Anodization of Twin Roll Cast Aluminum Sheets

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Anodization of aluminum alloys and its process parameters has been established based on material characteristics of conventional DC cast and hot rolled materials. There has been almost no detailed investigation to elucidate anodization behaviour of twin roll cast aluminum sheets. In the present study, twin roll casting was employed to produce materials exhibiting equivalent performance to those of conventional counterparts during anodization processes. New processing frames in chemical and electrochemical steps of anodization has been tested. Evolution of surface coating, associated pore size and surface features has been correlated with different combination of anodization parameters applied and compared with those of DC cast sheets. Optical microscope and FEG were used for characterization studies.

Keywords: Twin Roll Casting, anodization, FEG-SEM

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1.Introduction

Anodizing is one of the processes which add value to aluminum in application areas where aesthetic and durability needed. Originally, interest in the process of anodic aluminum oxidation is stimulated to cope with corrosion. Today, for Direct Chill casted (DC) aluminum parts, anodizing is a conventional surface modification process which can successfully be employed in various electrolytes and under various process parameters [1-6]. Recently, there has been studies on employing the perfectly organized nanoporetic structure of anodic oxide thin films as templates for nanowire and nanotube production [7-10].

However, anodization of aluminum alloys and all related process parameters have been developed for those materials produced with DC casting and hot rolling processing route. No interest has been given to Twin Roll Cast (TRC) aluminum products as far as anodizing is concerned. Moreover, the customers define the surface appearance of anodized TRC products as “brighter than that of DC products”, which means unaccaptable surface quality for them. Therefore, this study has been conducted in order to frame the optimum casting, heat treatment and anodization process parameters for obtaining the surface appearance as anodizing market desires. Main reason retarding the development in favor of TRC material is some surface features inherited from solidification characteristics of the casting method. These features significantly impares the surface quality after anodization. Surface segregations are among those becoming very severe if critical rules in casting process is violated. TRC aluminum has different microstructure than that of DC cast materials [11,12]. Water cooled caster rolls provide very high solidification rates (upto 800 ^{0}C/sec). Rapidly solidified outer skin, can be called featureless zone, has a supersaturated microstructure with very fine grains decorating this limited volume. This layer can still be present with the rolling and intermediate annealing unless it is exposed to any heating cycle resulting in any change in the characteristics of supersaturated layer.

Solidification rate decreases with the advancement of the strip between rolls due to the initially formed outer skin preventing heat transfer. Columnar grains occupying the quarter plane of the thickness and almost equiaxed ones present at the mid-plane exhibits typical through-thickness grain structure of a TRC cast strip. Response of the supersaturated layer to any electrochemical reaction is different than any microstructure that involves stable phases. In this paper, non-uniform grain size and intermetallic distribution originated from this non-equilibrium solidification conditions on the surface are reported. The effects of these non-uniformities on anodic oxide coating characteristics were investigated and compared to that of DC aluminum.

2. Experimental Procedure

The specimens employed in this study were produced by twin roll casting. For TRC products, anodizing current density is held constant and other parameters have been changed in order to have different surface features. Various surface features have been obtained by changing duration in etching and exposing the products in rolling and annealling practices. AA1050 (99.5%-99.6% Al) aluminum alloys were anodized under different surface preparation and anodizing parameters in sulphuric acid electrolyte (Table 1). The surface area of all samples were 4dm^2. The current densities are arranged such that 1-2 A is applied on 1 dm^2 of surface area. The resulting surface characteristics were compared with conventional DC cast, hot rolled and anodized specimen (DC), which is accepted as good quality by the customers and the consumers. In order to reveal the effect of etching on the homogenity of anodic oxide film, different etching times were employed on TRC1. TRC1 and TRC2 are in H14 and H24 tempers, respectively. The cold rolling and tempering sequence of the process employed to obtain H14 tempered materials causes the grains to recrystallize. On the other hand, processing route for obtaining H24 temper does not involve any recrystallization treatment. Final strength is achieved with the help of back-annealing and therefore initial grain structure of as-cast strip is retained. The coating parameters for all specimens were given in Table 2. The coating thicknesses were determined by cross-sectional metallography. As can be seen from Table 2, the anodic oxide coating thickness on DC cast specimen is much higher than those of TRC specimens even under lower current density values. For obtaining thicker coatings on TRC specimens, various current density, bath composition, surface preparation parameters should be tried and tested and then optimum parameters should be determined.

Table 1. *The compositions of the degreasing, etching, deoxidation and anodizing baths.*

Degreasing	Alkaline bath (5%)
Etching	Sodium Hydroxide (100 g/l), 45 g/l Al
Deoxidation	Nitric Acid (20%) and Fluoric Acid (5%)
Anodizing	Sulphuric Acid (180g/l), 5-15 g/l Al

Table 2. *Surface preperation and anodizing paramaters of specimens.*

	Specimen	TRC1	TRC1	TRC1	TRC2	TRC2	DC
Degreasing	T (^{0}C)	70	70	70	70	70	70
	t (min)	10	10	10	10	10	10
Etching	T (^{0}C)	70	70	70	60	70	50
	t (min)	20	12.5	5	10	10	10
Deoxidation	T (^{0}C)	30	30	30	RT	RT	RT
	t (min)	3	3	3	3	3	3
Anodizing	T (^{0}C)	23	23	23	23	23	20
	t (min)	20	20	20	20	15	10
	I (A)	6	6	6	6	6	4
	V (V)	10.3	10.2	10.2	10.3	10.2	15.5
	Material Thickness (mm)	2	2	2	1.5	1.5	0.5
	Temper	H14	H14	H14	H24	H24	H14
	Etched Thickness (µm)	84	55	20	50	56	35
	Coating Thickness (µm)	3.6	3.2	3.4	3.1	2.9	15
	Bare Surface Roughness, Ra(µm)	42			52		50

Specimen surfaces were examined metallographically by utilizing Zeiss AxioCam MRc5 optical microscope. The bare samples were ground with SiC paper, polished with 3 μm diamond and finished with colloidal silica. After electropolishing with Barker's solution, grain structures were observed under cross polarized light. Anodized specimens were polished for 45 seconds and etched in the same solution. The surfaces and the cross-sections of the anodized samples were examined by JEOL-JSM 7000F FEG-SEM. Anodized TRC1 and TRC2 were immersed in liquid nitrogen and then broken for cross-sectional investigations.

3. Results and Discussion

3.1. Visual Inspection

After the anodization of TRC1, TRC2 and DC specimens, they were visually investigated. As can be deduced from Fig.1, there exist some small "bright spots" on the anodized surface of TRC1. Spots can clearly be noticed after etching and they become more noticeable after anodizing. That appearance gives the impression that there are some uncoated areas on the surface. However, it is also evident that as the etching time increases, the quantity of those surface flaws decrease and the oxide coating seems to grow more uniformly and homogeneously. Although the surface preperation and the anodization parameters were not very much different than those of the first set of experiments, even for shorter anodization time; TRC2 exhibits homogeneous coating like that of DC. This behaviour could be attributed to TRC2 being in H24 temper that preserve as-cast grain structure with homogenously distributed intermetallics on the surface. In TRC2 the absence of recrystallization causes intermetallics to be dispersed more uniformly than those of TRC1 which was recrystallized because of the processing sequence of H14 temper. That non-recrystallized surface characteristic of TRC2 is similar to that of DC in the sense of uniform intermetallic particle distribution and this similarity leads to homogeneous surface coating characteristics.

As explained elsewhere [11, 12], there is a featureless and segregated zone on the surface of the aluminum produced by TRC because of the non-equilibrium cooling conditions. In addition to this, microstructure and chemical composition of the substrate were proved to have profound effects on the morphology of anodic oxide films [13,14,15]. In the present study, it is obtained that as etching time increases, more uniform anodic oxide film layers form. Therefore, it could be deduced that, in the case of TRC1, by etching more, one can get rid of this featureless and segregated zone and obtain more uniform anodic oxide coating. In order to clarify the reasons behind the different responses of the materials to very similar anodization parameters a series microscopic investigations were carried out.

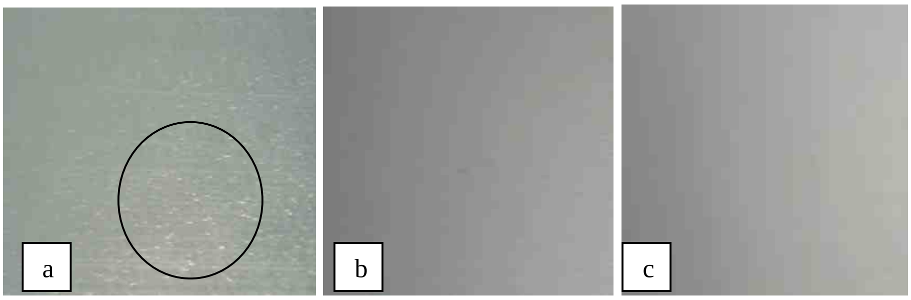

Figure 1. *Photographs of* ***a.*** *TRC1 after anodizing.* ***b.*** *TRC2 after anodizing.* ***c.*** *DC after anodizing.*

3.2. Metallographic Investigation

Metallographic studies were carried out on the bare and anodized surfaces of all specimens. Some regions exhibit few numbers of intermetallics on the surface of bare TRC1 (Fig. 2a and 2b). The images in Fig. 2a, 2b and 2c were taken from the same area of the specimen. The light colored region in Fig. 2a (that is, the dark colored region in Fig. 2b) has a very low concentration of intermetallic particles (Fig. 2e) and has much coarser grain structure (Fig. 2c).

The size and the shape of these regions are very close to the “bright spots” observed on the surface of the anodized specimens. Fig. 2d shows the region where the grains are finer and the concentration of the intermetallics are higher.

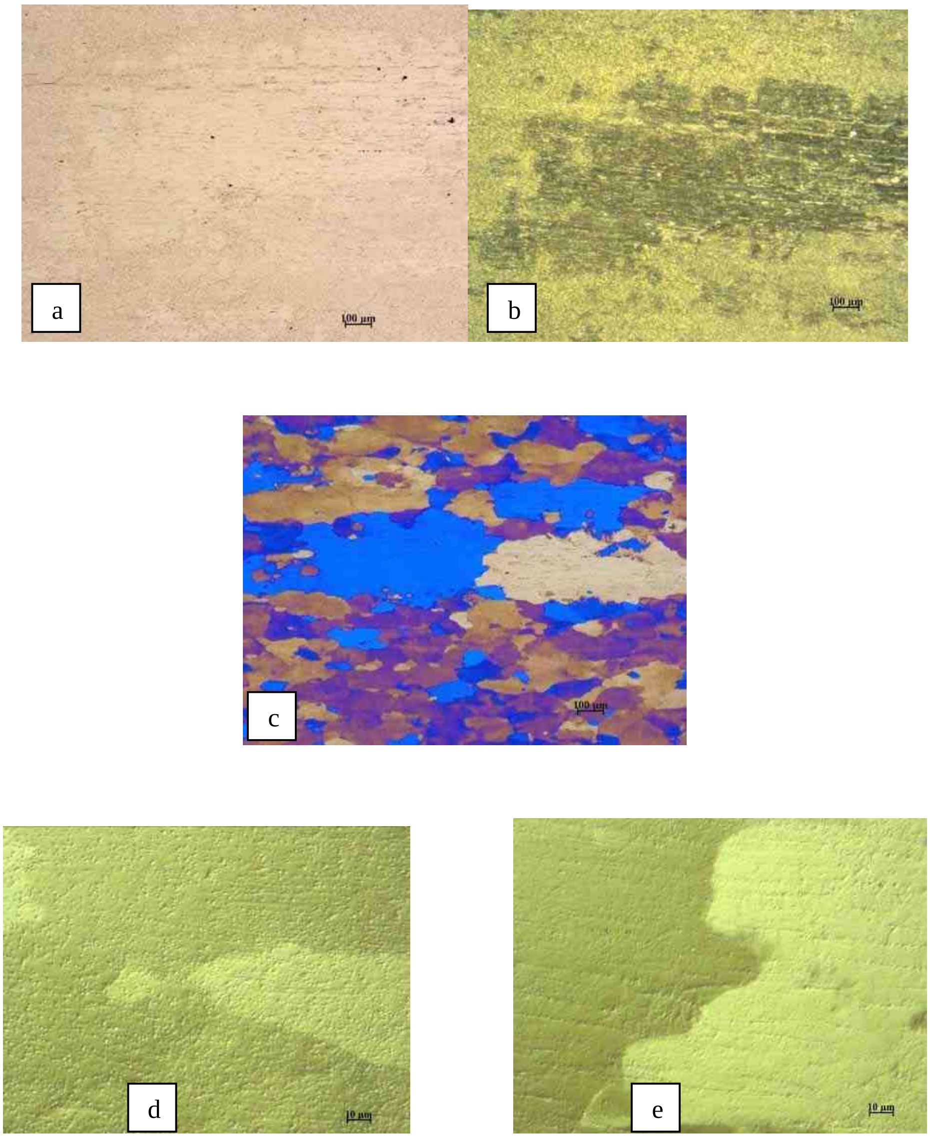

Figure 2.a. *Bright field image.* ***b.*** *Dark field image.* ***c.*** *Grain structure.* ***d.*** *Bright field image of fine grain sized region.* ***e.*** *Bright field image of coarse grain sized region.*

However, the grain size and intermetallic particle distribution on the surface of TRC2 are much more uniform (Fig.3) than that of TRC1. Surface characteristics of DC are very similar to that of TRC2 when intermetallic particle distribution are taken into consideration (Fig.4). The reason for the oxide coating appearance difference between these two specimens could be attributed to the mentioned surface characteristics.

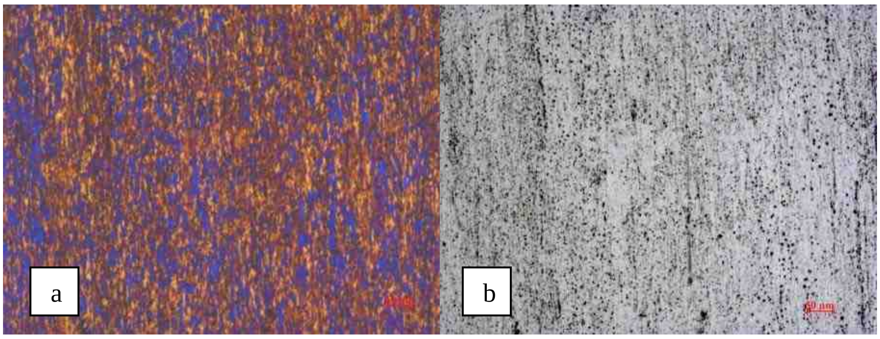

Figure 3.a. *Grain structure and* ***b.*** *distribution of intermetallics of bare TRC2.*

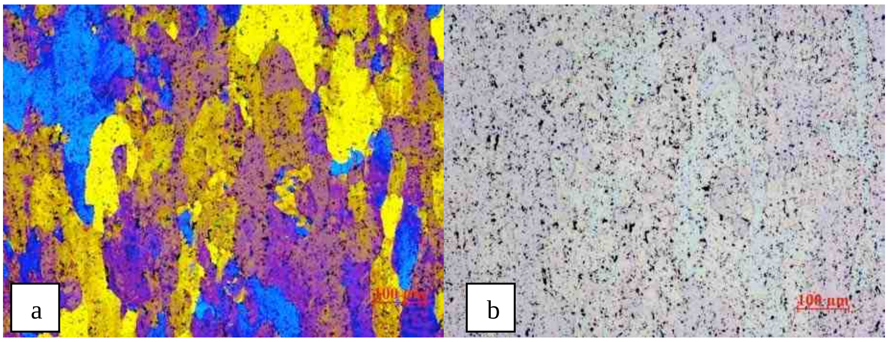

Figure 4.a. *Grain structure and* ***b.*** *Distribution of intermetallics of bare DC.*

The anodized, 45 seconds polished and etched specimens were investigated under the optical microscope in order to be convinced that the “bright spots” on the surface of TRC1 exactly coincide with the regions that have relatively low intermetallic concentration . The “bright spot” areas have been marked before the polishing process. The results revealed the fact that, the areas that have coarser grains and low intermetallic concentration exactly match the unwanted “bright spots” that have been encountered after the anodizing process. Fig. 5a and 5b indicates the problematic regions and Fig. 5c shows the border between the “uniformly coated” and the “bright spot” areas. The Fig. 5d and 5e represents the intermetallic distributions on the “uniformly coated” and the “bright spot” areas, respectively. Moreover, it is obvious that the intermetallic pits that have remained after etching has much higher concentration on the “uniformly coated” areas. However, the concentration is very low on “bright spot” regions.

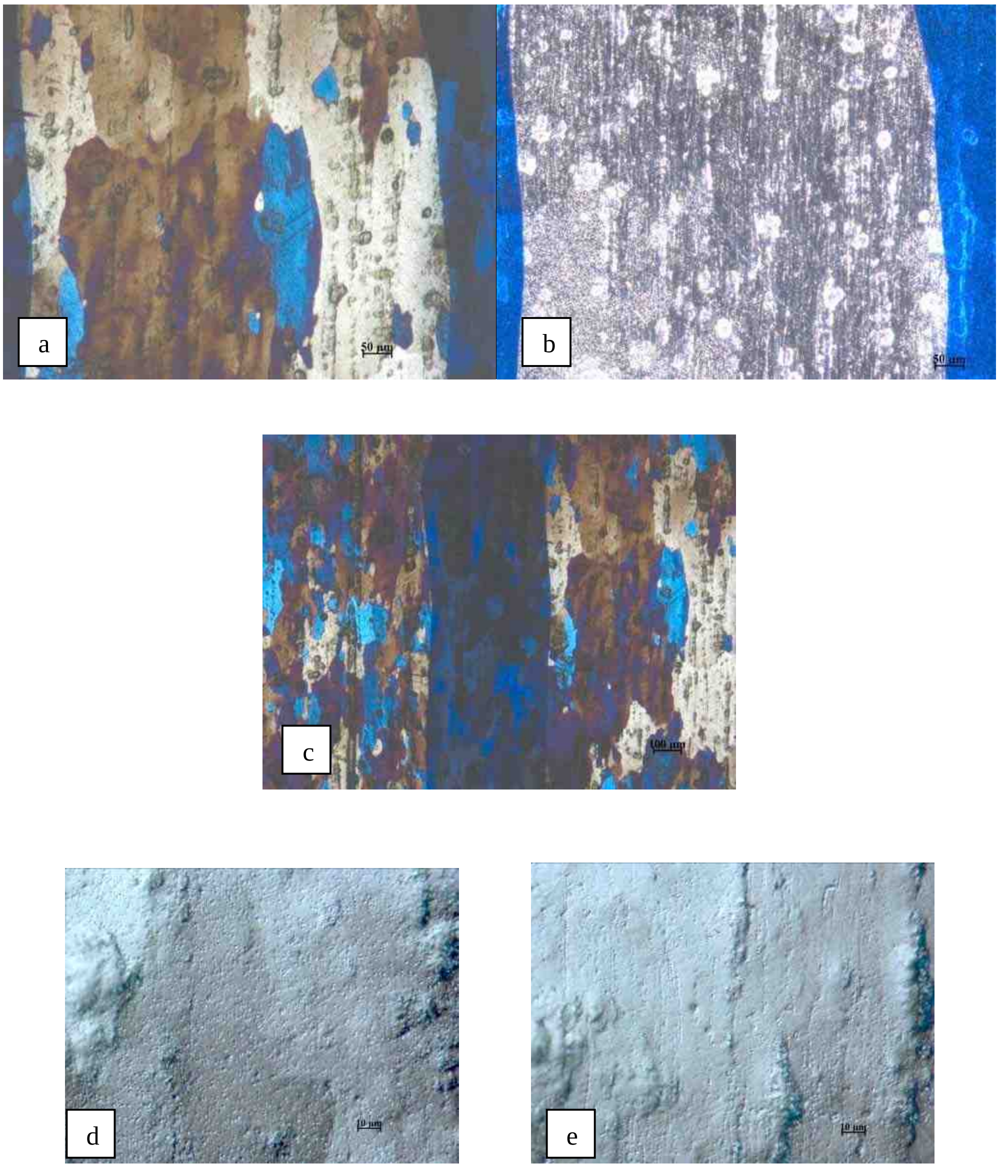

Figure 5.a. *Grain structure of “Bright Spot” area.* ***b.*** *Dark field “Bright Spot” area.* ***c.*** *The border between the “uniformly coated” and the “bright spot” areas.* ***d.*** *Bright field of “Uniformly Coated” area.* ***e.*** *Bright field of “Bright Spot” area.*

TRC1 exhibits non-uniform grain size distribution resulting from non-uniform distribution of intermetallics which can be explained in relation to the the restraining force exerted on the grain boundaries by second phase particles [16,17]. On the other hand, originating from the nature of the production process, the intermetallic particle and grain size distribution appeared uniformly on the surface of TRC2. Metallographic investigations carried out on anodized samples proved that intermetallic distribution has a significant effect on anodic oxide coating characteristics.

3.3. FEG-SEM Studies

In order to clarify the structural differences between surface and cross-sectional features of “uniformly coated” and “bright spot” regions, FEG-SEM investigations on TRC1 were carried out. There exist no significant differences between the coating thicknesses of the problematic and non-problematic regions (Fig.6), which are 3.68 μm and 3.72 μm, respectively. Although the “bright spot” regions on the surface seem to be left uncoated, FEG-SEM studies proved that all of the surface was successfully anodized. Moreover, Fig.7 and Fig.8 show the cross-sectional views of the problematic and non-problematic regions of the anodized specimens at 50000 and 80000 magnifications, respectively. Again, whole surface, including the “bright spot” areas, exhibits uniformly grown pores as in the case of anodized DC samples [1,2], indicating that the surface was uniformly coated.

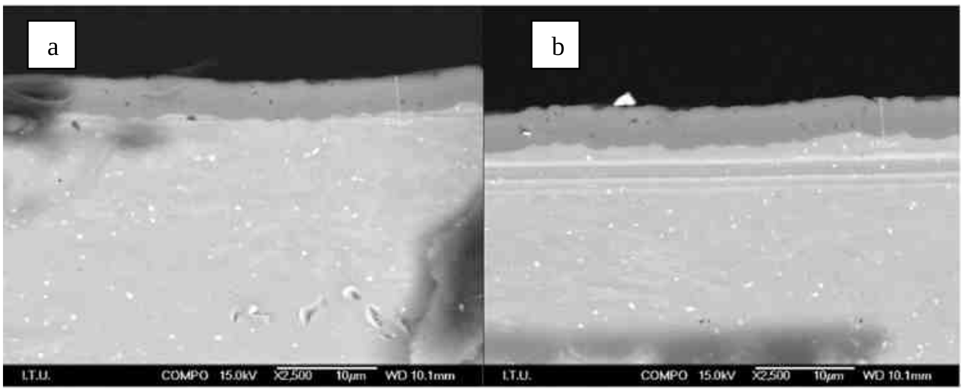

Figure 6.a. *Cross sectional view of the anodized specimen at “bright spot” region.* ***b.*** *Cross sectional view of the anodized specimen at “uniformly coated” region.*

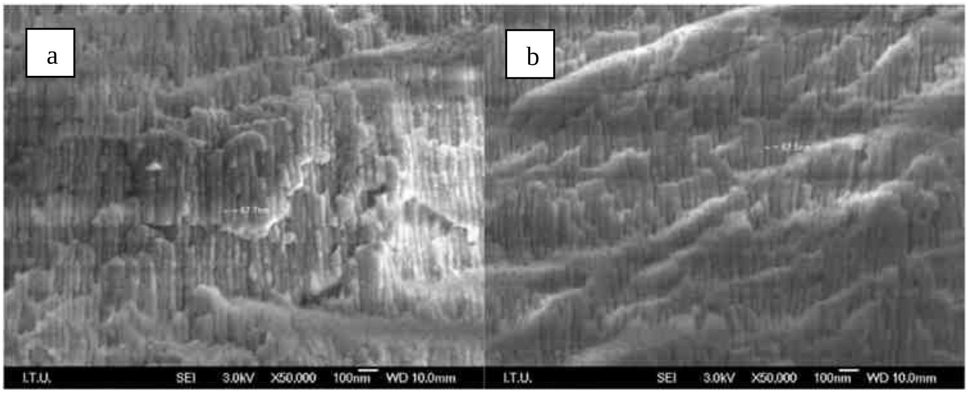

Figure 7.a. *Cross sectional view of the anodized specimen at "bright spot" region.* ***b.*** *Cross sectional view of the anodized specimen at "uniformly coated" region.*

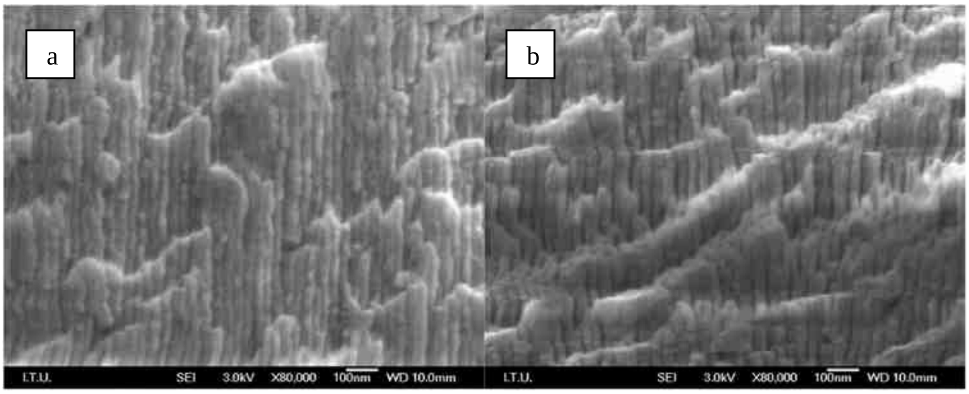

Figure 8.a. *Cross sectional view of the anodized specimen at "bright spot" region.* ***b.*** *Cross sectional view of the anodized specimen at "uniformly coated" region.*

As the orientation of the pores that lie close to the border between the anodic oxide coating and the aluminum is considered, the pores within the "bright spot" region seems to grow more orderly and smooth than those of non-problematic area (Fig. 9). Mostly, the latter contains some v-shaped grown pores which are most probably arise from the rougher substrate surface. It is interesting to note that, even the surface preperation technique is absolutely the same all over the substrate, the certain parts of the specimen has smoother surfaces and that these areas coincide with the regions with larger grains. It is denoted that the intermetallic particles are occluded in the oxide layer during anodization, so the substrate/oxide interface become locally rough [18,19]. Non-uniform intermetallic particle distribution between those two regions could be the reason for the different reactions of these two regions to the surface preperation method.

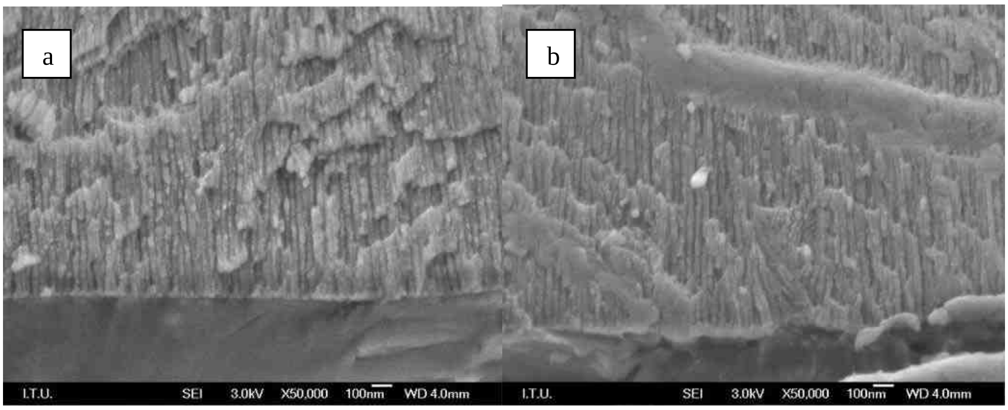

Figure 9.a. *Cross sectional view of the anodized specimen at "bright spot" region.* ***b.*** *Cross sectional view of the anodized specimen at "uniformly coated" region.*

Regarding the surface investigations of the oxide coatings, two different structures on the anodized surface of TRC1 were encountered. The "cellular structure" on the surface of the "bright spot" area are very fine and the sizes of the cells are homogeneous (Fig. 10a). On the contrary, the cell sizes within the "uniformly coated" area are coarser and not that uniform (Fig. 10b). No differences in cell sizes of TRC2 were reported.

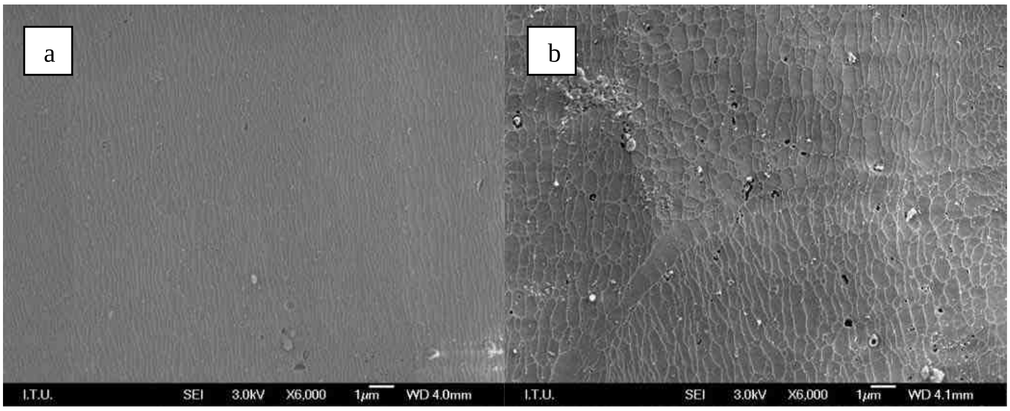

Figure 10.a. *Surface view of the anodized specimen at "bright spot" region.* ***b.*** *Surface view of the anodized specimen at "uniformly coated" region.*

Fig.10 shows the surface and the cross section of the TRC1 coating together. The "cellular structure" appearance of the anodized surface (Fig.10) could be attributed to the roughness of the anodized surface. The results of metallographic and FEG-SEM studies indicated that intermetallic distribution has a significant effect on anodic oxide coating characteristics. It was firstly reported by Cooke [20] that as the anodizing proceeds, intermetallic particle at the surface of the specimen is trapped in the coating leaving behind a mound on the aluminum/oxide interface and a dimple on the surface of the coating. These formations are said to scatter the light and reduce brightness. Therefore, the regions with low intermetallic concentration have less number of mounds and dimples and that leads us visually to perceive some "bright spots" on the surface.

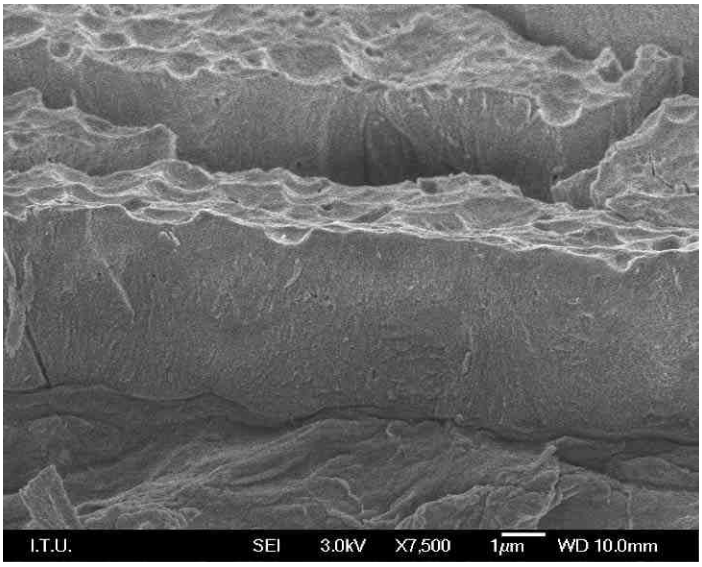

Figure 11.a. *Cross sectional view of the anodized specimen at "uniformly coated" region.*

4. Conclusion

1. As the etching time increases, more uniform anodic oxide film layers are obtained. This is attributed to the elimination of the featureless zone that is decorated with very fine intermetallic particles on the surface of the aluminum strip produced by TRC.

2. Thicknesses and the pore structure of the coatings have come out very similar all over TRC substrates, including the “bright spot” regions. “Bright spot” formation can be eliminated by employing longer etching times than are employed for DC cast aluminum. Moreover, optimum current density, bath composition and surface preparation parameters, which are thought to be effective on the resulting coating thickness, should be determined.

3. Non-uniform intermetallic particle distribution on the surface of TRC1 causes the formation of “bright spots” by altering the surface roughness of the aluminum/oxide interface and the coating surface. On the other hand, no differences in intermetallic distribution on TRC2 surface and therefore, no alterations on cell sizes at different regions of the coating were reported.

4. A series of thermo-mechanical processes will be employed to tailor the microstructural features on the as-cast strip surface. It is aimed to alter initially existing features, such as supersaturation, particle size and distribution, in the way of improving the response of the surface to the anodization process.

5. Since texture induced by the thermomechanical history of the aluminum strips is thought to be effective in the development of oxide film, further studies will be conducted on materials that are subjected to various heat treatments.

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