

THE APPLICATION OF ARC OXIDATION PROCESS ON ALUMINUM ALLOY

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Abstract - The aim of the present study is to investigate the coating deposition mechanism of aluminum alloys by means of micro arc oxidation. The surface characterizations were performed with X-ray diffractometry, scanning electron microscopy, surface roughness measurement equipment and microprocessor coating thickness gauge test. The results show that the micro-arc oxidized coatings on Al alloys show two distinct regions, i.e. a porous overlayer region consisting predominantly of γ -Al₂O₃ which was produced at the higher cooling rate, and a dense internal region consisting predominantly of α -Al₂O₃ which was generated at the lower cooling rate. They are well bonded on the Al substrate [1]. The thickness of the coatings significantly influenced the mechanical properties. In this study we have developed breakthrough surface treatment technology, opening up new horizons for light, valve metals [2].

Keywords - Micro Arc Oxidation, Aluminum Alloy.

Özet - Bu çalışmadaki amaç, Al alaşımların mikro ark oksidasyon yöntemi ile kaplama mekanizmalarının incelenmesidir. Yüzey karakterizasyonu X-ışınları difraksiyonu, SEM, yüzey pürüzlülüğü ölçüm cihazı ve mikro işlemci kaplama kalınlığı ölçüm testleriyle yapılmıştır. Sonuçlar, Al alaşımların üzerindeki mikro ark oksidasyon kaplamaların iki farklı bölgeyi gösterdiğini sergilemiştir. Porözlü üst tabaka bölgesinde baskın olarak γ -Al₂O₃ içermektedir ki, bu yüksek soğutma derecesinde oluşur. Diğer yoğun iç bölge ise baskın olarak α -Al₂O₃ içerir ki, bu da düşük soğutma derecesinde meydana gelir. Her iki bölgede, Al altlık üzerinde iyi bağlanmıştır [1]. Kaplamaların kalınlığı, mekanik özellikleri önemli şekilde etkilemektedir. Biz bu çalışmada hafif ve valf metallere yeni ufuklar açılması için yüzey işleme teknolojisini geliştirdik [2].

Anahtar kelimeler - Mikro Ark Oksidasyon, Alüminyum Alaşım.

I. INTRODUCTION

The practice of anodizing, or controlled oxidation, of aluminum and aluminum alloys is more than seven decades old. The primary intent of anodizing aluminum and aluminum alloy parts is to protect a highly reactive surface against corrosion in aqueous environments, such as humid air and sea water. Because the anodic coating can be produced in a variety of colors, painted anodized parts are used in architectural applications. Furthermore, because the anodization process produces a hard ceramic coating, many times harder than that of the substrate from which it is formed, anodic coatings are also used to protect aluminum parts from abrasion, especially sand abrasion [3].

Aluminum alloys combine many positive properties: a low density, a high strength, a high electrical and thermal conductivity and viscosity, a high corrosion resistance of many organic acids, seawater, good adaptability to manufacturing [4,5]. This makes them indispensable for many industries. For example, one can hardly imagine the aviation industry, food industry, power industry, building, etc. without application of aluminum alloys. At the same time there is a number of disadvantages as their low hardness, low module of elasticity, high chemical activity with many non-organic acids, low wear resistance. To avoid these disadvantages, one can produce aluminum oxide (Al₂O₃) on tool surfaces, since this coating is very hard and has high corrosion resistance. One of the known methods, which allow one to do this, is the micro-arc oxidation of the aluminum alloy by an electric arc in a special electrolyte [6].

The micro-arc oxidation (MAO) is one of the most promising types of surface treatment, which recently has been widely applied for production of multi-functional coatings, which found their application in many different industries. The micro arc oxidation relates to electro-chemical processes, but its feature is application of energy of electrical micro-discharges in an electrolyte in the surface of treated tools, which allows one to produce coatings of special properties.

This allows one to improve the ceramics-like coatings with a composition, structure and properties which can be regulated in a wide range, as well as to apply these coatings as wear and corrosion resistant, electric-insulating, heat-resistant as well as decorating coatings [7,8].

In such a way, the goal of this work was to investigate the structure and properties of Al_2O_3 coatings, which had been deposited to the Al alloy substrate using the micro-arc oxidation.

Traditional anodizing is an electrochemical oxidation process during which aluminum is the anode. The electric current passing through an electrolyte converts the metal surface to a durable aluminum oxide. The part to be anodized is connected to the positive terminal of a direct current (DC) power source, and a nonreactive metal, such as stainless steel, is connected to the negative terminal. The aluminum part, or the anode, and the stainless steel cathode are immersed in an electrolytic bath, and a DC voltage is applied across them. The potential difference is of the order of 20-100 V, and the current densities are 1-10 A/dm².

The electrolytic baths comprise aqueous solutions of chromic acid, orthophosphoric acid, sulfuric acid, oxalic acid, or combinations thereof. Because the electrolytic baths have appreciable resistivity, and because the anodization process itself is exothermic, the temperature of the electrolytic bath increases greatly during anodizing. Since the anodizing process is quite sensitive to temperature, the bath temperature is controlled rather closely by heat exchanger or refrigeration equipment [9].

There are many reasons to anodize a part. Followings are a few considerations and the industries that employ them:

- **Appearance:** Products look finished, cleaner, better and longer. Color enhances metal and promotes a solid, well-built appearance while removing the harsh metal look. Any aluminum product can be color anodized.
- **Corrosion resistance:** A smooth surface is retained while weathering is retarded. Useful for food handling and marine products.
- **Ease in cleaning:** Any anodized product will stay cleaner longer and are easier to clean when they do get dirty.
- **Abrasion resistance:** The treated metal is tough, harder than many abrasives, and is ideal for caul plates, tooling and air cylinder applications.
- **Non-galling:** Screws and other moving parts will not seize, drag or jam while wear in these areas is diminished. Examples include gun sights, instruments and screw threads.
- **Heat absorption:** Can provide uniform or selective heat absorption properties to aluminum for the food processing industry.

- **Heat Radiation:** Used as a method to finish electronic heat sinks and radiators [10].

Despite the many decades of experience and the expensive equipment employed by the traditional anodizing plants, the acid bath based DC anodizing process has several limitations. By the very nature of the low voltage DC power employed, the anodic coating is quite porous. Often the volume percent of pores is as much as 50%.

Additionally it takes many hours to produce a coating of a few tens of micrometers thick, because of the low current densities employed. The electrolytic baths comprise extremely low pH acidic electrolytes, and thus the process does not meet many of today's environmental regulations. The expensive equipment, such as the electric power supplies and heat exchanger, makes the process capital intensive.

The traditional process cannot be used for anodizing aluminum alloys containing high concentrations of Cu and Si, also it cannot be used for anodizing other reactive metals, such as Ti, Zr, Mg, etc., intermetallic compounds and metal matrix composites [9].

Despite all these disadvantages, among the different types of metal finishings, anodizing offers manufacturers many more options and combinations. Anodizing is not a plating process. Plating deposits materials onto a metal surface, whereas anodizing does not. The difference between plating and anodizing is that the oxide coating is integral with the metal substrate as opposed to being a metallic coating deposition. The resultant surface characteristics coupled with the inherent qualities of aluminum creates a metal of virtually unlimited capabilities. Anodizing services are needed in virtually any industry imaginable. From fashion jewelry and cosmetics, to aerospace; from the medical and military fields to the computer and high-tech electronic industries [10]. Anodizing is an electro magnetic process that can convert raw aluminum surfaces to an artificial oxide coating. This process is similar to the way a car battery uses an electrolyte, or acid to conduct electricity. A complicated series of steps are needed to perform anodizing correctly: Pre-cleaning, Etching, Deoxidizing, Anodizing, Dyeing, Sealing. For optimal results, careful rinsing is performed after each immersion. By adjusting immersion times, chemical concentrations, solution temperatures, mixtures, and electrical conditions, a variety of anodizing effects can be produced. A wide selection of surface finishes can be accomplished from very bright to dull matte along with one or more bright or subtle colors.

A common specification method for anodizing is known as the mil. spec. MIL-A-8625, for example, lists at least six types and two classes of electrolytically formed

anodic coatings on aluminum and aluminum alloys for non-architectural applications. Class and type designations are also used.

Table 1. Types of anodizing [11]

TYPE	DESCRIPTION	FINISH PROPERTIES
I	Chromic acid	Very few manufacturers offer this type of finish, due to the difficulty of disposing of the chromic waste. The alternative is usually Type II requests.
II	Sulfuric acid	This is the conventional, most widely used form of anodizing in use today. Coating typically is .0002 to .001 inches thick. This type also accepts a wide range of permanent color dyes in their true colors. The process offers moderate corrosion and abrasion resistance.
III	Sulfuric hard	This type offers the best possible anodize. Coating is thicker (from .001 to .003 inch), harder and more dense than Type II. This is accomplished by using higher voltages, acid concentrations and longer soak times than Type II. It also accepts dark permanent color dyes but with gray to gray-green tinges (from the thick anodic coating). Thickness is a combination of one-half penetration and one-half buildup on surfaces.

II. THE MICRO ARC OXIDATION PROCESS

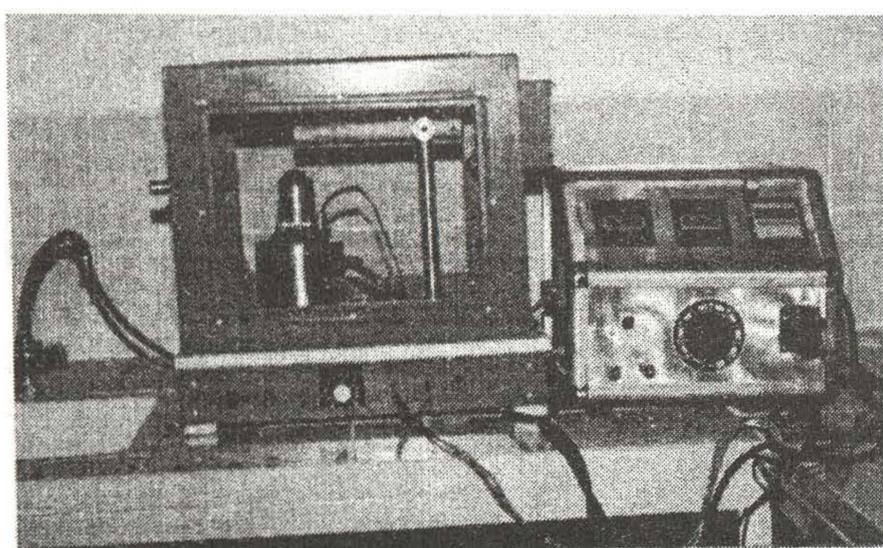


Figure 1. MAO System

Micro arc-discharge oxidation (MDO) is a cost-effective plasma electrolytic process which can be used to improve the wear resistance of aluminum alloy parts by creating a hard thick alumina coating on the component surface[12]. Micro arc oxidation (MAO), also called pulsed electrolytic oxidation (PEO) / pulse plasma anodisation / spark discharge anodizing, allows the deposition of

aluminum oxide coating on the surfaces of aluminum alloys. Micro arc oxidation is one of the most perspective methods of surface treatment receiving wide applications for obtaining of multifunctional coatings on metals and alloys. It is the development of the usual electrochemical process of anodizing, but has a number of differences. Essentially, it involves the modification of a conventional anodically grown oxide film by the application of an electric field greater than the dielectric breakdown field for the oxide. Discharges occur, and the resulting plasma-chemical reactions contribute to the growth of the coating. More significantly, local conditions of heat and pressure sinter and anneal the coating. Rapid cooling also modifies the oxide, resulting in a complex mixture of amorphous material and nanocrystalline phases.

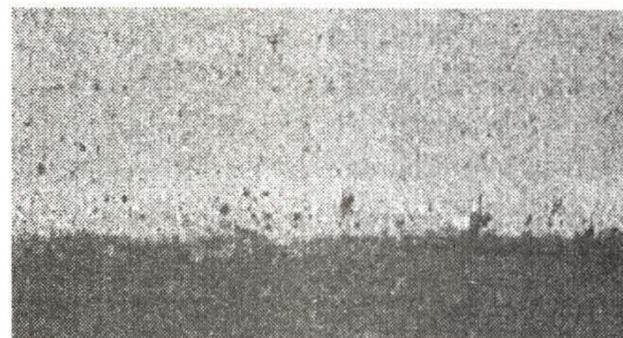


Figure 2. 50,88275 micron MAO coating on aluminium alloy (0,95% Mg, 3,85% Cu, 95,20% Al) [13]

The process may be applied to any valve metal such as aluminium, magnesium or titanium, and to a wide range of their alloys. Coating properties depend on the substrate alloy, but also on the electrolyte used and on the many parameters of the electrical system. On aluminum, dense alumina coatings (approximately 3% porosity) up to 130 microns thick can be formed, but more porous coatings up to 600 microns in thickness can also be formed by using different electrolytes. Typical alumina coatings consist of a relatively dense polycrystalline layer of alpha-alumina, with a softer, more porous layer of gamma-alumina formed on top [14]. The process combines electrochemical oxidation with a high voltage spark treatment in an alkaline electrolytic, resulting in aluminum oxide coating on the surfaces of Al based alloys. The process employs alkaline electrolytes whose composition is extremely critical to the coating rate and the properties of the anodic film that is formed. The pH of the electrolyte is in the range 8-12 and is thus environmentally sound.

MAO is carried out in weak-alkaline electrolytes at the voltage of alternating pulsed currents of an order above that of anodizing (up to 1000 V). The process employs alternating currents at high voltage and high current. Because of the high voltage, a microplasma surrounds the electrodes and the oxygen ions produced in the plasma diffuse through the anodic film into the aluminum substrate to react and form more anodic film.

It does not require the preliminary prepared surface and allows to obtain thick (up to 300-400 μ) coatings without ecology-dangerous refrigerating equipment. The high-

voltage and high-current allow the production of anodic films of the same thickness as that of the traditional process in a fraction of the time. MAO-coatings are characterised by very high hardness (up to 2000-2500 kg/mm², 1400-1700 HV), wear resistance and controllable porosity (2-5%). Because the voltages are higher than the breakdown voltage of the film formed, open channels are not necessary for sustaining the process and hence dense thick layers of non-porous film can be readily formed.

Because the process employs AC power, the productivity is increased. The power from an electrical utility supply can be used with proper controls to the electrochemical tank thus making the process less capital intensive. There is no need for power rectification and waveform smoothing. Because of the high density of the coating, practically there is no change in the dimension of the anodized part, and a completely finished part can be coated without major post-processing finishing operations. In some works about Micro arc oxidation process, also produces an outer soft coating of about 10% that may be buffed off; the remaining inner layer, is an extremely hard ceramic layer. It creates a thick ceramic coating, which exhibits excellent resistance to wear, heat and chemical corrosion. Additionally, the coating acts as an electrical insulator. There is no limitation on the desired thickness of the ceramic coating and the process is applicable to all alloys of Al, Mg, Ti, Zr and some composite materials. It is environmentally sound, totally different and far superior to current Hard Anodizing processes [3].

Micro arc oxidation is a novel technique to deposit ceramic coatings on the surface of valve metals and their alloys. Valve metals generally include Al, Mg, Ta, W, Zn and Zr. Such metals in their natural state are protected by thin, self healing, tightly adherent dielectric oxide films which resist the passage of current in the anodic direction. If using a valve metal as an anode, it is necessary to raise the potential of the valve metal surface to a high value in order to pass significant current through the anode. In MAO process, the anode made by valve metal materials is immersed in an aqueous solution, and the voltages as asymmetric alternating current are applied between the anode and the cathode [15].

MAO is used for imparting protective coating on all types of Al alloy components to enhance the service life several times. Ceramic aluminum oxide coating obtained by MAO has;

- Extremely high adhesion
- High Vickers hardness upto 25 GPa (1400-1700HV)
- High erosion & abrasion wear resistance
- High thermal shock resistance
- Dielectric properties (operates up to 500°C and dielectric breakdown occurs at a field of 10V per micron)

- Friction: polished coatings have a low friction coefficient (0.5 measured with respect to itself when dry, 0.1 when lubricated)
- Impregnation: coatings may be impregnated with polymers such as Teflon to modify their properties for specific applications
- Heat resistance: coating can withstand several seconds of 2000°C without undergoing any change
- Corrosion resistance: coated alloys can withstand over 7000 hours in a salt-fog test chamber

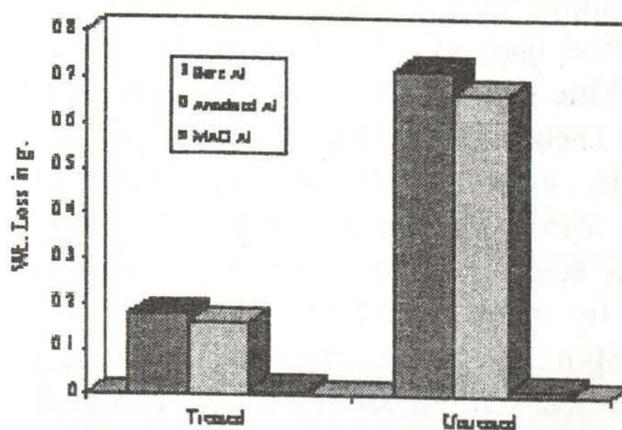


Figure 3. MAO

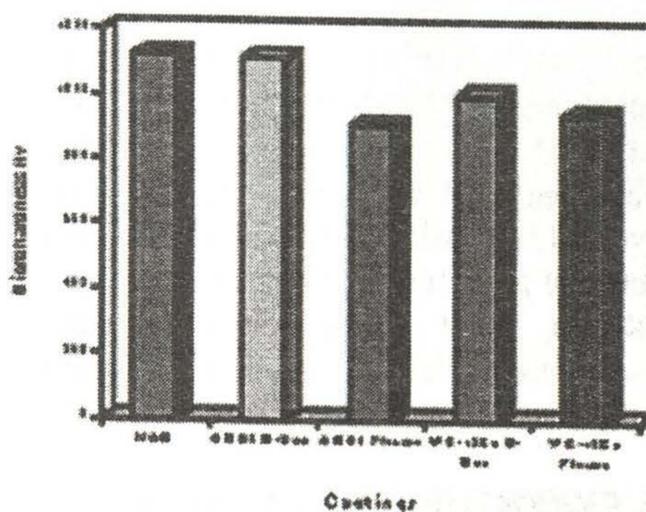


Figure 4. MAO Coating-HV Diagram

Above all, unlike with the traditional anodization process, aluminum alloy parts of any composition can be successfully anodized by the micro arc oxidation process. Even more importantly, a variety of ceramic "alloy" coatings, such as Al₂O₃-SiO₂, Al₂O₃-MgO, Al₂O₃-CaO, etc.

The Micro arc oxidation process is also suited for a hard coating inside surface of a part i.e. cylindrical, conical or spherical hollow parts. Many coating processes in the market, including chemical vapor deposition (CVD), physical vapor deposition (PVD), IVD, Plasma enhanced physical vapor deposition (PEPVD), sputtering and thermal spraying are unable to coat the inside surface of a long part.

Micro arc-discharges migrate on the being processed surface loaded into the electrolyte and exercise thermal,

plasma-chemical and hydrodynamics influence upon matrix metal, coating and electrolyte. It results in the formation of the ceramic-like coatings with the elemental and phase composition, structure and properties adjustable in a wide range. The MAO-coatings on aluminum alloys consist of three layers usually: thin transitive inner layer, the main working intermediate layer with the maximum hardness and minimum porosity consisting, in main, of $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$ and the outer friable technological layer, which can be removed afterwards if it is necessary [16,17].

MAO-technology application prolongs lifetime of the most important critical parts of machines and assemblies by 1.5-4.5 times. This technology ensures considerable cutting of expenses needed to buy spare parts and provide maintenance. Light and inexpensive aluminum or magnesium coated with the micro arc oxidation process can replace heavier steel or more expensive composite materials required by many manufacturing industries - including transportation, electronic, chemical, sports and others. Any desired coating thickness can be achieved with speedy production, economy of raw materials and total environmental safety.

Ceramic coatings made by MAO technology can be effectively used for hardening of Al parts in various areas of machinebuilding, such as engines manufacturing, hydraulics, textile industry, etc. It can be applied for pistons, diesel fuel pumps, valves thermo-couple cases for pyrolysis furnaces, batchers, parts for aggressive liquid pumps, front surface seals for rotary pumps, etc. Parts made of Al-alloy and treated by MAO-method can effectively substitute the parts made of heat treated steel, high-strength cast-iron, hard metal, ceramic, parts hardened by hard-chromium plating, hard-anodising and the parts made by gas-thermal spraying method [18].

III. EXPERIMENTAL DETAILS

The substrates of aluminum alloy rectangular coupons (Mg 0,95%, Cu 3,85%, Al the rest) with $50 \times 25 \times 5 \text{ mm}^3$, were cleaned in wet calcinated soda, rinsed with water to remove the mechanical contamination and degreased. Coating was formed using a MAO unit constructed in-house, which consisted of an insulated electrolyte bath and a high voltage asymmetric dc power supply. One output of the power supply was connected to the bath; the other was connected to the sample immersed in electrolyte. The electrolyte was prepared from a solution. The electrolyte temperature was controlled to remain lower than 70°C during treatment [15]. Coatings were fabricated by use of a micro arc oxidation technique where a voltage pulsed at mains frequency (50Hz) was selected in the range 300-350V, depositing time 35 to 70 min, average current density varying from 3-15 A/dm^2 . The basic parameters of MAO are the duration of the treatment τ , composition and the temperature of electrolyte, the averaged density of the current j and the ratio of the cathodic to anodic currents I_c / I_a on the

sample (it is under negative and positive potential alternately).

A scanning electron microscope (SEM) was employed for observation of the microstructure and surface morphology of the coatings before and after the various tests, and an EDX attachment was used for qualitative elemental chemical analysis. A scanning electron microscope (SEM) JEOL 840 A was employed for the observations of the surface and cross-section morphology of the coatings and analytic system (IXRF). Perthometer M1 is a portable equipment which is used to measure the roughness of the surface. Measurement interval is max. $150 \mu\text{m}$ and it has ISO 3274 quality. The thickness of the micro-arc oxidation coatings was measured with a microprocessor coating gauge. The Al alloy specimen and the wall of the stainless steel container were used as the anode and the cathode, respectively. The crystallographic characteristics and the phase composition of the coatings were investigated using a SHIMADZU XRD-6000 model and Cu X-ray tube ($\lambda=1.5405 \text{ Angstrom}$) X-ray diffractometer (Cu $K\alpha$ radiation).

IV. RESULTS AND DISCUSSION

IV.1 Phase Analysis

X-ray diffraction (XRD) studies of MAO coatings deposited in the current density range of $3 \text{ A}/\text{dm}^2 \leq j \leq 15 \text{ A}/\text{dm}^2$ show that these coatings consist mainly of, $\gamma\text{-Al}_2\text{O}_3$ and a few other impurities. Due to the very little content of impurities, we roughly think that MAO coatings are only composed of $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$. The difference in $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ content for the outlayer and internal layers of coatings is mainly caused by variation in the cooling rate of molten alumina in the micro-arc zone. Strongest 3 peaks we attributed were ;

No	Peak no	2Theta(deg)	d(A)	I/I ₁
1	2	44.8620	2.01876	100
2	1	38.6201	2.32944	44
3	4	65.2136	1.42947	33

We found sharply expressed peaks of $\gamma\text{-Al}_2\text{O}_3$ at 100, 44, and 33 as I/I₁. Also we did the same phase analysis for the substrate material by XRD and Cobalt X-ray tube, $\alpha=1,7902$;

$d\text{\AA}$	I/I ₁	hkl
2.338	100	111
2.024	47	200
1.431	22	220
1.221	24	311
1.1690	7	222
1.0124	2	400

As it was shown the substrate is aluminum.

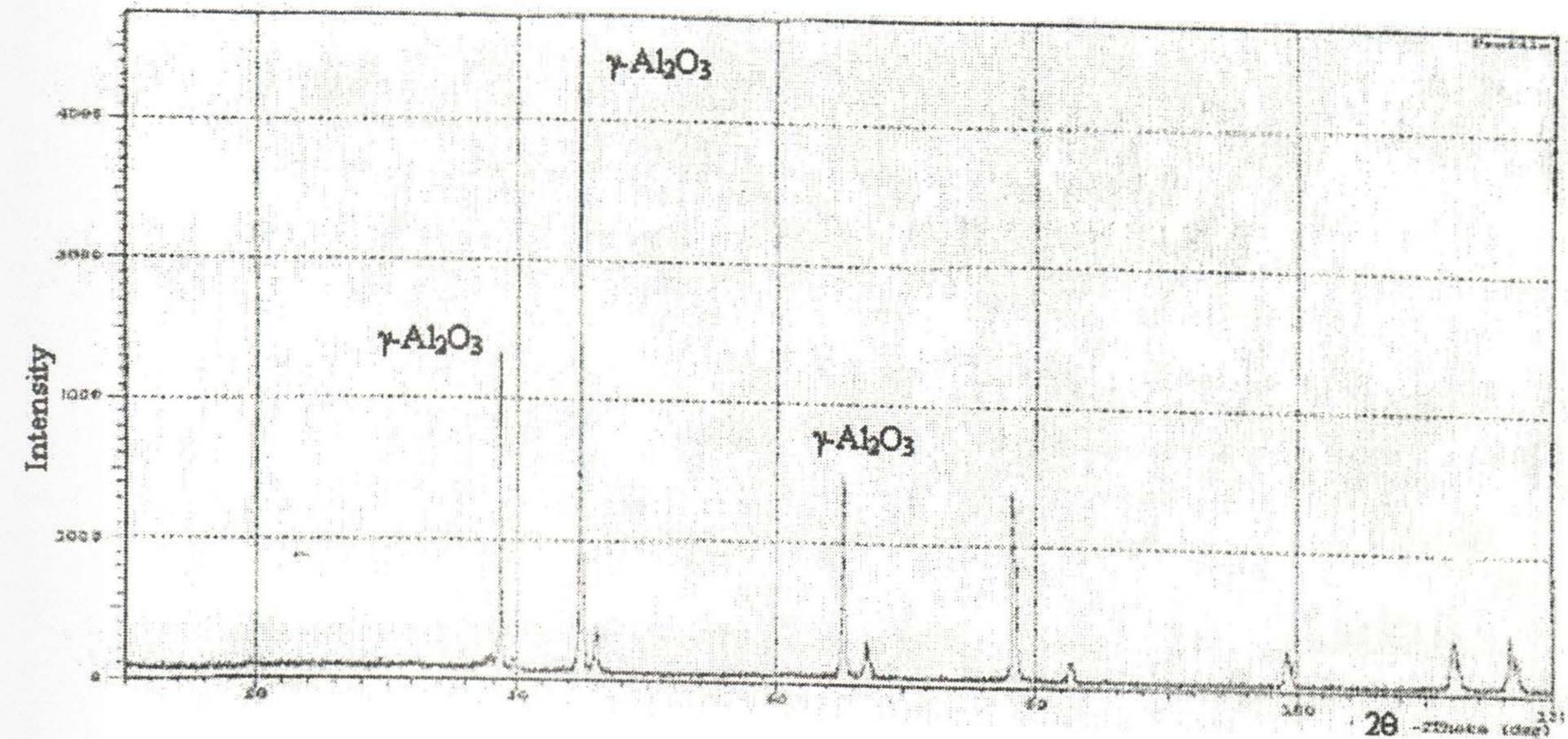
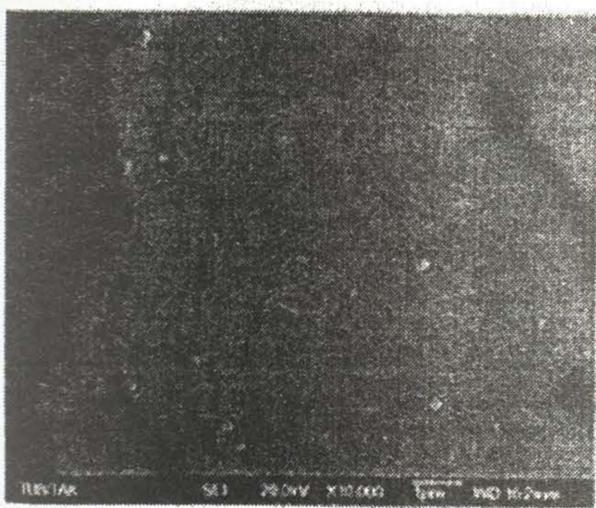


Figure 5. XRD

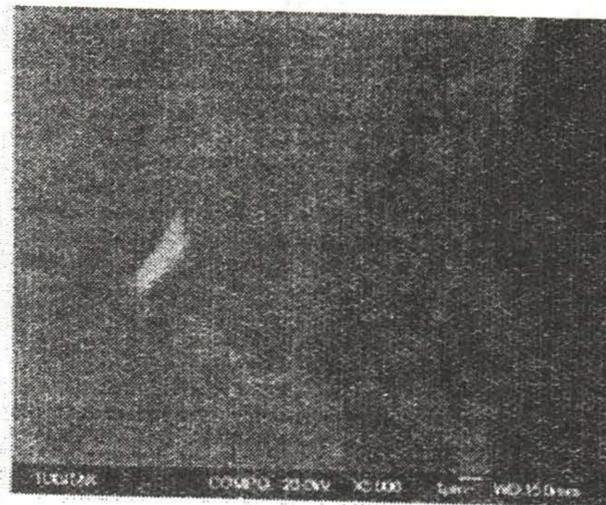
V.2 Analysis of Investigation of Sample Surface Morphology

Investigations of the surface morphology of the treated aluminum alloy was performed using the scanning electron microscope JEOL 840A-IXRF. Investigating the surface morphology of the aluminum alloy using the scanning microscopy, we found foreign regions. One can see them in SEM photos made for the treated sample surface (Fig.6a), coated surface and the matrix (Fig.6b). And energy-dispersive spectroscopic attachment was used for quantitative analysis at the other side as you see.



Element	Weight%	Atomic%
O K	51.47	64.14
Al K	48.53	35.86

Figure 6a. Coating Analysis of MAO process



Element	Weight%	Atomic%
Mg K	0.95	1.08
Al K	95.20	97.25
Cu K	3.85	1.67

Figure 6b. Matrix Analysis of MAO process

Also EDX analysis done to the sample. It was shown at the belows figure 7a and 7b.

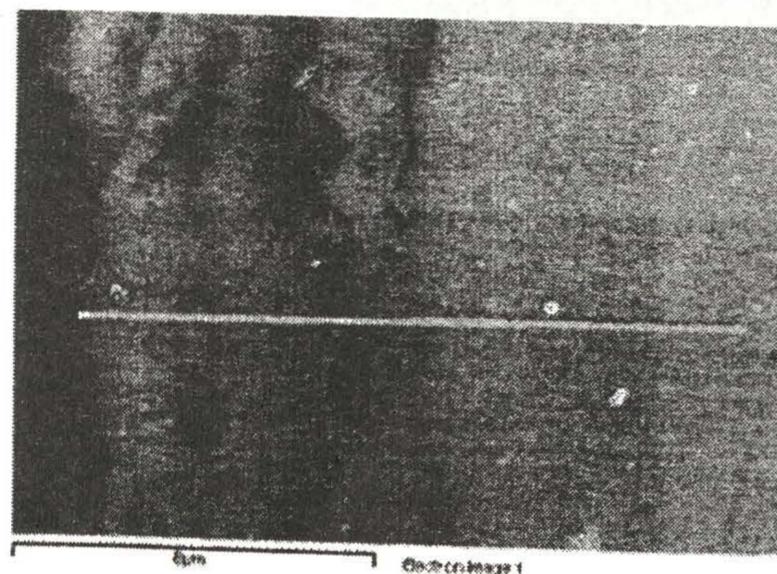


Figure 7a. EDX of MAO process

V. CONCLUSIONS

micro arc oxidation system was funded. This device is an electrolyte bath with transparent walls for observation. The MAO process occurs at room temperature in a very dilute and ecologically safe electrolyte. A typical electrolyte might include sodium phosphate, sodium hydroxide and hydrogen peroxide at concentrations of less than 5 gram per liter.

The result of this work was founding and then producing Al_2O_3 coatings on Al alloy with uniform element concentration over the whole depth. Based on the experiments mentioned above, MAO technology is superb and has more advantages over technology, ecology and economically, also the best surface quality.

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