Study of Early Stage Interaction of Oxygen with Al; Methods, Challenges and Difficulties

B. Fateh[a,1,3], G.A. Brooks[a,1], M. A. Rhamdhani[a,1], J. A. Taylor[a,2],
J. Davis[3] and M. Lowe[3]

(a) CAST Cooperative Research Centre (CAST CRC)
(1) HTP Group, Faculty of Engineering and Industrial Science, Swinburne University of Technology
(2) School of Mechanical & Mining Engineering, University of Queensland
(3) The Centre for Atom Optics and Ultrafast Spectroscopy (CAOUS), Swinburne University of Technology

Abstract

Aluminum is among the metals with the greatest affinity for oxygen. Aluminum oxidation occurs easily and rapidly; a surface film can be formed in order of milliseconds. Study of initial oxidation is very important as it concerns the first step of a metal's oxidation and corrosion behavior. Characteristics of the kinetics of early-stage oxidation are believed to have an important influence on the later steady-state growth. Modern sophisticated experimental studies such as scanning tunneling microscopy (STM), X-ray photo-electron spectroscopy (XPS), low energy electron diffractions (LEED), combining ellipsometry and auger electron microscopy have clarified some of the details of initial stage of both oxygen chemisorption and oxidation kinetics of Al. However, the experimental data are not consistent. Furthermore, the dynamics of absorption and oxidation process are much less understood. This paper reviews the methods, techniques and the challenges of Al initial stage oxidation process measurements and also introduces a new method for studying the oxide layer formation using ablation of the surface with an ultra-fast laser beam and fast imaging techniques.

Introduction

There are many aspects of Al melt handling and cast process that result in oxidation of Al and dross formation. Dross is an inhomogeneous complex mixture of aluminium oxides along with entrapped molten metal. Since dross contains 10 to 80 wt% of entrapped Al, poor melt handing practices can result in significant profit loss. Of particular importance is the generation of dross during pouring operations, when "fresh" metal is exposed to oxygen as a free surface is formed. Opportunities for dross reduction may be enhanced by a greater understanding of the kinetics of aluminium oxidation especially in molten phase.

When a clean surface of a metal is exposed to oxygen, the following processes are considered to occur:

(i) Oxygen is adsorbed on the surface and forms an adsorbed layer (chemisorption).

(ii) Matter exchanges between the adsorbed layer and the surface. Thus, the first layer of oxide appears through formation of islets of oxide nuclei. This process is also named as external semi-reaction by some authors [4]. It is considered in the majority of low temperature oxidation theories that both adsorption and oxidation occurs predominantly at grain boundaries and then spreads over the whole surface [5].

(iii) Matter transports through the oxide layer by solid sate diffusion of one or both of the reactant (in this case metal or oxygen)

(iv) Matter exchanges between diffused matter and the interfaced ions (internal semi-reaction [4]). In this case, the thickness of the oxide layer increases with time but the oxidation decelerates and finally reaches to stable plateau behaviour.

This explanation reveals that the first step of oxidation is expected to be governed by chemisorption but the last steps are expected to be controlled by diffusion process. Previous experimental work indicate that oxidation of metals are initially very rapid and follow linear first order kinetics. The initial fast linear oxidation is thought to be controlled by chemisorptions [6].Through further exposure to oxygen, the initial fast linear oxidation changes to slower logarithmic or parabolic growth rate behaviour [6].

Aluminium has a high affinity for oxygen and its oxidation occurs easily and rapidly. At room temperature Al is always covered with an oxide film of 2-3 nm in thickness [23]. At high temperature, the oxidation process is extremely fast and thus, it is very difficult to predict or measure the mechanism of oxidation at the initial stages.

According to the collision and kinetics theory of gases, for 1 cm^2 of a clean surface (which has about 10^{15} atoms) at room temperature and at the pressure of 1 atm., it will take nano-seconds to form a monolayer of the oxide, if we assume that all the oxygen that arrives at the surface reacts instantaneously. Therefore, a clean oxide-free surface is seldom found in nature and must be prepared. Defining a clean surface is a challenging step in studying the initial stage of oxidation. To prepare a clean surface and to remove surface scale, techniques such as *in-situ* sputtering or heating in hydrogen are employed [1]. Since normal weight gain methods are not sensitive enough to detect any changes that occur in time frames of less than a second, *in-situ* fast response surface analytical techniques should be employed for the measurement of Al initial oxidation. This phenomena has been extensively studied by different methods and techniques using mono-crystalline surfaces and in ultra high vacuum (UHV) chambers: such experimental techniques are low energy electron diffraction (LEED)[2,3], ellipsometery techniques [7-11], auger electron spectroscopy (AES) [12], scanning tunnelling microscopy (STM) [13-17], electron energy loss spectroscopy (EELS) [18-20], photoelectron spectroscopy (XPS) [21] and also medium energy ion scattering [22]. Results of these investigations show that oxygen is chemisorbed and then gradually converts to oxide. However, the details of the process are still unknown and

also there are great discrepancies among reported data for the observed onset of oxidation, oxygen sticking coefficient and coverage. We will discuss this issue latter in this paper.

In this paper, we review the several published papers on chemisorption and oxidation of Al surface, discuss some of the inconsistencies and finally introduce a new technique for visualizing the evaluation of surface change after being exposed to oxygen.

Literature review on early stage Al oxidation

The initial interaction of oxygen with Al solid surface has been studied by a number of groups in the past few decades. Lindmark *et al* employed an in situ ellipsometer for measurement of thin film aluminium oxidation [7]. Their experimental set up included three chambers: sputter, robot handler and oxidation chambers. In the sputter chamber, aluminium layers, with 3000 Å thickness, were deposited on top of silicon wafers. Then, the robot arm handler took a wafer and moved it through the robot handler chamber into the growth chamber. The pressure in the robot handler chamber was $8x10^{-8}$ torr. After the growth of the film, the wafer from the sputter chamber was moved by the robot arm, through the robot handler chamber and into oxidation chamber which had a base pressure $2x10^{-8}$ torr. This movement took about 1 minute.

The highly vacuumed oxidation chamber was equipped with a spectroscopic ellipsometer with a high intensity xenon light source lamp. The lamp produced light with wavelengths from 280-760 nm (a schematic of the experimental layout is shown in Fig. 1). In order to measure growth rate, oxygen was introduced into the oxidation chamber with the ultimate oxygen pressure of 20 torr and the ellipsometer was set to take data at 1 or 5 second intervals.
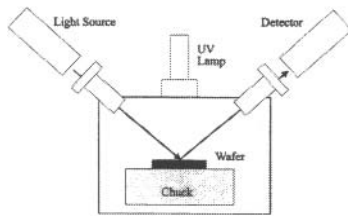

Figure 1. Schematic of the oxidation chamber outfitted with ellipsometer and UV lamp [7]

This set up has a certain disadvantage. The aluminium film suffers some oxidation during its journey from the sputter chamber to the oxidation chamber. Both Fig (1) and Fig (2) show oxide thickness prior to the time zero, the time when oxygen introduced to the chamber. As the authors pointed out even without the introduction of oxygen into the chamber, oxide growth was still seen. Thus, to measure oxide growth from a zero thickness on clean aluminium, an ultra-high vacuum system is required, which was not apparently the case in their study. Their report shows that during the exposure ψ decrease and Δ (ψ and Δ are two important ellipsometeric parameters which tan(Ψ) is the amplitude ratio and Δ is the phase shift upon reflection) increases sharply with time sharply (Fig. 2).

Figure 3 depicts the plot of changing thickness of Al and Al-oxide in time, based on the Lindmark *et al* [7] measured ψ and Δ data.

Two regimes can be seen in their data: a sharp transition from near zero to several angstrom thicknesses and then a slow logarithmic growth. The authors claim that the first regime describes the diffusion of metal ions to the surface and in the second regime the oxidation is limited by the tunnelling of electrons.
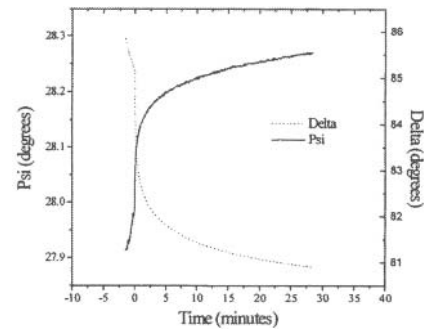

Figure 2. Plot of raw ψ and Δ data versus oxidation time, zero minute is the time when oxygen was let into the chamber [7]
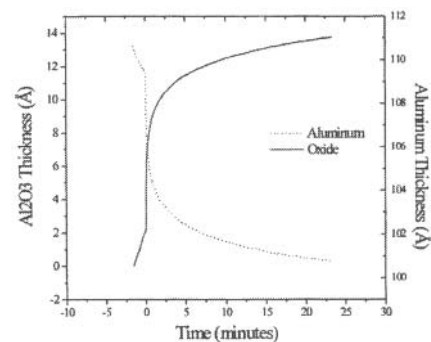

Figure 3. Plot of aluminum oxide and aluminum thickness versus oxidation time [7]

Kotenev [5, 9, 10] combined ellipsometry and electron microscopy for identifying the initial stages of Al oxidation (see Figure 4). A vacuum chamber with an electron spectrometer and an ellipsometer were combined. The experimental set up has been designed for complex investigation of the initial stages of gas-phase oxidation by means of ellipsometry, electron auger spectroscopy and low-energy electron diffraction with the usage of layer-by-layer etching of the surface with a beam of argon ions. In detail, his apparatus was set up as follows: a monochromatic radiation beam of laser (1) passed through a polarizer (2) and an electro-optical phase modulator (3). The phase shift between the orthogonally polarized radiation components with a frequency from a generator (6) was modulated. After a semi reflecting mirror, through the window (11), the radiation beam was incident on the specimen (12) placed in a high-vacuum analytical chamber (10) of the electron spectrometer. Then the beam being reflected by a concave mirror (13), it returned upon itself to a beam splitter (4), was reflected and passed through an analyzer (7), to a photo-receiver (8). The output signal of the receiver was sent to a control processing unit (9).

In the first chamber (16), an Al film of thickness 2000 Å was sprayed from a 99.99% Al source on a glass substrate. Then the sample moved to an analytical chamber (10) by means of a magnetic system. The chamber was under a vacuum of 10^{-10} torr. In order to make a fresh clean surface of Al, immediately before the experiment, the surface was cleaned by an argon beam. This is the advantage of Kotenev design compare to the previously described Lindmark set-up.
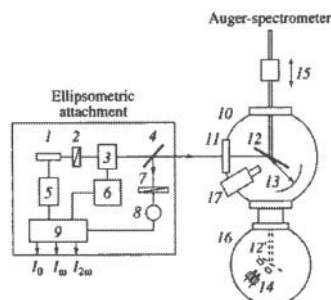

Figure 4. The set up for combining ellipsometric and electron-spectral measurements [9]

Figure 5 shows the experimental change of the ψ and Δ as a function of Langmuir value, L (1 L = 10 $^{-6}$ torr. s) in a constant pressure of 3×10^{-7} torr. Despite of Lindmark results, both ψ and Δ decrease with time. The ψ curve has an explicit minimum and all changes in Δ are negative.
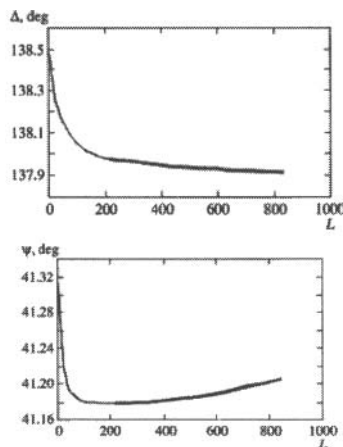

Figure 5. Change in the ellipsometric parameters ψ and Δ during the interaction between aluminum and oxygen of the rarefied atmosphere at room temperature vs. the dose of oxygen (1 L = 10 $^{-6}$ torr. s) [10]

Kotenev [5, 9, 10] sophisticated experimental set up revealed that the interaction between Al and oxygen at room temperature can be divided into 4 different stages. He claimed that the first stage corresponds to the formation and development of the first oxygen adsorption mono-layer, the second stage shows the growth of the second oxygen layer, the third stage belongs to formation of oxide nuclei and the fourth stages reveals the islet-like growth of a three dimensional amorphous oxide. These four stages are shown in Figure 6 and 7. Figure 6 shows the measured data of ellipsometry technique and Figure 7 the changes in auger-peak intensities and both are in good agreement in way of showing existing four stages of initial oxidation.

The change in thickness of the oxide layer as a function of Langmuir value, L, has been measured by Kotenev *et al*

(Fig. 8). Figure 8 depicts that the initial fast stages end at L < 100 with a thickness of around 10-12 nm. The slower stage corresponds to three dimensional growth of the oxide film.

Hayden *et al* [8] also studied oxygen chemisorption and oxidation of single crystal aluminium under different temperature and pressure conditions (range of 295-800 K and 10^{-9}-10^{-2} torr, respectively) using an ellipsometry technique.
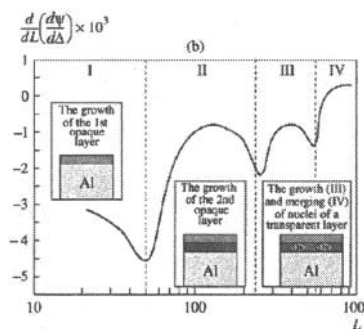

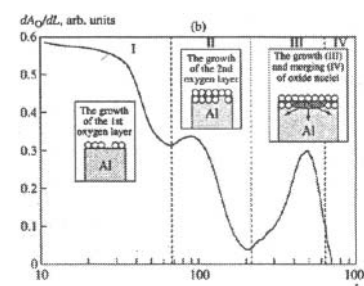Figure 6. The stages of early stage oxidation (Ellipsometric data) [9]

Figure 7. The stages of early stage oxidation (Auger-electroscopy data) [9]
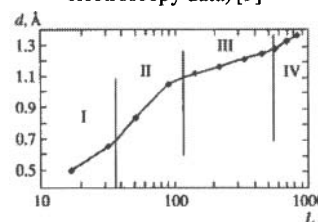

Figure 8. The change in the thickness of oxide layer at room temperature [10]

The authors reported that before each measurement, Al surface was electro-polished in a solution of perchloric acid and ethyl alcohol and then in-situ cleaned for preparing a single crystal Al. Their experiment carried out in an ultra-high vacuum (UHV) chamber equipped with LEED, Auger electroscopy and an automatic ellipsometer. Fig. 9 depicts their results of changes of ψ and Δ as a function of oxygen exposure (L) for various Al crystallographic faces at 5×10^{-7} torr and 295 K. It seems that, the results of Hayden *et al* confirmed the decreasing behaviour of both ψ and Δ. Their data reveals different oxidations rates for various Al single crystal faces, such as Al (111), Al (100) and Al(110).

The decrease of *ψ and Δ* as a function of oxidation and type of Al crystal face was also reported by Reichel *et al* [11], at 350 K and 1×10^{-4}Pa. Figure 10 shows the kinetics of ultra-thin (<1.5 nm) oxide-film growth on bare Al(100) and

727

Al(110) and Al(111) substrates measured by Reichel *et al* [11]. The figure shows that the oxidation kinetics on Al(100) and Al(110) can be subdivided into an initial, very fast and a subsequent very slow oxidation stage. However, on Al(111) at T≤ 450 K, no distinction between initial fast and a slow stage could be determined. Reichel *et al* [11] stated that this behaviour leads to an unexpected Al oxide growth at low temperature with respect to the rate of oxidation.
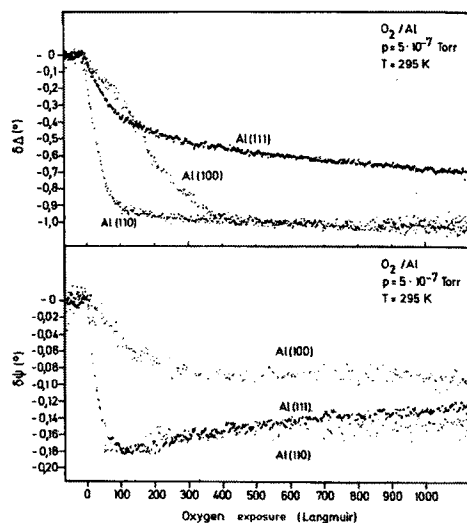

Figure 9. Changes of ψ and Δ during the oxygen interaction wit various Al crystal faces at 295 K and 5x10⁻⁷ Torr [8]
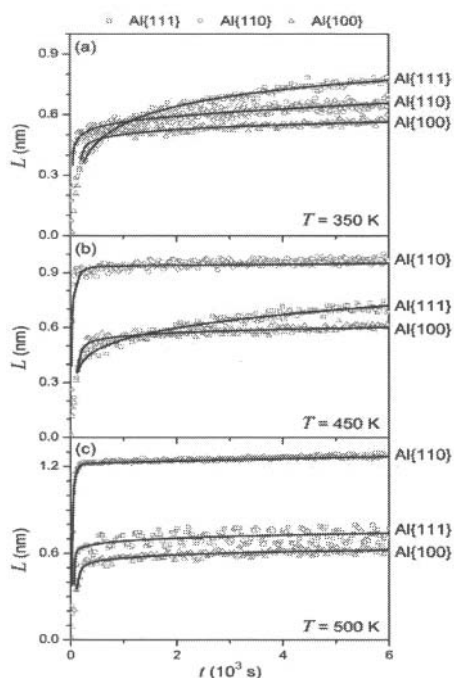

Figure 10. Experimental and fitted oxide-film growth for the oxidation of Al crystal faces at 350 K, 450 K and 500 K and and $p_{O2} = 1 \times 10^{-4}$ Pa [11]

Hayden *et al* [8] also reported the kinetics of the slow stages of Al(111) oxidation at 525 K under different pressures.

Figure 11 shows the semi-logarithmic plot of slowly increasing thickness of oxide film on an Al(111) substrate.

Hayden *et al* [8] found that at lower temperatures (less than 600 K) the oxidation rate follows a logarithmic rate law and holds a proportional dependence to the square root of the pressure ($p^{0.5}$). They also reported that at higher substrate temperature (600-800 K) the oxidation kinetics follows a parabolic relationship (Fig. 12). These measurements were carried out at a constant pressure of 1×10^{-4} Torr and calculated from changes of ellipsometric parameters.
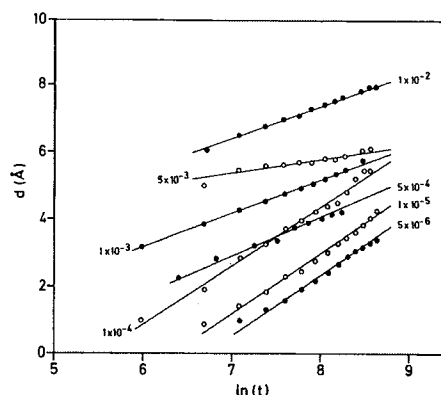

Figure 11. Slow increasing oxide thickness on Al(111) substrate at 525 K for various pressure of oxygen [8]
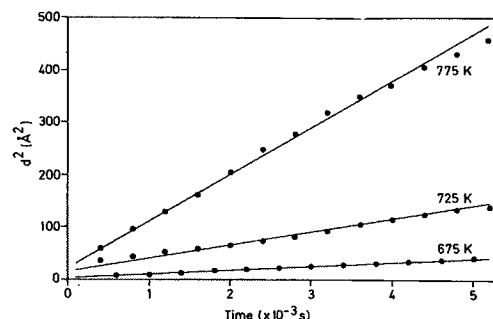

Figure 12. Plot of slow oxidation stage of Al{111} at p= 1x 10⁻⁴ Torr [8]

Benka and Steinbatz in 2003 [17] studied the oxidation of Al using secondary electron emission. The authors performed experiments in a UHV chamber with a base pressure of 1×10^{-10} mbar. Their Al sample was a 100 nm evaporated Al layer on a silicon wafer. In order to get a fresh non-oxidized Al surface, the samples were sputtered cleaned by Ar ions, but they had no means of measuring the structure of the Al surface. They found that electron emission yield depends on both oxygen pressure and exposure. They also claimed that at the beginning of oxygen exposure, the yield decreases and this behavior is due to chemisorption of oxygen, but when exposure continued the yield increased due to oxide formation (Results from their studies are shown in Figure 13).

Thus, the minimum yield corresponds to the end of chemisorption and the onset of oxidation process. As the figure shows, for pressure greater than 1×10^{-7} mbar, the onset of oxidation process occurs at 25 L ($1L = 10^{-6}$ torr.s). Other researchers have reported different values for the onset of oxidation from 100 L [10] up to 250 L [19]. A large discrepancy also exists for the reported sticking coefficient

728

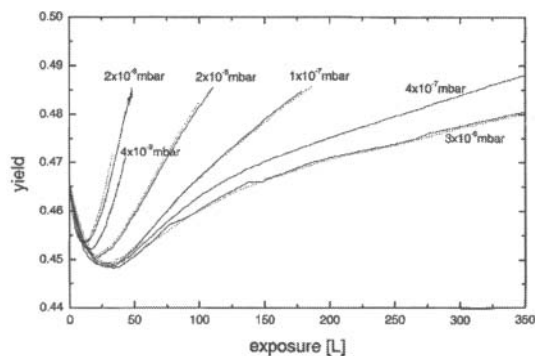of oxygen adsorption on Al, with values from 0.005 to 0.015 reported [14, 20].

Figure 13. Electron emission yields of Al as a function of exposure time for different oxygen pressure from 2 x 10^{-9} to 3x 10^{-6} [17]

Introduction of a new technique

Laser ablation is a technique for mass removal by coupling laser energy to the surface of a material. In recent years, femto-second laser ablation attracted a lot of attention because of small heat-affected-zone on the surface of target material [24].

A new method for studying the initial stages of oxidation, where a fresh surface of Al is prepared by removing the oxide layer using an ultra-fast laser ablation technique, has been developed at Swinburne University of Technology. Following ablation of the surface, the kinetics of solid Al oxidation is quantified by means of a fast imaging.

For the ablation of solid Al surface, the laser experimental set up was optimized. The sample was placed in a vacuum chamber with a silica window (50 mm diameter) for optical access. The chamber was connected to a rotary pump producing a vacuum of 2 mtorr (low vacuum range). Laser ablation and illumination light sources were focused through two different optical lenses (Fig. 14). A high speed camera was used to image the sample and was synchronised to a fast mechanical shutter in the ablating laser beam. In order to make shallow holes, the number of shots and laser intensity were optimised. The live images of ablated Al surface and the formation of sparks during laser ablation showed that 40 shots with 7-8 mW average power were enough to remove the oxide layer on the solid Al specimen. In order to capture images by high speed camera, a very strong light source was necessary. Thus, illumination of Al surface was a challenging issue. Focusing a very bright light source, using lenses and a fibre optic light, were optimized. The camera was adjusted to take 3000 frames per second in full resolution. Finally, the time evolution of the oxide layer growth on the ablated surface was recorded. Figure 14 shows a schematic set-up for the laser ablation and fast imaging technique. As the figure shows an ultra-fast laser beam (pulse duration in order of 100 femto-second =10^{-13} s) hits the Al surface through the objective lens. The BBO crystal (β-barium borate) is a crystal used for frequency doubling and coverting a red laser beam (wavelength= 800 nm) to a blue laser beam (wavelength= 400 nm). The blue laser allows more accurate focusing and more efficient absorption of the laser energy bu the material surface. A beam splitter

(neutral density filter) is used for adjusting different beam intensities.

Figure 15 shows the live captured images of time evolution of the oxide layer in 10 ms steps just after laser ablation. In the center of each image, the dark area depicts ablated surface of Al which is assumed to be a fresh Al. Image (a) was taken prior to ablation process and (b) was taken at the end of the ablation. Images (b), (c) and (d) were taken at 10 ms time intervals. Comparison between these images (inside the circle) clearly shows that surface is turning gradually to the color of surface prior to ablation, which most probably relates to the formation of an oxide layer on the fresh Al surface.

This result is promising and proves that this technique is a potentially suitable method to study the fast oxidation process in the millisecond time scale. Further studies on the image analysis techniques and measuring the rates of molten Al oxidation is in progress. For molten A oxidation studies, a high temperature stage is being incorporated into the apparatus described above and the result will be presented in subsequent publications.
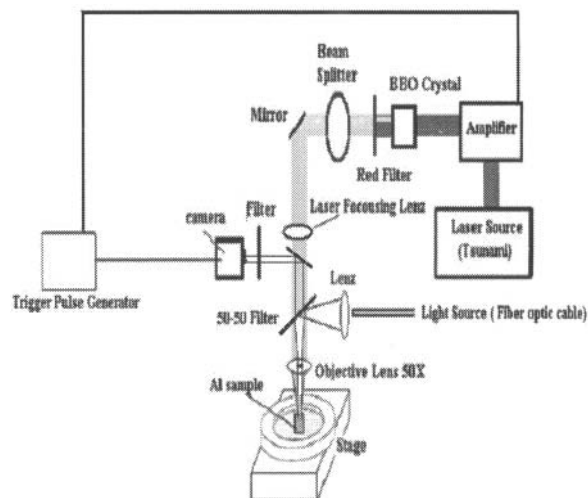

Figure 14. Schematic set up of laser ablation and fast imaging technique for visualizing the oxide formation on solid Al specimen
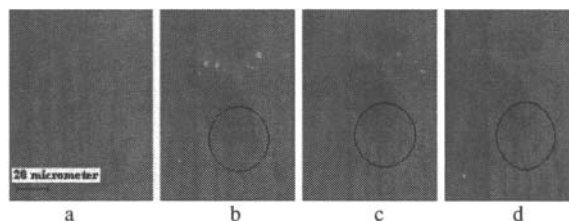

Figure 15. Live images of Al surface taken by fast camera (3000 fps)

a) Surface prior to ablation, b) surface just at the end of ablation c) 10 ms after ablation d) 20 ms after ablation

Conclusion

The interaction of solid Al and oxygen is rapid and complicated and it occurs in a stepwise process that is controlled by several parameters such as surface defects, crystal orientations and the method of preparing the fresh surface. For those reasons, there are inconsistencies between various data reported by different researchers. Table (1) reports the values of the measured Longmuir parameter (L= 10^{-6} torr.s) at which oxidation of aluminium surfaces commences, by different authors.

Table 1. Reported L values for the onset of Al oxidation

Author's Name	L value
Kotenev [5, 9, 10]	<100
Hayden et al [8]	for Al (111): 110 for Al (110): 30-50 for Al (100): 230-300
Benka and Steinbatz [17]	25
Reichel et al [11]	200-250
Zhukov et al [19]	250

Thus, there is considerable uncertainty in the literature about the point which Al oxidation commences. In general, all the experiments and varied techniques are carried out under ultra high vacuum conditions. There is no data available for oxidation process under low vacuum or normal pressure, nor is any kinetic data available for early stage molten Al oxidation. In this paper, a new technique has been introduced which may potentially provides better, faster surface treatment and also can be applied for measuring molten Al oxidation rate under lower vacuum or even normal pressure. This technique may allow observation of the initial stages of oxidation on very short-time scales, too.

References

1. A.S. Khanna; Introduction to High Temperature Oxidation and Corrosion; ASM International (2002), No. 06949G, ISBN: 0-87170-762-4

2. H.L. Yu, M.C. Muñoz and F. Soria, Surface Science 94 (1980), L184-L190

3. E.K. Lindmark, J.J. Nowak, M.T. Kief, Proceeding of SPIE Vol. 4099 (2000), pp 218-227

4. P. Sarrazin, A. Galerie and J. Fouletier, Mechanism of High Temperature Corrosion: a kinetic approach, Volumes 36-37 of Material Science Foundations (2008), ISBN: 0-87849-484-7

5. V.A. Kotenev, Protection of metals, Vol. 39. No.5, (2003) pp. 415-423

6. F.P. Fehlner and N.F. Mott, Vol. 2, No. 1, (1970) pp. 59-67

7. E.K. Lindmark, J.J. Nowak, M.T. Kief, Proceeding of SPIE Vol. 4099 (2000), pp 218-227

8. B.E. Hayden, W. Wyrobisch, W. Oppermann, S. Hachicha, P. Hofmann and A.M. Bradshaw, Surface Science, Volume 109, No. 1, Aug (1981), pp. 207-220

9. V.A. Kotenev, Protection of metals, Vol. 36. No.4, (2000) pp. 366-374

10. V.A. Kotenev, Protection of metals, Vol. 36. No.5, (2000) pp. 409-418

11. F. Reichel, L.P.H., Jeurgens, E.J. Mittemeijer, Acta Materialia 56 (12), (2008), pp. 2897-2907

12. L. Lauderback, S. Larson, Surf. Sci. 233 (1990) 276

13. H. Brune, J. Wintterlin, R. Behm, G. Ertl, Phys. Rev. Lett. 68 (1992) 624

14. H. Brune, J. Wintterlin, J. Trost, G. Ertl, J. Chem. Phys. 99 (1993) 2128

15. J. Trost, H. Brune, J. Wintterlin, R. Behm, G. Ertl, J. Chem. Phys. 108 (1998) 1740

16. M. Schmid, G. Leonardelli, R. Tscheließnig, A. Biedermann, P. Varga, Surf. Sci. 478 (2001) L355

17. O. Benka, M. Steinbatz, Surface Science 525 (2003) 207–214

18. J. Crowell, J. Chen, J. Yates, Surf. Sci. 165 (1986) 86

19. V. Zhukov, I. Popova, V. Vomenko, J. Yates, Surf. Sci. 441 (1999) 240

20. V. Zhukov, I. Popova, J. Jates, Surf. Sci. 441 (1999) 251

21. C. McConville, D. Seymour, D. Woodruff, S. Bao, Surf. Sci. 188 (1987) 1

22. D.O. Connor, E. Wouters, A. Denier van der Gon, J. Vrijmoeth, P. Zagwijn, W. Slijkerman, J. Frenken, J. van der Ven, Surf. Sci. 287/288 (1993) 438

23. P. G. Sheasby, R. Pinner, The Surface Treatment and Finishing of Aluminum and its Alloys, 2 (sixth ed.), Materials Park, Ohio & Stevenage, UK: ASM International & Finishing Publications, (2001) ISBN 0-904477-23-1

24. S.H. Kim, I. Sohn, S. Jeong, Applied Surface Science 255 (2009) 9717–9720

Correspondent author's email: behroozfateh@swin.edu.au