Polishing Phenomena of Aluminum Alloy using Photocatalyst and Cathilon dye under Utraviolet irradiation

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Abstract

A fundamental study on ultraviolet ray-aided machining (referred to as U-RAM) was conducted to evaluate its applicability to the polishing of aluminum alloy. Qualitative analysis with X-ray photoelectron spectroscopy (XPS) was used to estimate the chemical reaction induced on Al surfaces that were immersed in some solutions. Inductively coupled plasma spectroscopy (ICPS) was employed to quantitatively analyze the amount of oxidized/dissolved Al, Mg and Fe. The following conclusions were obtained by investigation of the aluminum alloy polishing process. Aluminum does not dissolve into TiO_2-solution, whereas a small amount of Al dissolves into Cathilon dye solution. Although only a small amount of Al dissolves into TiO_2-Cathilon dye solution in the absence of UV irradiation, the amount of Al dissolved increases slightly under UV irradiation with the formation of oxide, nitrogen oxide and nitride on the Al surface. In addition, a small amount of an aluminum chloride dissolves into TiO_2-Cathilon dye solution. An Al alloy (A5052) surface was made flat by polishing with TiO_2-Cathilon dye slurry under UV irradiation.

1. Introduction

Cu surfaces for an ultra-large-scale integration (ULSI) circuit are flattened using an abrasive-free slurry under ultraviolet ray (UV) irradiation as one of the chemical-mechanical planarization (CMP) technologies [1]. UV irradiation has been reported to be effective for the smoothing of diamond [2] and SiC [3] surfaces. These are several examples of polishing trials using UV irradiation. We have attempted UV-aided machining (U-RAM) of copper under UV irradiation [4-5]. A water-soluble luminous dye mixed with titanium dioxide or aluminum oxide was applied for polishing of the copper. It is also important to investigate the surfaces of anti-corrosive metals that have been flattened using U-RAM; therefore, polishing of a nickel cylinder was also examined using various polishing conditions with TiO_2 and Cathilon dye under UV irradiation [6].

However, the oxidation/dissolution of metals and the chemical reactions induced on the polished surface have not been examined to date. Therefore, a thorough investigation is required to clarify the polishing phenomena and mechanisms based on scientific considerations.

One of the fundamental studies concerning U-RAM is to clarify and discuss the polishing aspects of aluminum alloy. To evaluate the chemical reactions generated on pure aluminum (Al), Al plate was immersed in various solutions containing mixtures of a titanium dioxide photocatalyst and Cathilon dye in water. X-ray photoelectron spectroscopy (XPS) analysis of the Al surface was used to determine the chemical compounds generated in TiO_2 or Cathilon dye solutions and provide a qualitative estimate of the chemical compounds removed when polishing an aluminum alloy, such as A5052 examined here. Inductively coupled plasma spectroscopy (ICPS) is used to quantitatively analyze the amount of oxidized/dissolved Al, Mg and Fe from A5052 Al alloy. The present paper discusses the basic polishing phenomena of A5052 machined using U-RAM through qualitative XPS analysis and quantitative ICPS analysis.

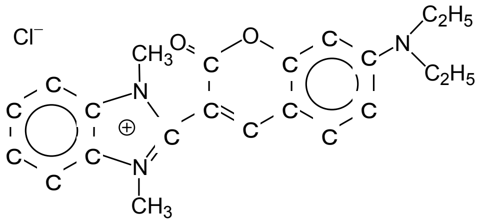


Fig. 1 Chemical structure of Cathilon dye

2. Experimental Procedure

2.1 Photocatalyst

Electrons and holes are generated in a thin layer on the surface of a TiO_2 photocatalyst when it is irradiated with UV at short wavelengths less than 380 nm and at high power over 0.1 μW/cm^2. An electron induces a reduction reaction, while a hole induces a strong oxidation reaction. If TiO_2 is mixed in a solution that contains a polymer, then decomposition of the polymer increases by the oxidation/reduction action of TiO_2, which leads to the generation of reactive oxygen species that can easily dissolve a metal into solution. TiO_2 particles with an average size of 0.18 μm and an anatase type were used in the current experiments.

2.2 Fluorescent substance

Cathilon dye is a luminous dye (Hodogaya Chemical Co.), the chemical structure of which is shown in **Fig. 1**. Cathilon dye consists of a high polymer ion that contains oxygen and nitrogen, and a chlorine ion in the solution state. When Cathilon dye is irradiated with UV with a wavelength of 254 nm, yellow light with a wavelength of 441 nm is emitted from the luminescent center of the dye.

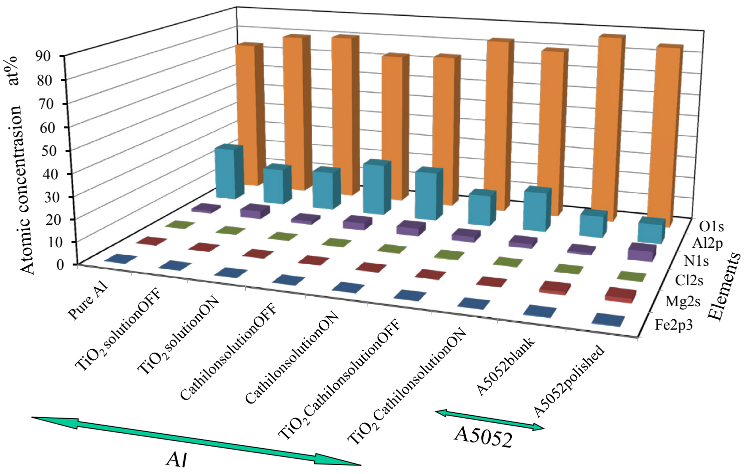


Fig. 2 Atomic concentration on the surface of Al/A5052

2.3 Metal Sample and Pre-Polishing Preparation

The purity of the Al plate used in the immersion test was over 99.0%. The thickness of the Al plate was 0.2 mm. Ion-exchanged water was used, where electrolytes such as residual chloride and organic substances were removed using a water-purification apparatus (SWAC-100, Shimazurika Co.). A solution of 15 mL ion-exchanged water mixed with 5 wt% TiO_2 and 2.5 wt% Cathilon dye was prepared in a beaker. UV of 253.7 nm and 60 μW/cm^2 was irradiated onto the Al plate immersed in the solution. The Al plate was stored in ethanol under refrigeration at 278 K.

An aluminum alloy sample of A5052 (Nikkei aluminum Co.) was obtained for polishing. The sample has a Vickers hardness of 159HV$_{500}$, and contains 0.25% Si, 0.4% Fe, 0.1% Cu, 0.1% Mn, 2.5% Mg, 0.1% Zn, 0.25% Cr with the balance Al. 3.5 mm thick disks of the A5052 alloy were cut from a 15 mm diameter rod. The surface of the sample was cut with diamond bite and polished using fine abrasive grits, previously.

ICPS (ICPS-8000, Shimadzu Co.) analyses of the elements dissolved in the mixed solution were determined quantitatively to the ppm level. Qualitative XPS (PHI 5400 XPS, Perkin-Elmer) analyses were conducted for the chemical compounds on the Al/A5052 surfaces. XPS analysis penetrates the surface to depths of several nanometers for the identification of the chemical composition. The atom concentration was calculated using the MultiPack software [7].

2.4 Experimental Procedure for U-RAM

Polishing of flat-surface samples was conducted using the UV irradiation polisher that was in-house built for the present subject, especially [5]. The satellite gear holds a pre-polished 15 mm diameter disk in the UV irradiation polisher. A micrometer was used to arrange three samples to equivalent heights. When a motor rotation is 100 rpm, the sample traces are off-set 12.64° in every rotation around a sun gear that leads to rotate the satellite gear, so that asample does not rotate on same traces. The rotation of sun gear used was 110 rpm with a load of 4.5 kPa for each sample. Corduroy is the polishing pad, which allows the transmission of UV radiation to the sample. A UV lamp (R-52G, UVP Co.) was used to supply UV radiation at a power of 800 μW/cm^2 and a short wavelength of 254 nm. A surface tester (SV-600 Mitutoyo Co.) was used to take ten measurements of surface roughness per sample for a polished surface to provide an average. We traced Vickers hardness testing marks on a sample. Both edges of marks were observed using scanning electron microscope (Keyence Co.). Chemical and mechanical polishing of the samples was accomplished by contact with the TiO_2 photocatalyst and Cathilon dye under a constant load.

Table 1 Chemical compounds on Al estimated from the XPS database

Al 2p 71.8-73.0eV	**C** 1s 284.5eV	**O** 1s 531.0eV	**N** 1s 398.1eV	**Cl** 2p 198.5eV	**OH**	**H**
Al_2O_3 71.1-75.9eV Aluminum (Ⅲ) oxide	**Al_4C_3** 73.6eV Aluminum Carbide (Decompose by water)	**Al_2O_3** 530.3-532.0eV Aluminum(Ⅲ) Oxide, Dialuminum (Ⅲ) trioxide	**AlN** 70.44-73.1eV Aluminum nitride **NO/Al** 396.8-407.4eV Nitrogen oxide on aluminum	**$AlCl_3$** 74.7eV Aluminum chloride **$AlCl_2$** (Ds-2p) 16.1eV Aluminum (Ⅱ) chloride Water soluble	**$Al(OH)_3$** 74.2-74.4eV Aluminum (Ⅲ) hydroxide No water soluble **$Al(OH)_3$** 531.1-531.53eV Aluminum trihydroxide No water soluble	**AlH_3** Aluminum Hydride (Though this is not found in XPS database, chemical form is shown.)

Table 2 Quantitative analysis of Al dissolution volume by ICPS

Group C : Immersing time=3.5h
Solution : 0.18μmTiO_2(5wt%)＋Cathilon(2.5wt％)+H_2O+UV:ON/OFF

Group	Solution	Content of Al ppm	Comments
C-1	TiO_2+Cathilon+H_2O (Immersing of Al)	1.5	Little solution of Al
C-2	TiO_2+Cathilon+H_2O+UV (Immersing of Al)	2.1	Little solution of Al

2.5 Estimation of Chemical Compounds Formed by Al Immersion Test

The oxygen, nitrogen and chlorine present in Cathilon dye, and the hydroxyl and hydrogen that form by the decomposition of water contribute to the chemical reaction of Al. It is necessary to verify the oxidation/dissolution of eight elements contained in A5052 to investigate the polishing phenomena of A5052. **Figure 2** shows the atomic concentrations (at%) of Al (blank), Al (immersed), A5052 (blank) and A5052 (polished) obtained by XPS analysis. The Al (blank) and Al (immersed) samples have large Al and O contents, and very small N and Cl contents. The A5052 (blank) and A5052 (polished) samples have large amounts of Al and O, very small amounts of N and Cl, a small Mg content, and no traceable Fe or other elements. Although Mg has a larger ionization tendency than Al, Mg dissolution was minimal during the immersion test of A5052 (this is described later in detail).

Table 1 shows the chemical compounds estimated from the XPS database (Internet reference: NIST X-ray Photoelectron Spectroscopy Database). Aluminum oxide (Al_2O_3) and its XPS spectrum is large (narrow analysis is shown later). Aluminum hydroxide is $Al(OH)_3$, nitrogen oxide is NO/Al, the nitride is AlN and two chlorides are $AlCl_2$ and $AlCl_3$. Chlorides are readily dissolved in water, so that Al^{2+} (Al^{3+}) ions are present in the solution. Although the Al_4C_3 carbide appears to form, it decomposes in water. There is no hydride present. Therefore, the chemical compounds on the aluminum surface are an oxide, a hydroxide, a nitrogen oxide, a nitride and a chloride.

3. Results and Discussion

A solution of TiO_2, Cathilon dye and H_2O (mixed-solution) was used to chemical and mechanical polishing of A5052. We discuss the polishing phenomena in relation to the chemical reactions during the immersion test in the absence or the presence of UV irradiation.

3.1 Identification of reaction by XPS and ICPS

Table 2 shows quantitative ICPS results for the Al surface immersed in a mixed-solution. The amount of dissolved Al increased slightly from 1.5 ppm in the absence of UV irradiation to 2.1 ppm in the presence of UV irradiation, when Al was immersed in a mixed-solution.

It is well known that pure Al is easily oxidized by oxygen in air and hydroxyl decomposed from water. The following chemical reactions form Al_2O_3 and $Al(OH)_3$ on the surface of Al:

$$2Al^{3+} + 3H_2O \leftrightarrows Al_2O_3 + 6H^+ \qquad (1)\ [8]$$

$$Al^{3+} + 3OH^- \leftrightarrows Al(OH)_3 \qquad (2)\ [9]$$

When TiO_2 decomposes H_2O in a mixed-solution, the reactive oxygen species of O^-, O^{2-}, O^{3-}, O and OH generate in solution under the photocatalytic action of TiO_2 [10]. The holes formed in TiO_2 do not oxidize Al, directly. Hydroxyl oxidizes Al in the absence of UV irradiation, although the reaction is weak.

$$TiO_2 + h\nu \rightarrow e^- + h^+ \qquad (3)\ [11]$$

$$H_2O + h^+ \rightarrow OH + H^+ \qquad (4)\ [11]$$

These reactions induce the following reaction:

$$Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \qquad (5)\ [12]$$

The water-immiscible solid of Al_2O_3 forms on the Al surface, so that the amount of dissolved Al in the mixed-solution is less. UV radiation promotes the photocatalytic reaction of TiO_2; however, the oxidation/dissolution of Al decreases by a reversible reaction between H and OH ($2H_2+O_2=2H_2O$).

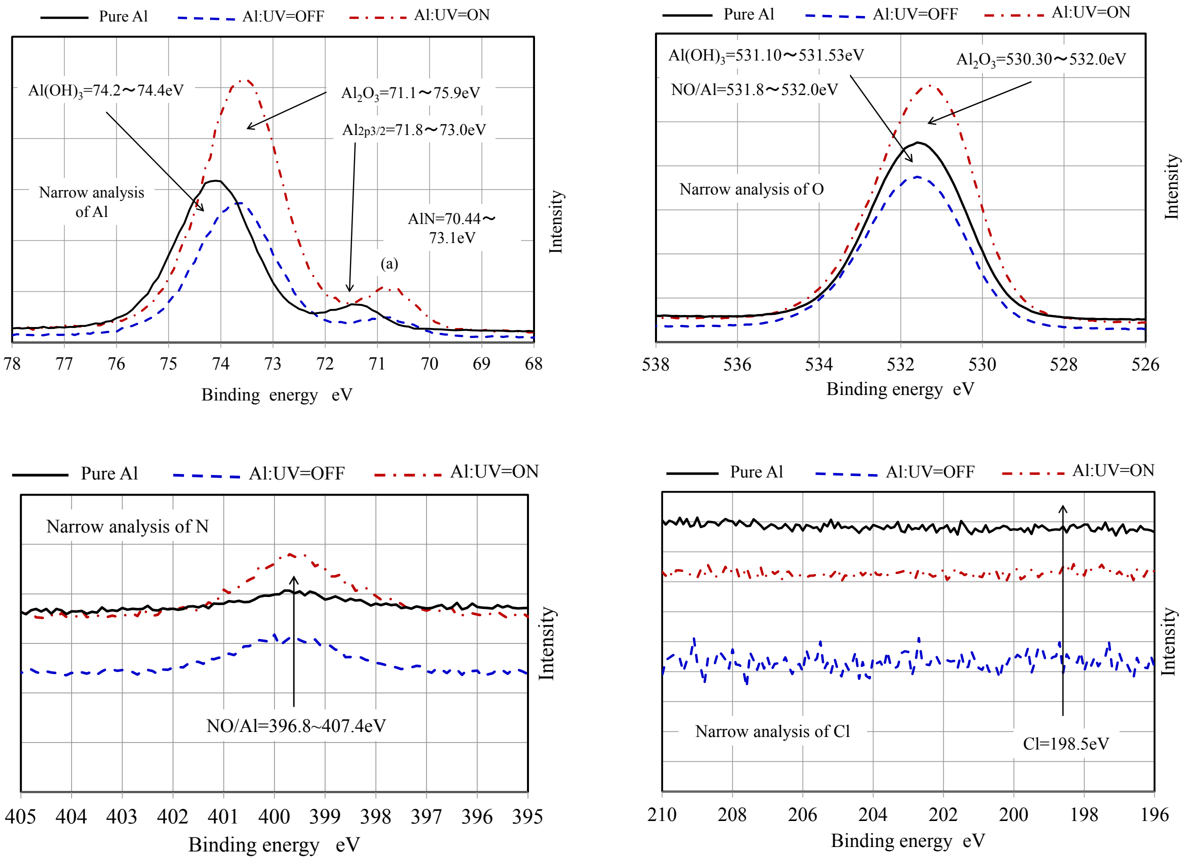


Fig. 3. Qualitative analysis of Al surface immersed in the mixed-solution.

We discuss the reaction of Al in a mixed-solution which the reaction factors are O, N and Cl of Cathilon dye. Elements involved with the chemical reaction are Cl^- ion, and N and O that are present in the polymer ion ($^+$) shown in Fig. 1.

$$Al \leftrightharpoons Al^{3+} + 3\ e^-$$

$$Al^{3+} + 3Cl^- \leftrightharpoons AlCl_3 \qquad (6)\ [8]$$

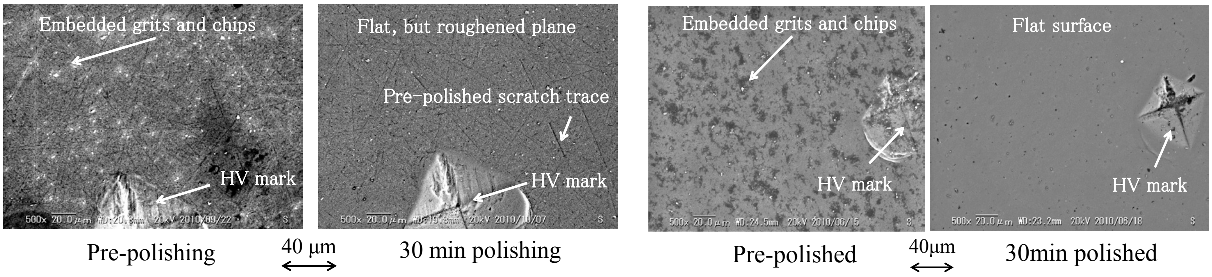
Al reacts with Cl to form $AlCl_3$, which is readily dissolved into the mixed-solution.

On the other hand, Cl^- acts as an electron donor. Both N and the O (electron donors) supply an electron, and Al acts as an electron acceptor. These lead to a reduction of Al on the surface. It appears that Al^{3+} forms a metal chelate by binding to N and O of Cathilon dye; however, it is difficult to identify the metal-chelate structure due to the large and complex polymer ion.

All chemical reactions shown in Eqs.(1)-(6) must cause in a mixed-solution immersed Al. It appears that the formation of Al_2O_3, NO/Al and AlN (described in the XPS analysis) consume more Al, so that there was no significant increase in $AlCl_3$ dissolved into the mixed-solution shown in Table 2.

Figure 3 shows XPS analysis results for the Al surface immersed in the mixed-solution. Narrow analysis of Al indicates that $Al(OH)_3$ forms on the Al surface because Al is easily oxidized. It was observed that Al_2O_3 forms on the Al surface immersed in the mixed-solution, as shown in the Al-narrow analysis. Its spectrum is large in UV irradiation. Narrow analysis of O indicates that $Al(OH)_3$ transforms to Al_2O_3 under UV irradiation. This causes a large spectrum for Al_2O_3 shown in the Al-narrow analysis. Narrow analysis of N indicated that NO/Al forms on the Al surface by reacting reaction with N in the air. The use of UV irradiation in U-RAM makes a spectrum large. N exists in Cathilon dye. UV of 254 nm provides larger decomposing energy than composing energy of C-N binding. UV irradiation appears to generate ionized nitrogen by the decomposition of Cathilon dye [6]. Ionized nitrogen contributes to the formation of AlN by dissolving into the mixed-solution. Narrow analysis of Cl indicates that a chloride is not formed on the Al surface, because no trace of Cl was evident. Table 2 shows that $AlCl_3$ is dissolved into the mixed-solution without UV irradiation. It appears that the formation of Al_2O_3, NO/Al and AlN consume more Al. The reduction from $AlCl_3$ to Al on the Al surface (shown in Eq.(6)) may cause slight solubility of Al in the mixed-solution under UV irradiation.

The oxidation of Al leads to the formation of Al_2O_3, and NO/Al and AlN form on the Al surface immersed in the TiO_2-Cathilon dye-solution. UV irradiation makes their spectra large as shown in Fig.3. Since the chemical reaction is large, Al-oxidization progresses in judging from the results shown in Fig.3. Mechanical polishing using TiO_2 or chemical polishing using Cathilon dye appears to make the newly formed surface of A5052 flat, interchangeably.



Pre-polishing 30 min polishing

UV:OFF(I)

Pre-polished 30min polished

UV:ON(S)

Fig. 4. Change of A5052 surface by polishing with and without U-RAM

3.2 Polishing with 0.18 µm TiO_2 particles, 0.5 wt% Cathilon dye and H_2O (mixed solution)

A5052 was previously polished to a surface roughness (Ra) of 10.2 nm without UV irradiation. **Figure 4** shows SEM micrographs of the change in the polished surface. The surface roughness was varied from 10.2 nm Ra to 10.4 nm Ra; however, no change of surface roughness appeared after 30 min polishing. A little chemical corrosion by TiO_2-Cathilon dye-solution in the absence of UV irradiation does not remove pre-scratched grooves. A5052 pre-polished to a surface roughness of 16.1 nm Ra was used for polishing with UV irradiation. The surface roughness abruptly decreased from 16.1 nm Ra to 7.0 nm Ra after 30 min polishing. The polished surface in the presence of UV irradiation is clean as shown in Fig. 4. A few embedded abrasive particles were evident; however, no pre-scratched grooves were observed due to the increased polishing effect with UV irradiation for the A5052 surface. However, it is difficult to discuss the difference in the surface conditions with respect to the XPS analysis. Then, the quantitative treatment of chemical-compounds formation with the XPS analysis still remains as the subject issue.

3.3 ICPS Analysis of A5052-Solution and XPS Analysis of A5052-Polished Surface

Table 3 shows quantitative ICPS analysis results for the A5052 immersion solution. The amount of Al dissolution was slightly larger than that shown in Table 2 under UV irradiation. This is because pure aluminum easily forms $Al(OH)_3$ and Al_2O_3, which prevents further dissolution of pure aluminum. The ionization tendency of Mg is larger than that of Al; therefore, $MgCl_2$ formed is easily dissolved in water. However, the 2.5 wt% of Mg composed in A5052 is significantly less than that of Al; therefore, the amount of Mg dissolved in a mixed-solution must be less. The very small XPS spectrum of Mg and $Mg(OH)_2$ for A5052 indicates only a small amount of Mg was dissolved. Table 3 shows the zero solubility of Fe in solution, in which is consistent with the XPS analysis. Therefore, the oxidation/dissolution of Al is the main mechanism for the polishing of A5052.

Table 3 Quantitative ICPS analysis for the amount of A5052-dissolution

Group D : Immersing time=3.5h
Solution : 0.18µmTiO_2(5wt%)＋Cathilon(2.5wt%)+H_2O+UV:ON/OFF

Group	Solution	Al ppm	Mg ppm	Fe ppm	Comments
D-1	TiO_2+Cathilon+H_2O (Immersing of A5052)	2.4	1.6	0.0	Little solution of elements
D-2	TiO_2+Cathilon+H_2O+UV (Immersing of A5052)	4.0	1.8	0.0	Little solution of elements

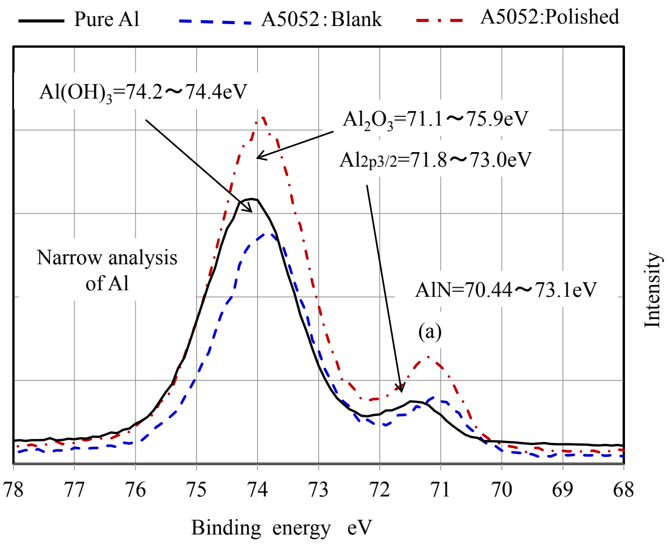


Fig. 5. Qualitative XPS analysis of the A5052 surface immersed in the mixed solution

Figure 5 shows XPS narrow analysis of the A5052 surface. The $Al_{2p3/2}$ spectrum appeared for the blank-A5052, and that of Al_2O_3 appeared for the polished-A5052. Thus, the formation of an oxide contributes to polishing and flattening of the A5052 surface.

4. Conclusions

The following conclusions were obtained from investigation of U-RAM with A5052 using quantitative ICPS analysis of a solution that dissolved Al, and using qualitative XPS surface analysis of Al immersed in a mixed-solution of TiO_2, Cathilon dye and H_2O.

1) Pure Al dissolves slightly into TiO_2-Cathilon dye solution, and the amount of dissolved Al increases slightly under UV irradiation.
2) Al forms an oxide, a nitrogen oxide and a nitride.
3) A chloride of Al dissolves into TiO_2-Cathilon dye solution.
4) The polishing process with TiO_2-Cathilon dye solution polishes and flattens the A5052 surface under UV irradiation.

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