by almost all peoples in the world. 240 colours are printed and 38 were used as the surface colours in this report, as shown in Table I. Colour numbers only are indicated in the tables and figures. The weight changes were determined in micrograms order using a microbalance (Sartorius 2405 type, 30 g max.) with heat treatment time.

3. Results

3.1. Heat treatment of pellets in different atmospheres

The results are shown in Table II. After surface oxidation of pellets between 800 and 1400 °C in N_2/O_2 (= 9) mixed gas, the pellets were covered by a white colour, confirmed as α-Al_2O_3 (corundum) from the XRD pattern. The molten aluminium sweated out from the inside of the pellet, and its surface was gold-coloured between 800 and 900 °C. On heating in nitrogen, the surface was white above 1300 °C, and a rose colour mixed with grey appeared between 800 and 1000 °C. Between 700 and 800 °C, the golden colour appeared in 2–60 min, as shown in Fig. 1.

In an argon atmosphere (lower p_{O_2} than nitrogen), a similar appearance to that in nitrogen was seen, but the coloration region is wider, as shown in Fig. 2. A yellow- or camel-coloured region appeared between 650 and 900 °C and a red-coloured region between 900 and 1000 °C. In an NH_3 atmosphere diluted by nitrogen (NH_3/N_2 = 0.8), the yellowish coloured region was limited to around 800 °C and to 30–60 min. In a hydrogen flow, golden colours are observed in the temperature range 700–1000 °C.

As mentioned above, the yellowish colour appeared after heat treatments between 650 and 900 °C under lower p_{O_2} than nitrogen. Its temperature range becomes wider in the order nitrogen–argon–hydrogen and the time when the yellowish colour appeared becomes shorter in this order. The coloration in an NH_3 atmosphere was very characteristic, being different from those in the other atmospheres. The golden colour region was seen the most widely in the argon atmosphere. The rose colour was always seen mixed with grey in the higher temperature region, than the golden colour range mentioned above.

3.2. Heat treatment of plates in different atmospheres

The results are summarized in Table III. Aluminium plates with a thickness of 0.5 mm heated in air showed a white colour above 1100 °C in 5 min. Yellow spots with oval shape (1–2 mm × 1.5 mm) were seen dispersed on the white surface oxidized at 1400 °C. These spots were estimated to form on the molten aluminium which sweated out from the inside through pin holes or cracks in the oxidized Al_2O_3 film. The same yellow spots (7 μm × 13 μm) were seen on the white plate in air at 1200 °C. With heat treatments in nitrogen and argon, the coloration region on the temperature–time diagram transfers to lower temperature than that for the pellets. The rose-coloured region is seen partly above 850 °C in nitrogen and between 650 and 800 °C in argon, and is always mixed with grey colour. There is no yellowish coloration in

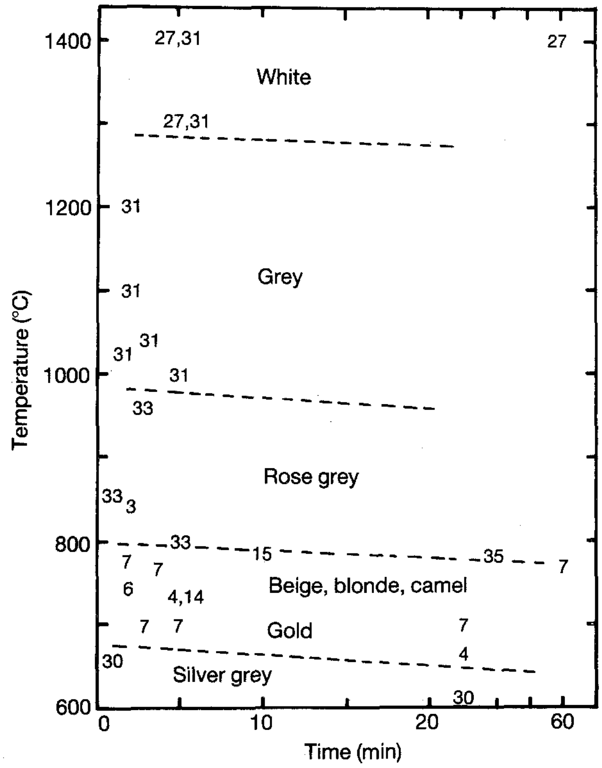

Figure 1 Colour distribution for aluminium pellets heated in nitrogen. Colour numbers are indicated in Table I.

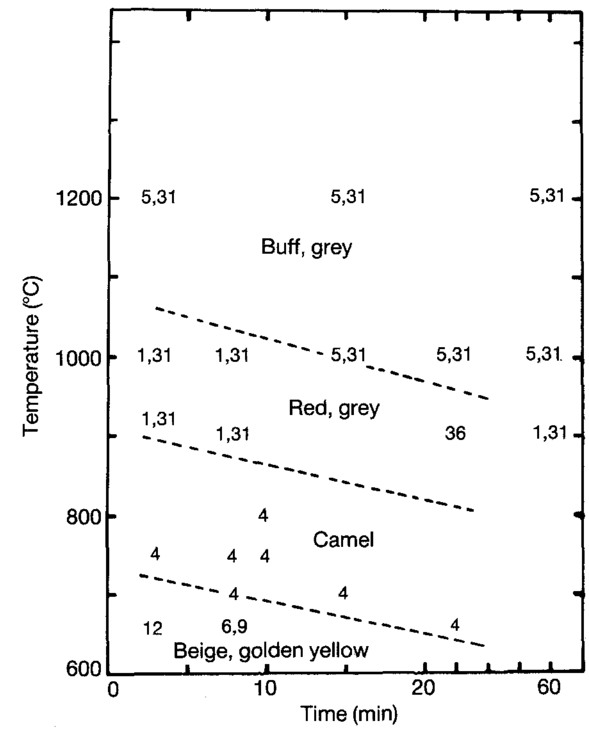

Figure 2 Colour distribution for aluminium pellets heated in argon. Colour numbers are indicated in Table I.

TABLE II Surface colorations of aluminium pellets. T, temperature; t, time; C, colour number in Table I

	N_2/O_2		N_2		Ar		NH_3/N_2		H_2	
T (°C)	t (min)	C	t (min)	C	t (min)	C	t (min)	C	t (min)	C
1400	5	31	5	27, 31						
			60	27						
1300	5	31	5	27, 31						
1200	5	31	2	31	3	5, 31	30	31	3	30
					15	5, 31				
					15	5, 31				
					60	5, 31				
1100	5	36	2	31					60	30
1050							10	31		
1040			3	31						
1020			2	31						
1000	5	36	5	31	3	1, 31	10	31	3	7
					8	1, 31	60	16, 31	15	30
					15	5, 31	90	31		
					30	5, 31				
					60	5, 31				
960			3	33						
920					3	1, 31				
900	5	35			8	1, 31	10	37	60	36
					30	36	30	37		
	60	36			60	1, 31				
850			1	33			10	36		
							60	11		
840			2	3						
820									3	7
800			5	33	10	4	5	36	60	1, 31
							10	35		
							30	12		
							60	12		
780			10	15						
			40	35						
780			2	7						
760			4	7						
			60	7						
750					3	4	10	11		
					8	4	30	8		
					10	4	60	7, 8		
740			2	6						
720			5	4, 14						
			5	7						
700			3	7	8	4	10	29, 31	3	4
			5	7	15	4			5	4
									15	11, 14
660			1	30	3	12				
			30	4	8	6, 9				
					30	4				
600			30	30			60	29, 31	30	30

nitrogen and argon atmospheres. Greenish colours are seen in hydrogen after 60 min. No large deformation of the original plates was observed even up to 1400 °C, in spite of fusion inside the plate.

3.3. Heat treatments of foils in different atmospheres

The results are summarized in Table IV. A commercial aluminium foil has two faces, lustrous and dull (wrong face). The colorations were similar for both faces but these differed slightly in the temperature at which the colours appeared.

On heat treatment in an argon atmosphere, a wide range of yellowish colorations was seen. Fairly pure yellowish colour was seen in the region of 700–1000 °C and after 3–60 min. A blonde colour appeared between 700 and 900 °C. The foil heated at 1000 °C for 3 min was partly coloured from blue to yellow along the argon flow direction. Another foil heated at 1200 °C for 3 min in argon similarly to the above, became coloured in the order blue–green–yellow–pink–silver.

On heat treatment in NH_3 diluted by nitrogen gas, the yellowish coloured region was narrow, and pink or purple mixed with grey colours were distributed in a region up to 900–1000 °C. After heat treatment in hydrogen, at 700 °C for 3 min, a golden colour was seen.

TABLE III Surface colorations of aluminium plates.

	Air		N_2		Ar		H_2	
T (°C)	*t* (min)	C	*t* (min)	C	*t* (min)	C	*t* (min)	C
1400	5	27, 31	2	31	30	31		
			5	6, 27, 31				
1300	5	27, 31	5	29, 31				
1200	5	27, 31	2	29, 31	15	31		
			5	6, 31	60	31		
1100	5	27, 31	2	31			60	20, 28
1040			3	31, 33				
1020			3	29, 31, 33				
1000	5	29, 31	5	6, 31, 32	3	6, 32		
					8	31		
					15	31		
					30	24, 31		
					60	31		
960			3	22, 31				
900	5	29, 31			30	28	60	20, 31
					60	31, 33		
850			1	31, 33				
840			3	31				
800	5	29, 31	5	31	10	30	60	17
780			40	29, 31				
780			10	30, 31				
770			2	30, 31				
760			1	29, 31				
			3	29, 31				
			5	29, 31				
750					8	33		
740			7	29, 31	15	32, 33		
720			3	29, 31				
			4	29, 31				
			5	29, 31				
700			3	29, 31	8	33	15	20, 31
			5	31				
680			1	29, 31				
660					3	35		
					30	32, 33		
600			5	29				

TABLE IV Surface colorations of lustrous and dull faces of aluminium foils.

	Lustrous face (A)				A, B-faces:		Dull face (B)			
	Ar		NH_3/N_2		H_2		Ar		NH_3/N_2	
T (°C)	*t* (min)	C	*t* (min)	C	*t* (min)	C	*t* (min)	C	*t* (min)	C
1200	3	2, 14, 22, 29	30	31					30	31
1100							7	29		
1000	3	14, 22	10	31	3	13, 14			10	31
			30	24, 31	3	23, 29			30	24, 31
			60	24, 31	15	23, 29			60	24, 31
900	10	6, 7, 14	10	23, 24, 26			10	6, 7, 25	10	23, 24, 26
			30	20, 23					30	20, 23
850	3	7, 14	10	18, 29			3	7, 14	10	32
	60	6, 7, 14	60	14, 34			60	6, 7, 25	60	4, 23, 24
800	3	7, 14	5	29			3	7, 14	5	29
	10	7, 14	10	21			10	7, 14	10	14
			30	32					30	32
			60	10, 14					60	14, 31, 38
750	5	29, 38	10	4, 14			5	4, 14, 38	10	4, 14
	8	38	30	29			8	38	30	29
	10	6	60	32			10	6	60	32
700	3	6, 14	10	29	3	14	3	6, 14	10	29
	8	28, 29					8	4, 12		
600			30	29	60	29			30	29

3.4. Heat treatments of vapour-deposited film

The film heated in air was coloured yellow at 1400 °C after 1 min and black at 720 °C. This coloration differs from the results for the plates which were white at 1400 °C. Because the thickness of the film was very thin, the amount oxidized was limited to the yellow colour.

3.5. SEM structure for the heat treated pellets

Pellets before heat treatment consisted of particles of 2–10 μm which formed by agglomeration of original particles of 1.5–3 μm (Fig. 3a). A plate heated at 1200 °C in air was covered with a thick oxide layer (Fig. 3b). Fig. 3c shows an oval shaped spot (7 μm × 13 μm) coloured yellow on the oxide layer of the above pellet; a melted and flat surface of aluminium metal is also seen there. The surface of a pellet heated at 740 °C in nitrogen and particles of 10–15 μm agglomerated to 20–50 μm by sintering are seen in Fig. 3d, while Fig. 3e shows the surface of a pellet heated at 750 °C in argon, which is similar to Fig. 3d. In both Fig. 3d and e, thin crystals of about 0.2 μm are seen on particles with a yellowish colour. Fig. 3f shows a surface heated at 1000 °C in hydrogen on which crystals of hexagonal plates (about 12 μm) exist. These are supposed to be α-alumina grown from aluminium vapour easily formed in hydrogen.

3.6. Weight increases with time in nitrogen and argon

Because the yellowish coloration appeared over wide region of the temperature–time diagram in the various

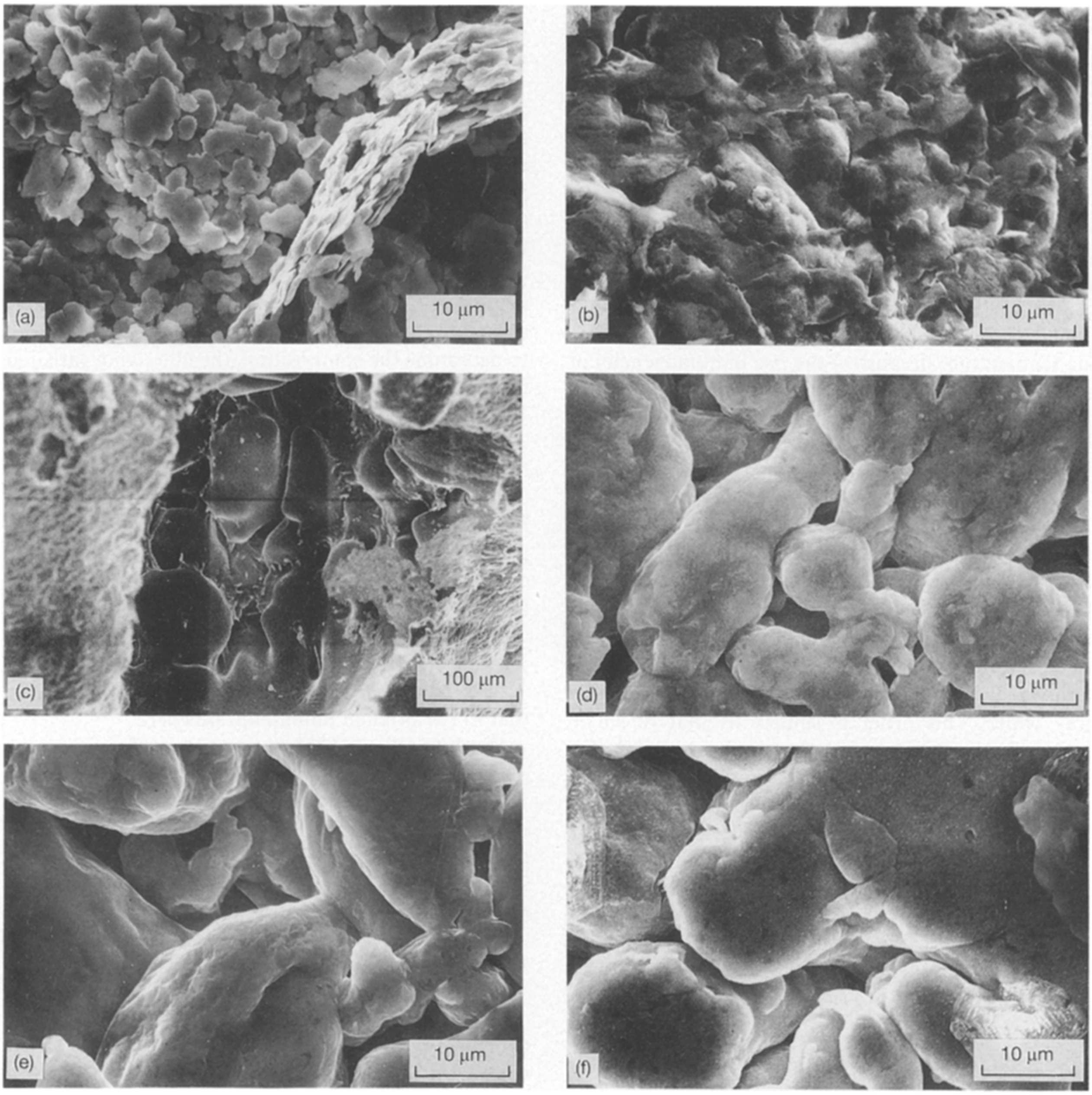

Figure 3 Scanning electron micrographs for heated aluminium surfaces. (a) Original surface of a compacted green pellet. (b) Pellet heated at 1200 °C for 10 min in air. (c) Oval shaped spot dispersed on pellet B. (d) Pellet heated at 740 °C for 2 min in nitrogen. (e) Pellet heated at 750 °C for 3 min in argon. (f) Pellet heated at 1000 °C for 15 min in hydrogen.

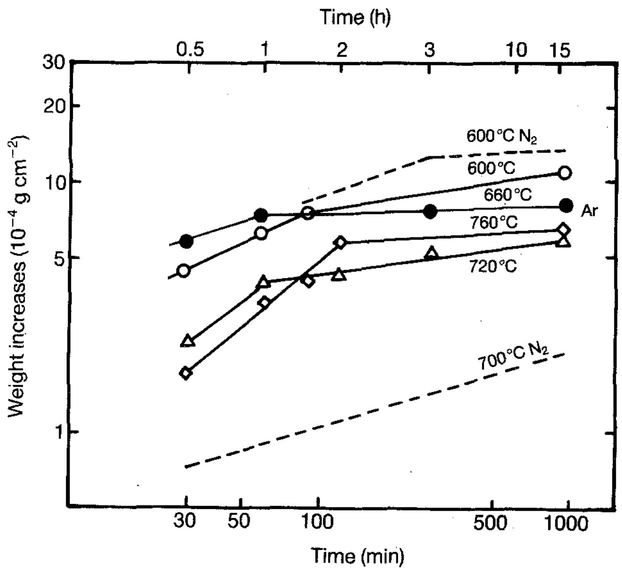

Figure 4 Weight increases of pellets in argon and nitrogen.

atmospheres, the pellet specimens were heated in nitrogen or argon flows in the temperature range 600–760 °C for up to 930 min and weight increases were determined with heating time using the microgram-ordered microbalance. The results are shown in a log–log diagram in Fig. 4. Diffusion-controlled oxidations with slopes of 0.56 ± 0.07 are seen up to about 100 min, followed by very small weight increases to 930 min. The weight increase in the initial stage of 1 h, decrease in the order 660–600–720–760 °C and have a characteristic feature across the melting temperature of 660 °C. The weight increases decrease with increasing temperature because of the rise in homogeneity of the oxide film. The thickness of the oxidized film is calculated to be 0.5–1.7 μm from the weight increases of 2×10^{-4}–6×10^{-4} g cm^{-2} using a density of 3.65 g cm^{-3} for γ-, δ- or θ-alumina [17, 18].

4. Discussion

4.1. Colour change

The colour changes illustrated in Figs 1 and 2 are summarized as the following order with increasing temperature:

Silver grey–blue–green–yellow–rose–red–purple–grey–white. This order is similar to that of single colours in the rainbow, but the purple appeared as a mixed colour seen only in interference colours. The order is very consistent with that in interference colours given by Kelly [19] or Kubota [20, 21] and also agrees well with that observed in an optical ray passing through a thin section of non-cubic mineral in a state of cross-nichols of a polarizing microscope [22]. For these reasons, the colour formed on the surface of the molten aluminium is presumed to be caused by interference.

4.2. Formation of coloured film

Thickness is estimated below 0.6–1.7 μm from the weight increases by oxidation in argon gas, as mentioned in Section 3.6. Hehn and Fromm [14] reported parabolic oxidation through a 1 μm amorphous oxide skin formed in vacuum. The yellowish film was formed on the smooth surface of the molten aluminium in the wide range 650–800 °C after up to 60 min in an argon or nitrogen gas flow. The interference colour formed on the smooth surface consisted of fine crystals of aluminium oxide. Yellow-coloured spots with an oval shape were dispersed on the white α-alumina layer produced at 1200 or 1400 °C in oxygen-rich atmospheres. These spots are thought to be the molten aluminium surface sweated through the α-alumina film oxidized during a few minutes of the cooling process in air.

4.3. Compounds formed on the aluminium surface

The formation process of the oxidized film corresponds to a diffusion-controlled one, as deduced from the slope (0.56 ± 0.07) in the initial stage as mentioned in Section 3.6. The homogeneous and dense thin film of aluminium oxide disturbs the transfer of oxygen molecules to the molten aluminium surface.

The composition of the oxidized film of molten aluminium metal below 1000 °C has been reported as amorphous, γ, and η forms [3, 5, 8, 9, 14] which transform to the α-form above 1000 °C. It was reported [18] that dehydration products of boehmite ($Al_2O_3 \cdot H_2O$) are in the order γ- to δ-phases with increasing temperature, and those of bayerite ($Al_2O_3 \cdot 3H_2O$) are in the order η- to θ-phases. Those of gibbsite ($Al_2O_3 \cdot 3H_2O$) are χ to κ [23]. Such phases appear in the temperature range 250–850 °C. In order to determine the composition, the films were gathered from many yellowish coloured specimens obtained at 750 °C after 10 min in argon and examined by XRD. The presence of lower temperature phases (χ, η, and γ) of transition aluminas which formed in the temperature range 250–750 °C from the above aluminium hydrates, was detected from the presence of small peaks at 46.0° and 67.0° of 2θ [17, 24]. Although they could not be clearly distinguished from the higher forms (κ, θ and δ), the possibility of the lower temperature form occurring is stronger by looking at the positions of the peaks. In addition, an amorphous hill with a maximum at 19° occurs which is higher than that in the original aluminium powders.

De Vita *et al.* [25] reported the formation of Al_3O_3N on molten aluminium in nitrogen at 700–800 °C. Ito *et al.* [26] recently described aluminium previously oxidized to 1 wt % oxygen content easily reacting up to 98% to AlN with nitrogen at 900 °C for 2 h. Thus the coloration of the pellet in nitrogen involves nitridation accompanied by oxidation between 700 and 800 °C, and the formation of AlN or aluminium oxynitride is possible.

5. Conclusion

When pellets, plates, foils and deposited thin films of aluminium were heat treated for up to 60 min in the temperature range 600–1400 °C under various atmospheres of air, N_2/O_2 (= 9), nitrogen, argon, NH_3/N_2

and hydrogen. Under all conditions surface colours were produced in the order silver grey–blue–green–yellow–camel–rose–pink–purple–grey above the melting temperature of aluminium. Weight increases were determined after heat treatments for up to 90 min. From the above results, it is found that the colours were caused by the interference colour of the thin aluminium oxide film produced on the smooth surface of the melt. The yellowish and golden colours appeared over a wide range of temperature, time and atmospheres.

Acknowledgements

The author thanks Mr K. Aihara, Mr Y. Kobayashi, Mr Y. Miyake and Mr A. Ohanru for their help in the experimental work.

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Received 13 August 1992
and accepted 8 June 1993