Study on coloring of aluminum alloys by Microplasma oxidation (MPO) technique

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Abstract

Over the past years, great scientific and industrial achievements have been made in the domain of existing many coloring technologies of aluminum alloys for different applications ,mostly, coloring after anodizing for decoration and physical applications. However, the coloring after anodizing process strongly depends on thickness and color of Al_2O_3 thin film , and on its porosity and their distribution which can affect the hardness of alumina layer. Also, this technology requires sequenced processes and controlled conditions to get the desired color. The MPO technology has recently been studied as a novel and effective means to provide improved properties such as thick and hard ceramic coating with excellent load-bearing and wear resistance properties on aluminum alloys. In the present study, the MPO technique was used for deposition of ceramic layers colored with different colors and hardness better than those produced by anodizing . This study is expected to promote the research in coloring of aluminum alloys so as to meet the increased demands for colored aluminum alloys for hard environmental applications ,where, such know-how can not be gained easily from the literature and the internet.

الخلاصة

ظهرت خلال السنوات الأخيرة تطورات بحثية وصناعية في مجال تلوين سبائك الألمنيوم بطرق مختلفة ولأغراض مختلفة , أشهرها التلوين بعد الانودة لأغراض الديكور والتطبيقات الفيزيائية .على كل حال, التلوين بعد الانودة يعتمد على عدة عوامل أهمها سمك ولون غشاء الالومينا Al_2O_3 المتكون قبل التلوين وكثافة المسامات وتوزيعها فيه وهي المؤثرة في صلادة الغشاء , وكذلك التلوين بعد الانودة يتميز نسبيا بالتعقيد الناتج من سلسة الخطوات والظروف الواجب توفرها للحصول على اللون المطلوب.

حديثا, أثبتت تكنولوجيا الأكسدة بالبلازما المايكروية MPO الحديثة تفوقها الاقتصادي والفني على باقي التقنيات في الترسيب السريع لطبقات سيراميكية سميكة ، صلدة جداً ،مقاومة للتآكل وملائمة لظروف التحميل الترايبولوجية الشديدة. في هذا البحث, تم استخدام هذه التكنولوجيا في تلوين سبائك الألمنيوم بألوان مختلفة ذات صلادة أعلى من صلادة الطبقات الملونة بعد الانودة , كخطوة قد تسهم في تطوير البحث في هذا المجال في ظل تزايد الطلب على الألمنيوم الملون ملائم للظروف الجوية الشديدة خصوصا وان الشركات والبحوث المتوفرة لاتعطي تفاصيل دقيقة عن أسرار عملها في هذا المجال.

1. Introduction

Coloring of light metals such as aluminum and its alloys has been attracting increasing attention over the past years , especially(K. Sharma et al, 1997 ; M. F. Shaffei et al, 2001 ; X. Hu et al, 2009 ;Yann Goueffon et al, 2010;Yann Goueffon, et al , 2009) in coloring with gold ,bronze and other colors for the decoration, household, roof paneling and construction applications; black coloring for physical applications

,such as, light and anti-dust applications. Furthermore, thin film deposited by anodizing of aluminum alloys(K. Sharma et al, 1997 ; M. F. Shaffei et al, 2001 ; X. Hu et al, 2009 ;Yann Goueffon et al, 2010;Yann Goueffon, et al , 2009) , can be colored by using of dyestuff , non-organic paints , and electrolytic deposition of metal salts. However, coloring after anodizing depends on the color and thickness of Al_2O_3 film before coloring , also, color properties such as stability, uniformity , constancy and environment resistance require thick Al_2O_3 film (more than 25μm). Recently, such properties could be overcome by using of multi-processes including AC-colring after DC –anodizing ,then coloring by immersion(K. Sharma et al, 1997 ; M. F. Shaffei et al, 2001 ; X. Hu et al, 2009 ;Yann Goueffon et al, 2010;Yann Goueffon, et al , 2009).

Generally, it may be known that the researchers and companies founded in the internet can not give the know-how or precision details about their works.

The microplasma oxidation MPO technology (B. Rajasekaran et al, 2008; Fa-he CAO, 2008; Jun L., ,2007; Samir H.A. and Qian HC, 2004 ; Samir H.A., 2005;Samir H.A. and Qian HC , 2005;Samir H, ,2009;Yang bin, 2008) has recently been studied as a rapid, novel and effective means to provide thick and hard ceramic coating with excellent load bearing and wear resistance properties on light alloy materials-particularly aluminum alloys. The MPO, is an unconventional plasma–chemical-electro-chemical treatment. It operates at potentials above the breakdown voltage of an original oxide film growing on the surface of a passivated metal anode dipped in an aqueous solution containing modifying elements to be incorporated in the resulting coatings L O Snizhko, et al, 2004.

From the viewpoint of the aforementioned properties and demands ,this study presents our researches on coloring of aluminum alloys by MPO technique. It is expected that this study will be helpful to promote the using of colored aluminum alloys in hard conditions and environments .

2 Experimental Details

2.1 Materials and Specimens

2A12 aluminum alloy disc coupons with size of Φ_{out} 25 mm × 3 mm were used. The nominal composition of 2A12 aluminum alloys is given in Table 1. Prior to coating the specimens were polished by emery papers followed by buff polishing to a surface roughness of R_a 0.04μm, cleaned with detergent and then washed with distilled water.

Table1 Elemental composition and mechanical properties of 2A12 aluminum alloys

Mechanical properties		Elemental composition							
Hardness (HV)	135								
Yield strength (MPa)	344	Element	Si	Fe	Cu	Mn	Mg	Zn	Al
Tensile strength (MPa)	441	%	0.50	0.50	3.8-4.9	0.3-0.9	1.2-1.8	0.30	Bal.

2.2 MPO Coating

MPO coatings were fabricated by use of a home-made microplasma oxidation MPO unit with power of 150 kW, voltage of 0-600 V, current of 0-250 A, and frequency of 50-500 Hz .As shown in Fig.1, the unit consists of an insulated electrolyte bath, a high voltage AC power supply, a stainless steel container with a sample-holder used as an electrolyte cell, stirring and cooling systems. One output of the power supply was connected to the bath; the other was connected to the sample immersed in electrolyte. The electrolytes for coloring were prepared for all the experiments from a solution of different compounds (according to the required color) in distilled- water. During the oxidation process, the electrolyte was mixed and cooled to prevent heating over 30^oC.

The deposition process was controlled to produce an alumina layer of thickness 25-35 µm. Then the coated Al alloy specimen was detached from the sample-holder, rinsed with cold then hot water and dried in warm air.

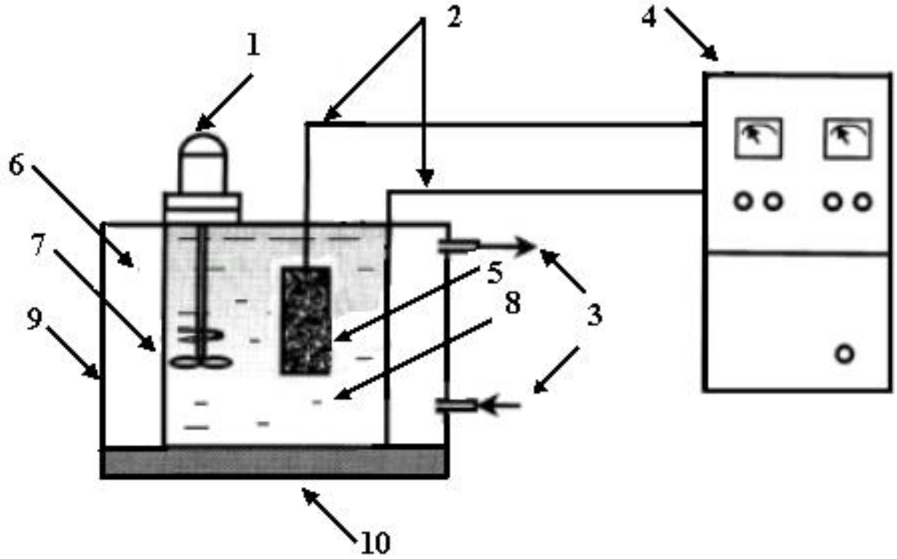


Fig.1. Schematic diagram of microplasma oxidation.1-stirring system, 2-connecting wires, 3-cooling system, 4-high voltage power supply, 5-sample, 6-cooling bath, 7-stainless steel container, 8-aqueous solution, 9-plastic case, 10-insulating plate **2.3 Coating Characterization**

A scanning electron microscope (SEM) KYKY 1000B (China, Chongqing University) was employed for the observation of the surface and cross-section morphology of the coatings. The thickness of coatings was measured with ED-300 coating thickness equipment.

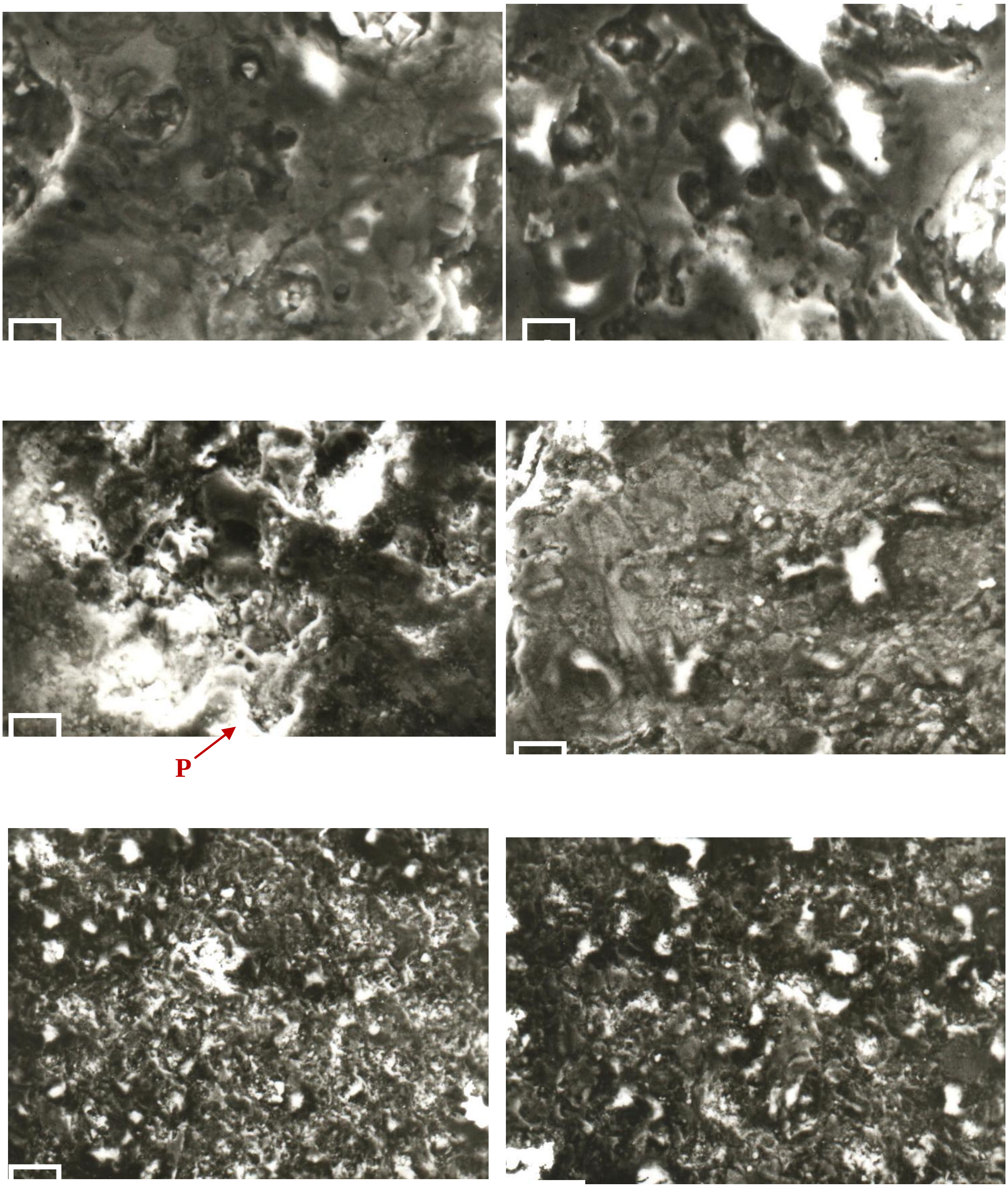
The coating hardness was evaluated using a Mitutoyo MVK G1 microhardness tester

with Vickers indenter, at a load of 50 g.

3. Results and Discussion

3.1 SEM observations

Fig.2 shows the micrographs of some coated samples. It may be clear that the Al_20_3 oxide layers prepared in this work were characterized by a porous structure due to the local thermal action of the sparks and high temperature sintering in the micro arc zone. The pores (P) were clear in fig.2a-c and high in fig.2a, b in comparison with the others .The non-uniform distribution of porosity observed in fig.2a, b could be the main reason for the decreasing in their hardness to 750- 720 HV(Samir H.A,2009) . However ,porous elimination needs modified current mode conditions which can result in the interruption of the formation of localized discharges arcs, thereby pores sealing (Yerokhin,1998). Generally, the density of porosity was different depending on electrolyte composition .Also, this can prove that the structure and properties of coatings depend on deposition techniques and parameters .



Experiment	1	2	3	4	5	6

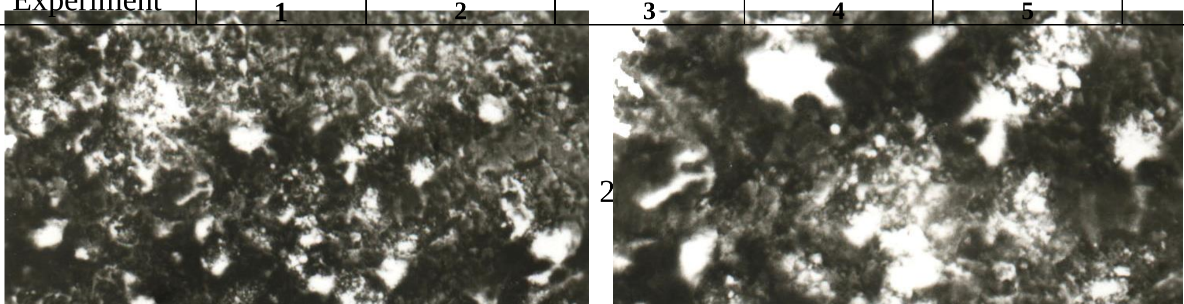


Table2 Process parameters and results of experiments on coloring by MPO technique

Parameters and Results / Electrolytes (g/l)	290-320 volt 90 min Gray 950 HV	340 volt 0.3 A 38 °C 50 min Black 925 HV	350 volt 1.1 A 40 °C 35 min dark gray 870 HV	340 volt 0.4 A 40 °C 60 min frog skin –like 800 HV	320-350 volt 1 A 35 min black 750 HV	340 volt 1 A 40 °C 35 min black 920 HV
KoH	2	2	2.5	2	3	3
$(NH_4)_2MoO_3$		2	5	6	9	9
NaF		1.5				
Na_2WoO_4		6				
Na_2SiO_3	7	10	7	7	10	2
NaoH		1.5	1.5			
Na_3Po_4	7		6	15		
$C_4H_5Na_3O_7$	3		3	1.5		
Na_3Mo_4				4		
Na_2Wo_4	3		4	4	8	8
Na_2MoO_4	3				7	10
Na_3Vo_4	3			3		
K_2CrO_4						2
KH_2Po_4						3
$(NaPo_3)_6$	7					
Experiment	**7**	**8**	**9**	**10**	**11**	
Parameters and Results / Electrolytes (g/l)	360 volt 1.5 A 40 min dark gray-black 1050 HV	340 volt 1.5 A, 38 °C 30 min green points-pitted beige 980 HV	310 volt 1 A 30 min black 900 HV	260 volt 1.6 A 30 min bright gray/ red 1100 HV	340 volt 40 min 1 A gray/ blak 720 HV	
KoH	3	3				
$(NH_4)_2MoO_3$	9	5		8	0.6%	
NaF	3	3	2	2		
Na_2WoO_4						
Na_2SiO_3			10	3	0.5%	
NaoH			3			
Na_3Po_4						
$C_4H_5Na_3O_7$			5			
Na_3Mo_4						
Na_2Wo_4			8		0.8%	
Na_2MoO_4			3		0.6%	
KH_2Po_4	5	5		5		
$Na_2B_4O_7$	5	5	5	5		
$(NaPo_3)_6$					0.5%	

$K_2Fe(CN)_6$	3	2		2.5		

3.2 Description of Coloring

Results from coloring, colors and their hardness and deposition parameters are given in table 2. In MPO technology ,the aluminum sample is immersed as anode in the electrolyte, then breakdown voltage is applied between the anode and the cathode to make many sparks moving rapidly over the substrate, resulting in synthesizing of complex compounds(composed of oxide of substrate material and modifying elements in the electrolyte)for growing of oxide layer. Final stable voltage of deposition(volt), current (A), final electrolyte temp.(^oC),deposition time min),color (after rinsing and

visual inspection) and hardness (HV), are given up the table. Results indicate the possibility of coloring of aluminum alloys with different colors depending on electrolyte composition and deposition parameters . The electrolyets were composed of salts, fluorides, compounds for metal passivation, modifying compounds, compounds for strong metal dissolution, and substances that increase the electrolyte conductivity and provide the oxide layer with stabilizing elements. Hardness results from table 2 were better than those recorded(Samir H.A,2005) for anodized thin film although the increasing of electrolyte temperature and porous structure obtained after some experiments. The results could indicate that the sample hardness of exp.10 was exhibited the highest value (1100 HV) among the others, while , the sample hardness of exp.11 was exhibited the lowest value (720 HV). Probably, the porous structure variation could strongly affect hardness results (Samir H.A,2009) . Also, the electrolytes temp. which were not in the desirable range can affect the structure growing ,thereby, hardness distribution . Anyhow, samples of exp.1 were exhibited good surface finish and their hardness improved by adding of vanadium compounds. Hardness and the dark of color of samples from exp.2 improved by increasing the concentration of $(NH_4)_2MoO_3$ to 7 g/l. samples of exp.3 were exhibited good surface finish and the adding of $C_4H_5Na_3O_7$ could result in the black coloring. In the exp.4,5 and 6 the voltage could be increased easily . Samples of exp.7 were exhibited high hardness although the colors were not in the required level. Samples of exp.8 and 9 were exhibited good hardness. Samples of exp.10 were exhibited the highest hardness, but the color changed to" red color" when the concentration of $(NH_4)_2MoO_3$ and $KMnO_4$ to 11 g/l and 1 g/l, respectively. For exp.11, the color changed to black when the concentrations of the electrolyte modified to Na_2SiO_3 0,5% , $(NaPo_3)_6$ 0,5% , Na_2MoO_4 1%, $(NH_4)_2MoO_3$ 0,9 % , Na_2WoO_4 0.8%. Anyhow, these experiments were carried out at Chongqing University (China) during the doctoral work of the author as an attempt in coloring of aluminum alloys . Furthermore, future work in this area should take into account more investigation in optical properties , such as color adsorption; in density of porosity.

4 Conclusions

Based on the experiments mentioned above, the following points could arise from the present study :

1- The controlled micoplasma oxidation(MPO) technique could be used for coloring of aluminum alloys and deposition of thick and hard ceramic layers .
2- Colors like gray, black, dark gray, frog skin-like and green points-bitted could be obtained with hardness in the range of (720- 1100 HV), and at deposition conditions of : 260-360 volt, 0,3- 1.6 ampere, 30- 60 min and maximum temperature 40 ^{o}C .
3- Hardness results were better than those of anodize film although the increasing of electrolyte temperature and porous structure obtained after some experiments.
4- Coloring by using of MPO technique shows great promise for the research in coloring of aluminum alloys so as to meet the increased demands for colored aluminum alloys for hard environmental applications ,where, such know-how can not be gained easily from the literature and the internet.

5. References

Fa-he CAO, Long-yong LIN, Zhao ZHANG, Jian-qing ZHANG, and Chu-nan CAO, (2008). "Environmental friendly plasma electrolytic oxidation of AM60 magnesium alloy and its corrosion resistance",Transactions of Nonferrous Metals Society of China, Volume 18, Issue 2, April, Pages240-247.

Jun L., Peng W,Litain H and Jinqcheng H, (2007). Tribological properties of duplex MAO/DLC coatings on magnesium alloy using combined microarc oxidation and filtered cathodic arc deposition, Materials science and engineering,454-455, 164-169.

Samir H, (2009). Study the Properties of Microplasma Oxidation Coatings (MPO) Deposited on Aluminum Alloy under modified Conditions, Journal of kerbella university , in press.

Samir H.A. and Qian HC (2004). Comments on process of duplex coatings on aluminum alloys , Journal of central south university of technology,11(3) 239-245.

Samir H.A. and Qian HC , (2004). A perspective of micro plasma oxidation (MPO) and vapor deposition coatings in surface engineering of aluminum alloys . Journal of Chongqing university,3(2) 4-11.

Samir H.A. and Qian HC , (2005). Deposition of duplex Al_2O_3/TiN coatings on aluminum alloys for tribological applications using a combined microplasma oxidation (MPO) and arc ion plating (AIP),Wear.

Samir H.A., (2005). A study on Al_2O_3/TiN duplex coatings to improve the tribological properties of aluminum alloys under heavy load –bearing conditions, Ph.D thesis , Chongqing university, China.

Shaffei, M. F. ; Abd El-Rehim, S. S. ; Shaaban, N. A. and Huisen, H. S. (2001). "Electrolytic coloring of anodic aluminum for selective solar absorbing films", Metal Finishing, Volume 99, Issue 12, December, Pages 27-30.

Sharma, A. K. ; Bhojraj, H.; Kaila, V. K. and Narayanamurthy , H. (1997). "Anodizing and inorganic black coloring of aluminum alloys for space applications", Metal Finishing, Volume 95, Issue 12, December, Page 14 Rajasekaran, B.; Ganesh Sundara Raman, S.; Rama Krishna, L. ; Joshi, S.V. and Sundararajan, G. (2008). "Influence of microarc oxidation and hard anodizing on plain fatigue and fretting fatigue behaviour of Al–Mg–Si alloy", Surface and Coatings Technology, Volume 202, Issue 8, 15 January, Pages 1462-1469.

Snizhko, L O; Yerokhin, A ; Pilkington, A; Gurevina, N L ; Misnyankin, D O; Leyland, A.and Matthews A. (2004). anodic processes in plasma electrolytic oxidation of aluminum in alkaline solutions' Electrochemica Acta ,2004,49 2085-2095.

X. Hu, Y.J. Pu, Z.Y. and Ling, Y. Li, (2009). " Coloring of aluminum using photonic crystals of porous alumina with electrodeposited Ag Optical Materials", Volume 32, Issue 2, December, Pages 382-386. Yann Goueffon, Laurent Arurault, Sandra Fontorbes, Catherine Mabru, Claire Tonon, and Pascale Guigu (2010). Chemical characteristics," mechanical and thermo-optical properties of black anodic films prepared on 7175 aluminium alloy for space applications",Materials Chemistry and Physics, In Press, Available online 22 January.

Yang bin,(2008). 'Ceramic coating for parts of microscope ' US Patent 7345817.

Yann Goueffon, Catherine Mabru, Michel Labarrère, Laurent Arurault, Claire Tonon, and Pascale Guigue, (2009). "Mechanical behavior of black anodic films on 7175 aluminium alloy for space applications",Surface and Coatings Technology, Volume 204, Issues 6-7, 25 December 2009, Pages 1013-1017

Yann Goueffon, Laurent Arurault, Catherine Mabru, Claire Tonon, and Pascale Guigue," Black anodic coatings for space applications: Study of the process parameters, characteristics and mechanical properties" , Journal of Materials Processing Technology, Volume 209, Issue 11, 21 June 2009, Pages 5145-5151.

Yerokhin,(1998). 'Method for forming coatings by electrolyte discharge and coatings formed thereby' United States Patent, 5720866.