REPRODUCIBILITY OF THE SURFACE CHARACTERISTICS OF ANODIZED AA2024-T3 AIRCRAFT ALLOY WITH DEPOSITED Ce-CONVERSION COATING

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ABSTRACT

The establishment of any technology requires data verification regarding the repeatability and reproducibility of the obtained products. It includes the capability to repeat the properties of the respective products, in order to ensure quality reproduction. Namely, the ability of reproducing the characteristics of the final products determines the reliability of the used technological regime. In the present study a large amount of data was collected and analyzed. The data contain information for the color characteristics and the hydrophobicity of 28 samples of the AA2024-T3 aircraft alloy, coated with combined oxide layers. The coating primers were formed by means of anodization and subsequent sealing with cerium oxide layers. The combination of these methods results in the formation of hybrid layers, composed of Anodic Aluminum Oxide (AAO) and Cerium Conversion Coating (CeCC). Finally, the combined AAO-CeCC protective coatings were submitted to a total of 56 measurements and the obtained results underwent statistical data treatment.

As a main result, the acquired statistical data have revealed a high level of repeatability, and can be used as a standard for the further production of similar coating systems.

Keywords: AA2024-T3 aircraft alloy, anodic aluminum oxide (AAO), cerium conversion coatings (CeCC), color characteristics and hydrophobicity, statistical data treatment.

INTRODUCTION

Almost all metallic products require to be coated, before being put on the commercial market. Other than an attractive appearance, the coatings must also ensure reliable long-term protection of the respective works against corrosion. In this sense, it has been established, that all types of coatings and protective layers should meet a number of various requirements, in order to be implemented in the industrial practice, as shown in Fig. 1 [1, 2].

Another additional property of recent increasing interest is the antibacterial effect, achieved by elaboration of advanced biometric photoactive layers, such as the proposed by Bryaskova et al. [3] and Philipova et al. [4].

The performance of the protective layers depends mainly on the method and conditions of coating deposition and also on the preliminary treatments, carried out prior to the actual coating process [5, 6]. On the other hand, the deposition technologies must also provide remarkable durability of the properties and characteristics of the resulting coatings, especially when the products are to be exploited outdoors [7]. Besides, in accordance with the application purpose of the respective coatings, these should possess additional properties,

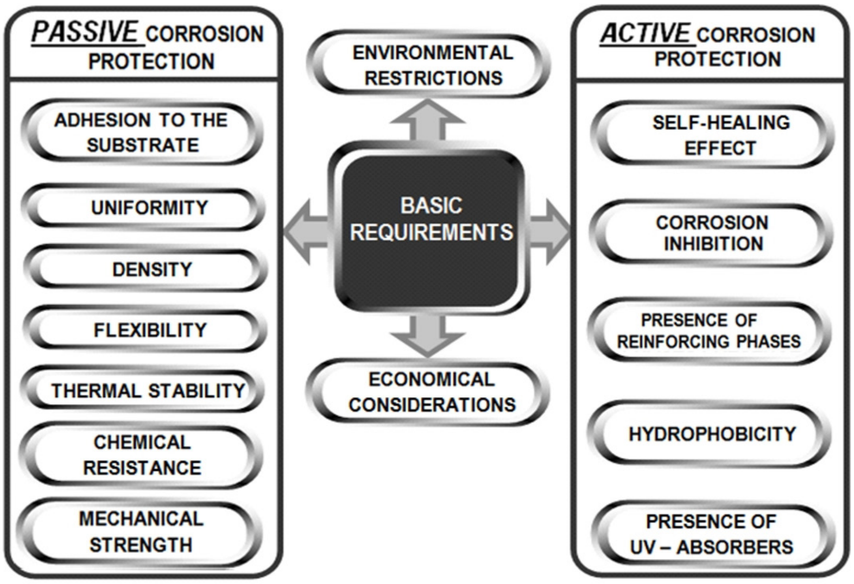

Fig. 1. Requirements for an industrial coating according to [1, 2].

as well. For instance, various machine elements, such as steam turbine blades, aircraft and boat propellers, require protective coatings with enhanced microhardness and thermal stability, for instance the spray deposited ceramic Al_2O_3 protective layers proposed by Savinkin et al. [8]. Anodization is another, widely used method for the formation of highly-ordered Al_2O_3 films [9]. Although this electrochemical method is a well-known basic approach for formation of Al_2O_3 films with highly textured surfaces [10] and even templates for production of nanomaterials with defined dimensions [11], it still remains an object of intensive scientific research activities [12, 13]. Indeed, it was undoubtedly evinced that anodic aluminum oxide (AAO) layers, formed by means of anodization, employed as a primary treatment process, highly extend the endurance of Al-based products [9, 14, 15]. Furthermore, it was demonstrated that the formed porous AAO layers could be easily modified by incorporation of nickel and/or copper [16], silver [17, 18], zinc [19] and multicomponent nanoparticles [20].

Moreover, the formation of cerium conversion coatings (CeCC) is becoming an alternative to the already banned chromium conversion coatings (CCC) [2, 7]. An additional benefit of the Ce-compounds is their proven corrosion inhibition efficiency [21 - 24].

In this sense, it was recently established that the combination of anodization and deposition of cerium-based conversion primers provides a reliable base for further deposition of organic layers [2, 24], such as the recently proposed enhanced epoxides [25, 26], as well as for other types of advanced mid- and finishing layers [27 - 30]. This is a result of the proven barrier properties of the AAO layers, which are further enhanced by the deposition of cerium oxide primer layers [2, 24, 31, 32].

The present paper summarizes the results of statistical treatment of data on the surface properties of a relatively large number of AA2024-T3 samples, with grown AAO layers, sealed by CeCC. The collected and analyzed data from the color evaluation and the assessment of their hydrophobicity should serve as an accuracy standard for layers, acquired by means of AAO formation and subsequent CeCC sealing.

EXPERIMENTAL

Sample preparation

In order to acquire sufficient numerical data for statistical analysis, 28 samples cut from the AA2024-T3 aircraft alloy underwent three subsequent surface treatment procedures, as described in Table 1.

Performed measurements

Color characteristics

The color characteristics of all 28 samples were acquired using a *Lovibond* tintometer. Two measurements were performed on separate sites of the treated area of each sample, located near the geometric center. The purpose was to determine the repeatability between each

Table 1. Surface treatments and conditions.

Treatment / Procedure	Medium	Duration	Temperature	Current density
Preliminary treatment	50 g dm^{-3} NaOH	2 min	50°C	
	HNO_3:H_2O (1:1)	2 min	ambient	
	tap and distilled water	1 min	ambient	
Anodization	15 wt. % H_2SO_4	50 min	ambient	15 mA cm^{-2}
Ce conversion coating deposition	0.025 M $CeCl_3$ 0.025 M $(NH_4)_2Ce(NO_3)_5$ 5 cm^3 dm^{-3} 30 % H_2O_2	5 min	50°C	

two results, acquired from one and the same sample surface, in order to detect any color variation.

The results were further treated by the method of the small statistics, assuming a probability of P = 0.1 %.

Surface hydrophobicity

The hydrophobicity was evaluated by measuring the contact angle between sessile drops of distilled water and the respective sample surfaces, fixed in a horizontal position. The sample positioning and the respective contact angle measurements were performed using a "Theta Lite" high precision optical device, product of Biolin Scientific (UK), coupled with specialized "One attention" software (Finland). The constant volume of the drops (0.15 mL) was ensured using a "Gastight 1001" precise screw syringe, product of Hamilton Co. (USA), where each one was dropped from a 10 mm height onto the respective sample. The measurements were coincided with taking 12 photographs per second, for a total of 10 sec. of data collection. All collected numerical data for the contact angle between the sessile drops and the respective surfaces were recorded 10 sec. after dropping.

Statistical data processing

All 28 samples were submitted to the above-described measurement procedures twice, at different points of the respective surface areas. This approach has enabled to collect 56 values for each of the measured parameters, described in detail in the next paragraphs. The method of small statistics requires 7 subsequent steps, in order to determine the average values and the expected data dissipation constraints.

The used abbreviations in the algorithm, illustrated in Fig. 2, correspond to various attributes of the obtained via statistical treatment final result. And so, the measured values (**MV**) are appointed as $\mathbf{MV_n}$, where **n** corresponds to the number of the respective consecutive measurement. After arranging them in ascending order $\mathbf{MV_1}$ corresponds to the lowest determined value, whereas the highest is given with $\mathbf{MV_n}$. The difference between them shows the result deviation amplitude (**RDA**) or in other words, the difference between the highest and the lowest measured values. The **RDA** reveals the precision of the measurements, but is not related to their accuracy. Here, it is worth noting, that the accuracy is related to the probability for coincidence between the final result value and the real value of the given measure. In turn, the final result is the average mean value $\mathbf{M_{av}}$, acquired from all performed measurements. Prior to its determination, it is necessary to perform a *Q-test procedure*, in order to define the reliability of the acquired lowest $\mathbf{MV_1}$ and highest $\mathbf{MV_n}$ values, respectively. If the respective $\mathbf{Q_1}$ or $\mathbf{Q_n}$ are lower than unit (i.e., $\mathbf{Q_1 < 1}$ and $\mathbf{Q_n < 1}$) the values are considered reliable. Each result, returning values $\mathbf{Q_1 \geq 1}$ or $\mathbf{Q_n \geq 1}$, is omitted from further calculations, considering it a result of a random error. Ultimately, only the reliable results are included in the calculations for the determination of $\mathbf{M_{av}}$.

The most important attribute of the statistically treated results is the so-called standard deviation **s.** It serves to define the respective confidential range constraints **ΔY**, which predetermine the precision of any other measurement in the respective dimension. Also, it should be noted that the position of the last digit of $\mathbf{MV_{av}}$ coincides with the first digit of **ΔY**. As illustrated in Fig. 2 the correct calculation of the **ΔY** value, requires data regarding the *Student* t-criterion. Its value is to be found and selected from tables [34, 35], according to the number of the measurements of the

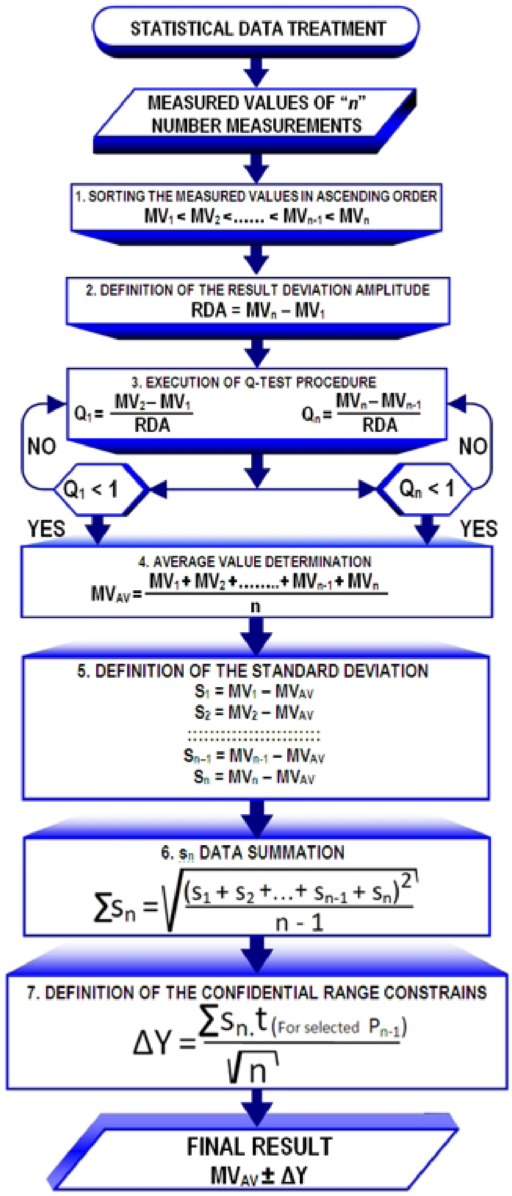

Fig. 2. Sequence of statistical data processing.

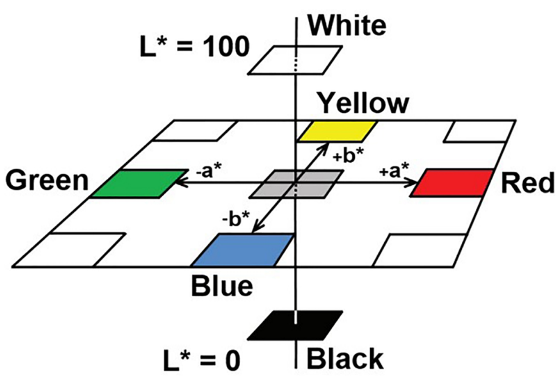

Fig. 3. Illustration of the CIE L*a*b*, 3D-coordinate system for color evaluation [24].

given parameter (n) and the probability (P). Actually, in these tables [34, 35], the t-criterion values are represented for n-1 number of measurements, because only a single measurement (n = 1) of any given parameter does not allow the determination of the accuracy and precision of the respective data acquisition. Indeed, the correct performance of any scientific research requires repetitions of the measurements, in order to guarantee result reliability regarding the characterization of the respective object of investigation. Finally, the commented in the next paragraphs obtained results will be used as a reference for determination of the results reproducibility of future investigations.

RESULTS AND DISCUSSION

Data on color characteristics

The color characteristics can be quantified according to various color space systems, developed for color description and for guaranteeing the color reproducibility in various industrial fields. Thus, for instance, the color variations are an undoubted indication for the deterioration of various nutrition products or for the aging rate of various textiles, ceramics or plastics, as well as painted or coated final products and facilities, especially designed for outdoor exploitation.

In this sense, especially the detrimental effect of UV-light and atmospheric humidity on corrosion protective coatings often results in the change of color of the respective surfaces. In the case of organic paints UV irradiation results either in bond cleavage or UV-enhanced oxidation [2, 24]. The inorganic coatings, like chromium conversion coatings, suffer changes in the oxidation state of the composing elements. For instance, the Cr(III)-compounds possess a greenish color, which due to oxidation converts to orange, typical for the Cr(VI) ones. Hence, the determination of the repeatability and reproducibility of the color characteristics is of key importance for establishment of technological reliability of the proposed surface treatment approaches, serving as a standard for the obtained protective primer coatings. Consequently, the results obtained by the present study will serve as indicators for the preciseness of the described technological regime.

For the needs of the present investigation, the color characteristics were characterized by employing the CIE L*a*b* color space, illustrated in Fig. 3, following [30, 33].

Table 2. Processed data on the parameter values of the used color space after. Result attributes of the obtained color characteristics for the performed measurements.

Parameter	L^*	a^*	b^*
Minimal value	$L^*_{min} = 74.56$	$a^*_{min} = -5.460$	$b^*_{min} = 28.39$
Maximal value	$L^*_{max} = 85.67$	$a^*_{max} = -1.150$	$b^*_{max} = 62.40$
Result deviation amplitude	$RDA_{L^*} = 11.09$	$RDA_{a^*} = -4.310$	$RDA_{b^*} = 34.01$
Average value	$L^*_{av} = 82.25$	$a^*_{av} = -4.047$	$b^*_{av} = 46.79$
Q_1	0.002254	0.000	0.000
Q_n	0.02976	0.1415	0.1415
Σs_n	0.080	0.170	-0.170
s	0.01089	0.02313	0.02313
ΔY	0.005102	0.01084	0.01084
Final result	**$L^*_{56} = 82.248 \pm 0.005$**	**$a^*_{56} = -4.05 \pm 0.01$**	**$b^*_{56} = 46.79 \pm 0.01$**

This system is developed for the description of the color characteristics of the light reflected from solid objects, illuminated with white light. It is composed by three relative coordinates **L^***, **a^*** and **b^***. There, the height **L^*** ranges from **L^*** = 0 (black) to **L^*** = 100 (white), the length **a^*** may adopt negative (green) or positive (red) values and finally, the width **b^*** may also be negative (blue) or positive (yellow).

The obtained results for the color characteristics of the AAO-CeCC combined coating primers are summarized in Table 2.

Thus, the data in Table 2 show that the samples are bright, according to the obtained **L^*_{56}** value with a distinct yellowish tonality, defined by **b^*_{56}** and an insignificant greenish hue, determined by **a^*_{56}**. Besides, the results reveal that the color characteristics of the samples possess remarkable repeatability, expressed by the narrow confidence interval. The confidential range constraints **ΔY**, differ around 5×10^{-3} for **L^*_{56}** and 1×10^{-2} for **a^*_{56}** and **b^*_{56}**, respectively**.** Further, it is worth noting, that these values are defined after 56 measurements, using the respective *Student* criterion, which according to data tables [34, 35] has a value of $t = 3.473$, for P = 0.1 % probability.

Surface properties

The surface properties of the initially formed coatings predetermine the adhesion of the next layers, which are to be deposited in order to obtain a multilayered coating system, providing all requirements, described in Fig. 1. The surface properties of the samples were determined by a sessile drop technique, which enables their assessment with satisfying repeatability. Examples for contact angles between a water drop and

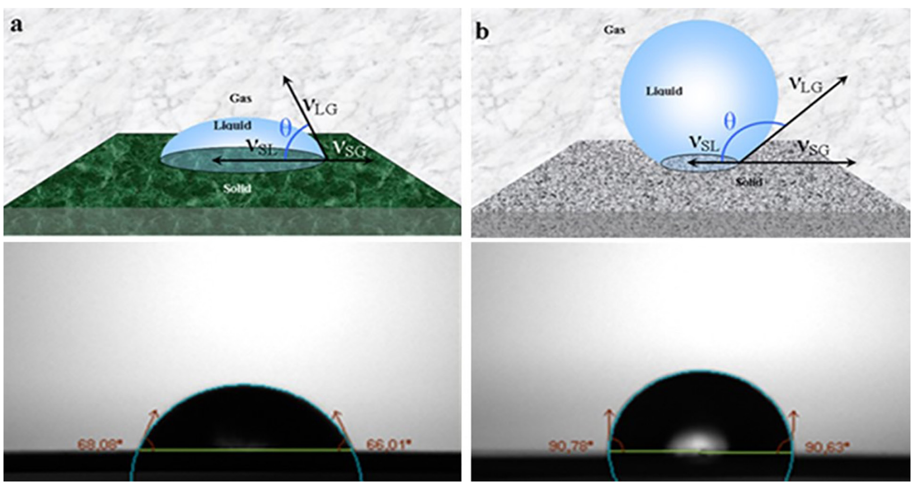

Fig. 4. Examples for contact angles between hydrophilic (a) and hydrophobic (b) surfaces.

Table 3. Contact angle results acquired after statistical data treatment.

Parameter	Contact angle mean value attributes
Minimal value	9.08
Maximal value	51.81
Result deviation amplitude (RDA)	42.73
Average value (M_{av})	28.024
Q_1	0.1727
Q_n	0.1121
Σs_n	0.2400
s	0.03236
ΔY	0.01502
Final result	**θ_{56} = 28.02 ± 0.01 °**

a hydrophilic (a) and a hydrophobic (b) surface are illustrated in Fig. 4.

The contact angle measurements were also executed in duplicate for each sample, in order to acquire a total of 56 results. The obtained data were further treated following once more the algorithm illustrated in Fig. 2. The obtained by the respective statistical analysis results are summarized in Table 3.

The contact angle measurements have shown rather low precision, compared to the results of the color characterization. Indeed, the data in Table 3 show that the **RDA** is about twice higher than $\mathbf{M}_{av}$, which can be attributed to the roughness of the metallic surface, prior to the formation of AAO and subsequent CeCC deposition. The apparent lower precision of the contact angle values is a result of the initial roughness of the samples and the selective dissolution of intermetallic inclusions during the preliminary treatments. Nevertheless, the final result in Table 3 reveals the definitely hydrophilic properties of the investigated surfaces, probably due to the aqueous solutions, used for formation of the coating. As a main result, the water in these solutions results in the hydration of the surface layers, during their formation. This fact indicates that the already formed AAO - CeCC combined surface layers are suitable for further coating only by waterborne polymeric intermediate coating layers. In turn, these layers must be further coated with hydrophobic finishes, in order to guarantee the required for long-term outdoor service hydrophobicity.

Despite the low precision of the measured contact angle result, its accuracy can be accepted as reliable, because of the high number of measurements performed. It has predetermined confidential range constraints **ΔY** of only 0.03569 % of the average value $\mathbf{M}_{av}$ of the contact angle.

CONCLUSIONS

The present research summarizes the results, acquired by a large number (56) of measurements on 28 samples of AA2024-T3, coated by combined AAO-CeCC coatings. Unlike the majority of the research works, devoted to the elaboration of corrosion protective coating primers, the present study is dedicated to the collection of data, acquired from a large number of samples, treated in the same manner i.e., with no change in the conditions of film formation. Hence, all samples were submitted to the same pretreatment procedures, since the aim was to evaluate the data repeatability.

The sequence of these procedures was: preliminary surface treatment, anodization and final sealing by cerium conversion coating formation. Some properties of the obtained combined AAO-CeCC coating primers were studied, namely their color characteristics and hydrophobicity. The obtained results were then submitted to statistical data treatment.

The results have shown that the obtained coating primers possess bright yellow color with an insignificant green hue. All color attribute measurements have shown a significant rate of repeatability, precision and accuracy.

The additional contact angle measurements have shown that the formed AAO-CeCC coating primers are definitely hydrophilic and the obtained results are accurate, despite the lower precision rate. Finally, it was supposed that this lower precision rate of the contact angle measurements is a result of the sample surface roughness and the preliminary surface treatments.

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