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MCDM selection of pulse parameters for best tribological performance of $Cr-Al_2O_3$ nano-composite co-deposited from trivalent chromium bath

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A B S T R A C T

Optimum operating parameters for pulse co-deposition of nano-Al_2O_3 with Cr from a trivalent chromium bath onto Cu cathode are selected by using “technique for order performance by similarity to ideal solution” (TOPSIS), “VIšekriterijumsko KOmpromisno Rangiranje” (VIKOR), “elimination and choice expressing the reality” (ELECTRE) and “complex proportional assessment” (CORPAS) accompanied with analytic hierarchy processing (AHP) to compare methods for achievement of the best tribological coating performance. Criteria for appropriate selection include wear loss, corrosion resistance, micro-hardness, bath condition and current efficiency. Results ascertain the best $Cr-Al_2O_3$ nano-composite coating with 40% duty cycle, 10 Hz current frequency and 1 g/L nano-Al_2O_3 dispersed into the electrolyte bath. Comparison of the different calculated Speraman's coefficients weighed with the «subjective» analytic hierarchy process indicates more consistent results than «objective» entropy technique. The study clarifies the comparative capability of the weighing and the ranking methods in choosing the best way to make consistent final results independent of the level of knowledge and standpoints of the researchers. Recommendation of subjective rather than objective weighing apparatus to the MCDM researchers is therefore a constructive achievement.

1. Introduction

Previous studies have shown profound impact of nanoparticle presence, current mode, current density, pulse frequency and duty cycle on microstructure, microhardness and corrosion resistance of the electrodeposited $Cr-Al_2O_3$ coatings [1]. Ranking of premium parameters for any specific usage is an imperative stage of a material selection method [2–4]. Various criteria must be considered for best achievement. From two or more sets of parameters, best ranking with respect to a specific application can be attained by using multi criteria decision-making (MCDM) procedure [5,6]. Different techniques encompassing entropy [7], analytic hierarchy processing (AHP) [8], complex proportional assessment (CORPAS) [9], elimination and choice expressing the reality (ELECTRE) [10], technique for order performance by similarity to ideal solution (TOPSIS) [11] and VIšekriterijumsko KOmpromisno Rangiranje (VIKOR) methods [12] have been discussed extensively by different researchers to facilitate the material selection procedures and to reach appropriate conclusions [7–12].

This study considers wear loss, corrosion behavior, hardness and current efficiency as selection criteria for evaluation of the optimal conditions for the best co-deposition of $Cr-Al_2O_3$ nano-composite onto copper substrate from a trivalent chromium bath. Although chromium electroplating from traditional bath of Cr(VI) has more than 120 years precedent [1,13], owing to the toxic nature of hexavalent chromium bath [13–17], Cr trivalent bath is used as a harmless electrolyte for co-deposition of chromium-aluminum oxide nano-composite onto Cu cathode with the aim of enhancement of wear and corrosion resistance and tribological behavior improvement [18,19]. Spearman's coefficients were calculated to find the direction of association of acquiring ranks and proximity of results obtained via different approaches.

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2. Experimental procedure

2.1. Materials and electroplating system

Nano−particles of α−Al_2O_3 from Nanostructured & Amorphous Materials Inc. were added to Cr(III) bath for co-electrodeposition on a copper substrate with Cr layer. Prior to electrodeposition, the substrate was abraded with abrasive paper No.1000 SiC while eradicated to 0.05−0.1 μm roughness. The substrate was then rinsed in distilled water and ultrasonically degreased with acetone for 30 min.

Electroplating bath contained 50 nm diameter Al_2O_3 nano-particles. It was stirred for 1 h prior to the electrodeposition. In all experiments, the cathode was washed with distilled water and ethanol. Then it was activated with a dilute (5 wt%) HCl solution for 20 s. The activated cathode was then immediately placed into the electroplating bath. Magnetic stirring at 200 rpm sustained dispersion of the particles and prohibited them from any possible sedimentation during the electrodeposition. Schematic representation of the system used is depicted in Fig. 1.

Composition of the electrolyte and operating parameters of the electrodeposition process are summarized in Table 1. Experiments were conducted in a three-electrode electrochemical cell monitored with potentiostat/galvanostat AUTOLAB model PGSTAT302N. The polarization curves were depicted at a sweep rate of 1 mV/s in 0.5 M NaCl solution at room temperature. The hardness of the coatings was measured by a Vicker's micro hardness (HV) indenter applying 25 g load for 10 s. The Average of 5 readings were quoted for each hardness number. The wear resistance was estimated by pin-on-plate SRV vibrant wear tester (The counterpart was steel ball with a diameter of 10 mm) under the unlubricated condition with the humidity of 40% and the temperature of 25 °C. All wear tests were carried out under 20 N load and frequency of 10 Hz. More details are as given in a previous publication [1].

Table 1
Bath composition and electrodeposition parameters used in this research.

Substance	M/L
$CrCl_3 \cdot 6H_2O$	0.4
Glycine	0.5
H_3BO_3	0.5
NaCl	0.5
NH_4Cl	0.5
NH_4Br	0.2
$AlCl_3 \cdot 6H_2O$	0.01
Process parameter	**Amount/Type**
Temperature	30 ± 1 °C
Plating time	20 min
Anode	Platinum
Cathode	Copper
pH	2.7
Agitation	Magnetic stirring (200 rpm)
Average current density	20 A/dm^2
Current	Direct or pulsating
Duty cycle	20, 40, 60 and 80%
Frequency	5, 10, 15, 20, 25, 30 Hz

2.2. Applied selection methods

Weighting procedure was used by all applied selection methods.

2.2.1. AHP method

The analytic hierarchy process is a subjective method first introduced by Saaty [20]. It seems to be the most advantageous and prevalent method of MCDM with significant capability to solve arduous problems of the materials selection. This method decomposes the problem of an intricate issue into a hierarchy system [21]. The main idea behind it is to obtain ratio scales from pairwise comparisons [22]. In summary, the procedure is as follows:

Step 1: Develop a hierarchical structure

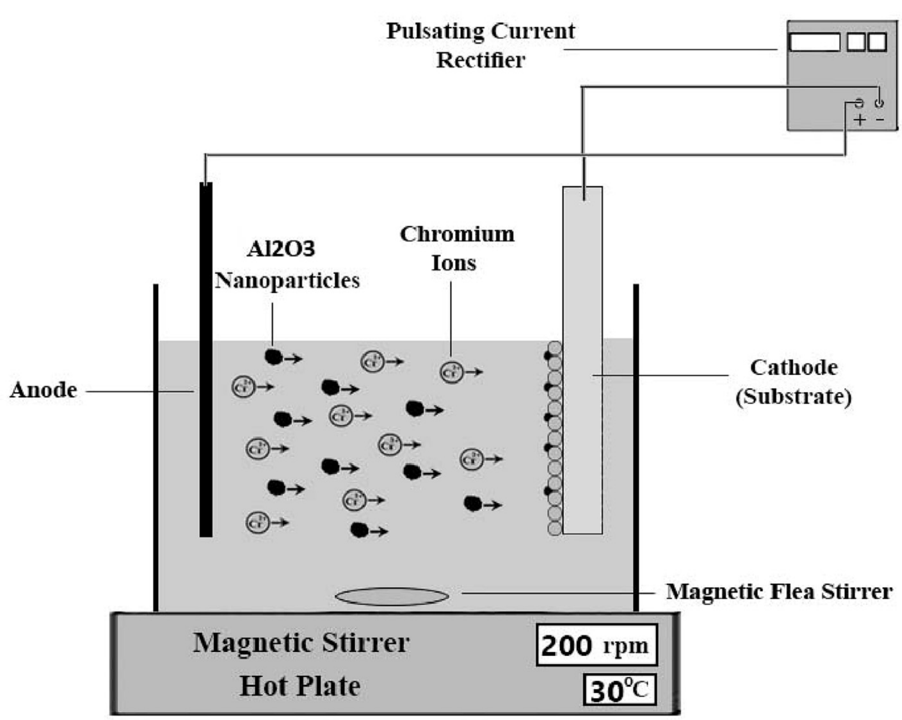

Fig. 1. Schematic illustration of the nano-composite electrodeposition system.

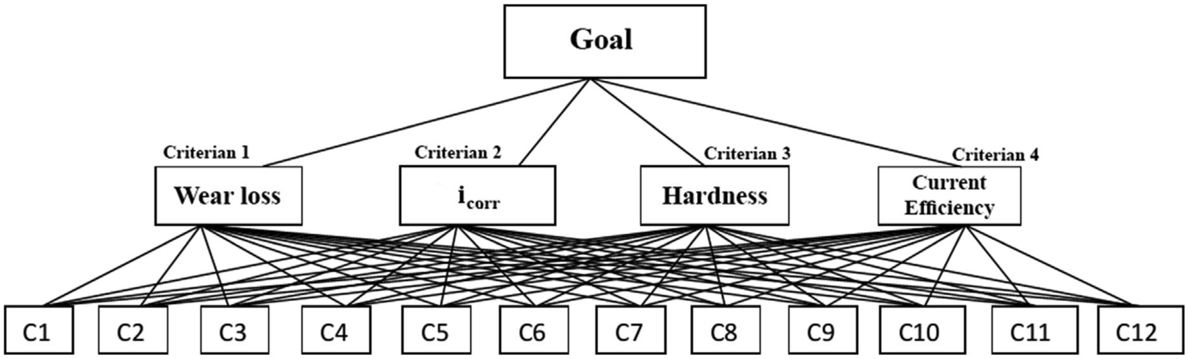

Fig. 2. Decision-making hierarchy structure of this research.

First step is to decompose a complicated decision problem to an organized hierarchy. AHP breaks down a complex multi-criteria decision-making problem into a hierarchy of interrelated decision elements (criteria and decision alternatives). The objectives, criteria and alternatives are arranged in a hierarchical structure similar to the family tree shown in Fig. 2.

Step 2: Pairwise comparisons

The participating decision makers provide pairwise comparisons of the alternatives and the criteria for each level of the hierarchy to gain the weight factor and criteria significance on the current level with respect to the specified criteria at a higher level. As shown in Table 2 this weight factor expresses a measure of the relative importance of the criteria for the decision maker. In AHP method the paired comparison is constructed by allocating values from 1 to 9 to declare the influence of each element in the decision of the two element properties. The meaning of the comparison scale used in the weighting of two elements can easily be demonstrated by using Table 3 [23]. The final outcome of the pairwise comparison on n criteria can be summarized in an $(n \times n)$ assessment matrix A.

$$\begin{pmatrix} 1 & a_{12} & \cdots & a_{1n} \\ a_{21} & 1 & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & 1 \end{pmatrix} \tag{1}$$

If a_{ij} is the element of row i column j of the matrix, then the lower diametric element is obtained by using [23]:

$$a_{ji} = \frac{1}{a_{ij}} \tag{2}$$

Considering "n" as the number of criteria in this assessment, the number of comparisons to accomplish this method can be achieved by the following relation [21]:

$$No.\ of\ Comparisons = \frac{n(n-1)}{2} \tag{3}$$

Step 3: Relative weight calculation

Depending on pair-wise comparison process results, the eigenvector of the decision matrix will be determined as the priority vector of the features compared. This is to demonstrate their relative weights with consideration of the features located one level higher in the hierarchy. At this step, some mathematical procedures are done to normalize and calculate the relative weights for each matrix. By normalizing each column and averaging the resulting rows, the weights of the matrixes could be obtained. The averaged numbers correspond to weights (priority) of each factor.

Step 4: Consistency ratio

Consistency ratio (CR) is a ratio for corroboration of the results that are gained by pair-wised comparisons and it can be a reliable ratio to ensure the accuracy of the relative weights. This ratio can assist assertion of inconsistencies in the evaluation procedure. Consistency ratio (CR) depends on consistency index (CI) and random consistency index (RI) and it can be calculated by the following formula:

$$CR = \frac{CI}{RI} \tag{4}$$

where the consistency index (CI) can be computed from the following formula:

$$CI = \frac{\lambda_{max} - n}{n - 1} \tag{5}$$

The RI values in Eq. (5) are shown in Table 4. As is seen, the random consistency index (RI) depends only on the rank of the matrix (n) [23,25].

According to AHP method, when the consistency ratio (CR) becomes less than 0.1, the result are reliable so that more assessment

Table 2
The relative importance of each criterion.

Criterion	Wear loss (mg)	i_{corr} (μACm^{-2})	Hardness (HV)	Current Efficiency (%)
Wear loss (mg)	1	2	4	7
i_{corr} (μACm^{-2})	0.5	1	3	5
Hardness (HV)	0.25	0.33	1	2
Current Efficiency (%)	0.14	0.2	0.5	1

Table 3
Pair comparison evaluation scale [24].

Relative Importance	Definition
1	Equal Importance
3	Weak Dominance
5	Strong Dominance
7	Demonstrated Dominance
9	Absolute Dominance
2, 4, 6, 8	Intermediate Dominance

Table 4
Values of the random consistency index (RI) as a function of the matrix rank (n) [21].

n	1	2	3	4	5	6	7	8	9	10
RI	0	0	0.58	0.9	1.12	1.24	1.32	1.41	1.45	1.49

is not needed [23]. For CR values larger than 0.1, the judgment is not consistent and re-evaluation is required.

2.2.2. Entropy method

This is an advantageous technique introduced by Shannon [26] for elimination of the subjective factors of the weighting methods. Its main purpose is to generate common measurable scales for all criteria. Unlike the AHP method that uses knowledge and standpoints of experts to acquire relative weights, entropy method utilizes measured data to generate more harmonic results. Normalized decision matrix first should be obtained by the following relation:

$$f_{ij} = \frac{X_{ij}}{\sqrt{\sum_{i=1}^{m} X_{ij}^2}} \tag{6}$$

where i receives the values 1, 2, …, m, j receives 1, 2, …, n and f_{ij} is a normalized priority measure of the ith alternative with respect to the jth criterion.

The entropy value (H_i) can then be calculated by using Eq. (7);

$$H_i = -k\sum_{j=1}^{n} f_{ij}\ln f_{ij} \tag{7}$$

where k is a constant evaluated from Eq. (8):

$$k = \frac{1}{\ln n} \tag{8}$$

where n is the number of alternatives.

Next, according to the entropy value, weights of each criterion can be calculated by using Eq. (9):

$$W_i = \frac{(1-H_i)}{\left(m - \sum_{i=1}^{m} H_i\right)} \tag{9}$$

The higher the relative weight, the more important and the more effective the criterion is.

2.2.2.1. VIKOR method.

This method first was introduced by Opricovic [12]. It helps ascertainment of compromise-solution and weight-stability intervals gained by given weights from the AHP and the entropy process. VIKOR is one of the most applied multi-criteria decision making (MCDM) methods utilized for intricate systems. It determines rank of the best choice from among a pool of alternatives in presence of conflicting criteria. The concept of VIKOR is the closeness to the ideal solution; so that the process of ranking could be accomplished by comparing the measure of proximity to the ideal solution [27]. An important feature of this method is its selection of best alternative with highest group usefulness and lowest regret utility. The positive aspect of VIKOR is that it can be utilized in arduous conditions with multiple-criteria [28]. This exclusivity is obtained by using the L_p-metric (Formula (10)) in the compromising programming method [29].

$$L_{P,i} = \left\{\sum_{j=1}^{n}\left[\frac{W_j\left(f_j^* - f_{ij}\right)}{\left(f_j^* - f_j^-\right)}\right]^P\right\}^{\frac{1}{P}} \tag{10}$$

Where $1 \le P \le \infty;\ i = 1, 2, \ldots, m.$

The following steps declare briefly the procedure taken by VIKOR:

Step 1: Assessing the normalized decision matrix.

The normalized decision matrix can be calculated by using Eq. (6).

Step 2: Assessing the ideal solutions and the negative-ideal solution.

The best f_i^* and the worst f_i^- can be acquired as follows:

$$A^* = \left\{\left(\max f_{ij} | i = 1, 2, \ldots, m \text{ and } j = 1, 2, \ldots, n\right\} = \left\{f_1^*, f_2^*, \ldots, f_j^*, \ldots, f_n^*\right\} \tag{11}$$

$$A^- = \left\{\left(\min f_{ij} | i = 1, 2, \ldots, m \text{ and } j = 1, 2, \ldots, n\right\} = \left\{f_1^-, f_2^-, \ldots, f_j^-, \ldots, f_n^-\right\} \tag{12}$$

where m is the number of alternatives and n is the number of criteria.

Step 3: Calculating the regret and the utility measures.

S_i and R_i demonstrate the utility measure and the regret measure, respectively and W_j represents the criteria weights which express the relative importance of the jth criterion. S_i and R_i can be calculated for each of the alternatives by the following relations:

$$S_i = \sum_{j=1}^{n}\frac{W_j\left(f_j^* - f_{ij}\right)}{\left(f_j^* - f_j^-\right)} \tag{13}$$

$$R_i = \underset{j}{MAX}\left[\frac{W_j\left(f_j^* - f_{ij}\right)}{\left(f_j^* - f_j^-\right)}\right] \tag{14}$$

Step 4: Calculate the VIKOR index

The VIKOR index for each alternative is given by:

$$Q_i = \nu\left[\frac{S_i - S^*}{(S^- - S^*)}\right] + (1+\nu)\left[\frac{R_i - R^*}{(R^- - R^*)}\right] \tag{15}$$

where $S^* = \min_i S_i$, $S^- = \max_i S_i$, $R^* = \min_i R_i$ and $R^- = \max_i R_i$. Here, v is the majority of criteria or the maximum group utility which is usually set to 0.5 [12,30,31].

Step 5: Ranking the alternatives.

Now the preference order can be ranked according to VIKOR value. The best alternative is the solution with the nearest measure to the ideal solution so the alternative with the highest VIKOR index is assigned as the best solution [27]. The process of ranking with VIKOR method can be accomplished with different values of criteria weights, assessing the influence of criteria weights on proposed compromise solution. The VIKOR method ascertains the weight stability intervals, using the methodology introduced by Opricovic [12].

2.2.3. TOPSIS method

TOPSIS is one of the most applied and practical methods for decision making that determines the best alternative that is nearest to the ideal solution and farthest from the negative ideal solution. This method that was first developed by Hwang and Yoon [32] can be summarized as follows:

Step 1: The first step in this method like the others is to construct the normalized matrix by using Eq. (6).

Step 2: The second step is to generate the weighted normalized matrix as follows:

$$V = F.W = \begin{pmatrix} w_1f_{11} & w_2f_{12} & \cdots & w_nf_{1n} \\ w_1f_{21} & w_2f_{22} & \cdots & w_nf_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ w_1f_{m1} & w_2f_{m2} & \cdots & w_nf_{mn} \end{pmatrix} \quad (16)$$

n and m are the numbers of criteria and alternatives, respectively.

Step 3: This step is to ascertain the ideal and negative ideal solutions as mentioned before, by Eq. (17) and Eq. (18). Maximum and minimum values of standard v calculated for different coating criteria are listed in Table 12. Best (ideal) and worst (non-ideal) values of each criterion are shown by v^+ and v^- codes, respectively. Closeness to the ideal value is a measure of the ideality extent. Using Eqs. (9) and (10) respectively.

$$V^+ = \{(\max v_{ij}|j\in J_1), (\min v_{ij}|j\in J_2),\ i = 1,2,3,\ldots,\ m\} = \left\{V_1^+, V_2^+, \ldots, V_n^+\right\} \quad (17)$$

$$V^- = \{(\min v_{ij}|\ j\in J_1), (\max v_{ij}|j\in J_2),\ i = 1,2,3,\ldots,m\} = \left\{V_1^-, V_2^-,\ \ldots, V_n^-\right\} \quad (18)$$

Step 4: In this stage by utilizing the n-dimensional Euclidean distance method, the distance of all alternatives from ideal and negative ideal solution are calculated by using Eq. (19) and Eq. (20):

$$S_i^+ = \left\{\sum_{j=1}^{n}\left(V_{ij} - V_j^+\right)^2\right\}^{\frac{1}{2}} j = 1,2,\ldots,n\ i = 1,2,\ldots m \quad (19)$$

$$S_i^- = \left\{\sum_{j=1}^{n}\left(V_{ij} - V_j^-\right)^2\right\}^{\frac{1}{2}} j = 1,2,\ldots,n\ i = 1,2,\ldots m \quad (20)$$

Step 5: The relative closeness of each alternative to the ideal solution is computed by Eq. (21), as mentioned below:

$$Q_i = \frac{S_{i-}}{S_{i*} + S_{i-}} \quad (21)$$

where the best rank is for the alternative with a higher value for relative closeness that means the alternative with the lowest distance from an ideal solution and highest distance from the negative solution.

2.2.4. COPRAS method

This method that was first introduced by Zavadskas and Kaklauskas [33] has numerous advantageous in comparison with other methods mentioned above. It is easier and more transparent and it can be utilized for graphical exegesis. This method like the others give preference to the alternatives based on their ideal and negative ideal solution and it can opt the best alternative among a pool of alternatives regarding their similar features and criteria. The following steps express the way that COPRAS method uses to find the best material among a pool of presented materials.

Step 1: like the other methods the first step always is constructing the weighted normalized matrix as it is mentioned in Eq. (6) and Eq. (16).

Step 2: In this step the useful criteria and non-useful criteria must be determined. Then the sum of the maximizing criterion and minimizing criterion must be calculated as follows:

$$S_{i+} = \sum_{j=1}^{k} d_{ij} \quad (22)$$

$$S_{i-} = \sum_{j=k+1}^{n} d_{ij} \quad (23)$$

The maximizing criteria are the ones that the higher value is more advantageous and appropriate for the final results of the coating.

Step 3: The final step is to calculate the relative importance of each alternative by using Eq. (23). The best alternative is the one with higher relative importance.

$$Q_i = S_{i+} + \frac{\sum_{i=1}^{n} S_{i-}}{S_{i-}\sum_{i=1}^{n}\frac{1}{S_{i-}}} \quad (24)$$

2.2.5. ELECTRE method

Another useful method that was first proposed by Roy [34] to choose the best alternative from the given set of alternatives is elimination and choice expressing the reality (ELECTRE) method. This method that is widely used by recent papers can handle both quantitative and qualitative alternatives [35]. This method utilizes outranking relations to rank and determines preferences for the alternatives. Following steps can assist to find the ranking by the ELECTRE method:

Step 1: As it is mentioned in the other methods, first it is necessary to find the weighted normalized matrix by using Eq. (6) and Eq. (16).

Step 2: After computing the weighted normalized decision matrix, the criteria should be divided into two parts by using the following formulas. The set of criteria is divided into concordance and discordance parts. Concordance criteria are the ones that having higher value would be more beneficial and conversely the lower value by discordance criteria would be advantageous.

$$A_{kl} = \left\{j|\ v_{kj} \geq v_{lj}\right\} \quad (25)$$

$$D_{kl} = \left\{j|\ v_{kj} \geq v_{lj}\right\} \quad (26)$$

Step 3: In this stage the concordance and discordance index are calculated by using Eq. (27) and Eq. (28), respectively.

$$I_{kl} = \sum W_j \quad (27)$$

$$NI_{kl} = \frac{Max\left|v_{kj} - v_{lj}\right|,\ j\in D_{k,l}}{Max\left|v_{kj} - v_{lj}\right|,\ j\in All} \quad (28)$$

Step 4: By using the data that is gained in the previous step, the concordant and discordant matrix can be constructed as follows:

$$NI = \begin{pmatrix} - & NI_{1,2} & NI_{1,3} & \cdots & NI_{1,m} \\ NI_{2,1} & - & NI_{2,3} & \cdots & NI_{2,m} \\ \vdots & \vdots & - & \vdots & \vdots \\ \vdots & \vdots & \vdots & - & \vdots \\ NI_{m,1} & NI_{m,2} & \cdots & NI_{m(m-1)} & - \end{pmatrix} \quad (29)$$

$$I = \begin{pmatrix} - & I_{1,2} & I_{1,3} & \cdots & I_{1,m} \\ I_{2,1} & - & I_{2,3} & \cdots & I_{2,m} \\ \vdots & \vdots & - & \vdots & \vdots \\ \vdots & \vdots & \vdots & - & \vdots \\ I_{m,1} & I_{m,2} & \cdots & I_{m(m-1)} & - \end{pmatrix} \quad (30)$$

Step 5: In this step by using Eq. (31) and Eq. (32), the preference and indifference threshold of this matrix is calculated and by comparing the previous matrix with this new threshold, the new effective concordant and discordant matrix is constructed by using the Formula (32) and (33):

$$\bar{I} = \sum_{l=1}^{m} \sum_{k=1}^{m} \frac{I_{k,l}}{m\,(m-1)} \tag{31}$$

$$F_{kl} = \begin{cases} 1 & I_{kl} \geq \bar{I} \\ 0 & I_{kl} < \bar{I} \end{cases} \tag{32}$$

$$\bar{NI} = \sum_{l=1}^{m} \sum_{k=1}^{m} \frac{NI_{k,l}}{m(m-1)} \tag{33}$$

$$G_{kl} = \begin{cases} 1 & NI_{kl} \leq \overline{NI} \\ 0 & NI_{kl} > \overline{NI} \end{cases} \tag{34}$$

Step 6: The final step is multiplying the concordant and discordant matrix to construct the general effective matrix.

$$H_{k,l} = F_{k,l} \cdot G_{k,l} \tag{35}$$

The best alternative is the one that has a higher value in the following Equation.

$$Q_n = \sum_{l=1}^{l} H_{n,l} - \sum_{k=1}^{k} H_{k,n} \tag{36}$$

3. Results and discussion

3.1. Morphology and wear resistance

Effect of duty cycle on volume percent of alumina nanoparticles included into the composite matrix is shown in Fig. 3. From this figure, it can be deduced that the coatings produced by pulsating current has higher uniformity than direct current. Electrodeposited composite coatings prepared under pulse current conditions has higher incorporation percentages than those produced with direct current. The most imperative reason for this is that in the process of electrodeposition with pulse current, there is a relaxation time (off time) for each pulse cycle during which there is no electrochemical reaction. Particles attain and gather around the cathode surfaces while having their adsorbed ions at their outer layer. Hence, at pulse current, too many particles with their adsorbed ions will be aggregated on the coating [1].

As has been mentioned elsewhere [36,37], nanoparticles directly influence the grain size of the coating due to the following reasons. First, the presence of Al_2O_3 nanoparticle increases appropriate places for germination of Cr which enhances the rate of germination so that the grain size of the coating will decrease [38,39]. Second, Al_2O_3 nanoparticles are obstacles to grain growth [37]. For as much as the lower grain size of the coating can enhance the coating performance, so the higher concentration of Al_2O_3 nanoparticles in the electrolyte is a good aspect of these coatings because it can assist to have more compact and smoother coating.

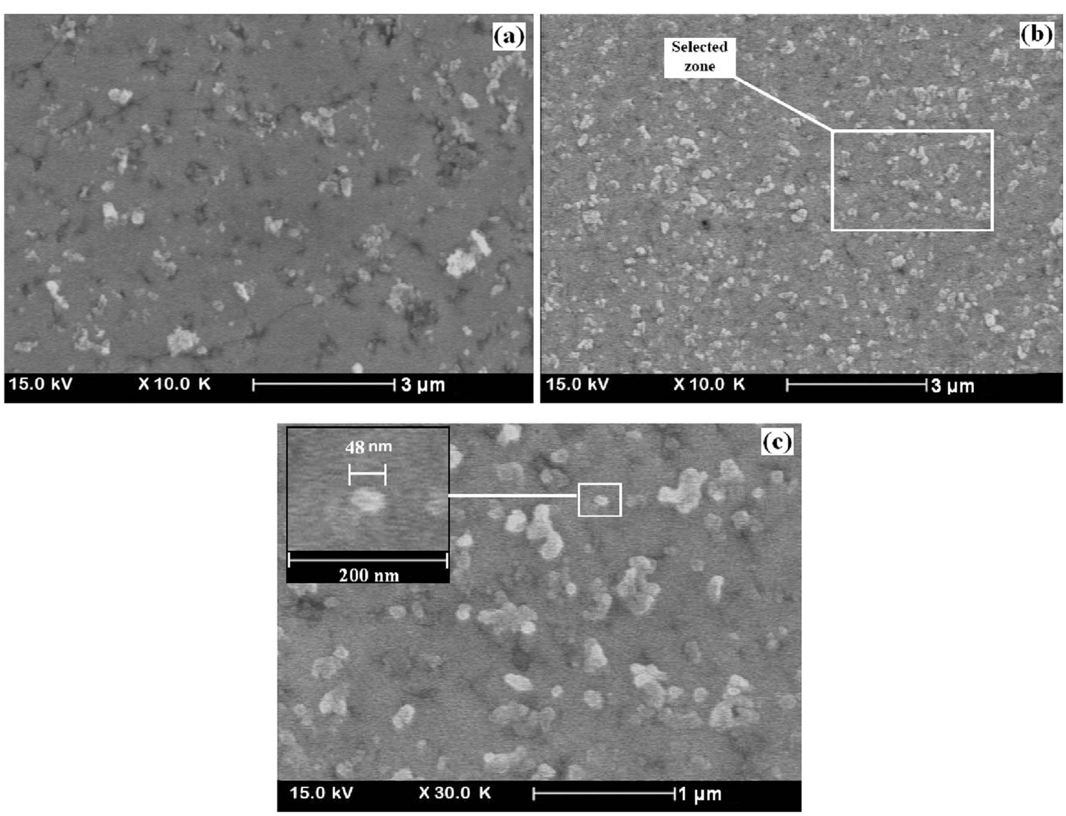

Fig. 3. SEM micrograph of composite coatings electrodeposited from a bath containing 1 g/l alumina with (a) direct current and (b) pulse current having duty cycle of 40% and frequency of 10 Hz (c) selected zone.

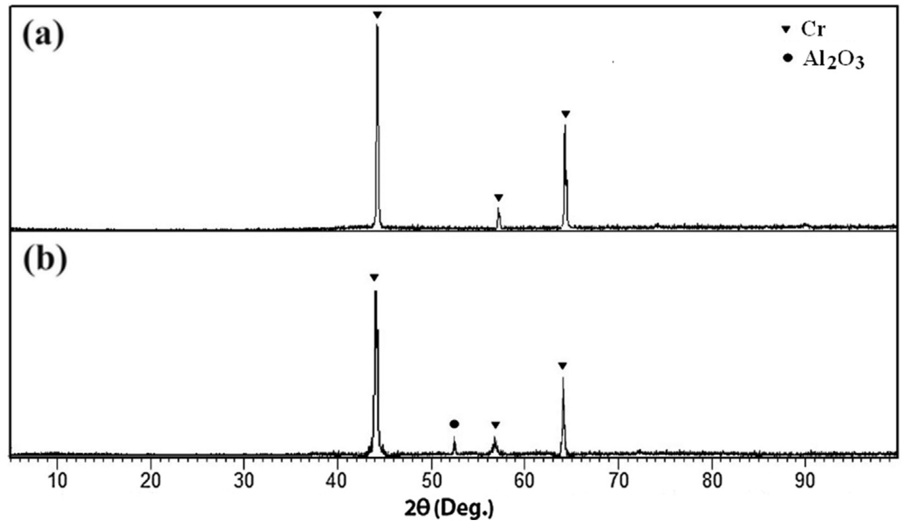

Fig. 4. XRD results (a) before and (b) after adding Al_2O_3 nanoparticles.

As it can be seen in Fig. 4, a small peak of Al_2O_3 is visible and it is evidence of presence of Al_2O_3 in the coating [40]. By using the Scherrer equation, the grain size of the coatings before and after adding Al_2O_3 can be calculated as follows:

$$t = \frac{0.9\,\lambda}{B\cos\theta_B} \tag{37}$$

where t is the mean size of the grains, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity and θ is the Bragg angle [41].

By comparing the grain size of both coatings developed, it can be deduced that the crystal size is minimized in the composite coating after adding Al_2O_3.

Effect of duty cycle and current frequency on wear resistance of Cr–Al_2O_3 nano-composite is shown in Fig. 5. From Fig. 5a, it is seen that the lowest wear loss (mg value) is achieved at 40% duty cycle. With 20% duty cycle, due to the high peak of the applied current, the produced deposits were powdery with poor adhesion so that the result is a recognizable decrease in wear resistance of the coatings. Above 40% duty cycle, the amount of alumina incorporation decreases. Hence, by increasing the duty cycle and decreasing of alumina nanoparticles, lower wear resistance is resulted.

It is observable in Fig. 5b that higher wear resistance is gained at lower pulse frequencies. As mentioned before, the incorporation percentages of the particles will increase by decreasing the current frequency [1]. By decreasing the frequency and increasing the amount of nanoparticles in the coatings, a significant increase will be observed in the wear resistance profile of the composite coating.

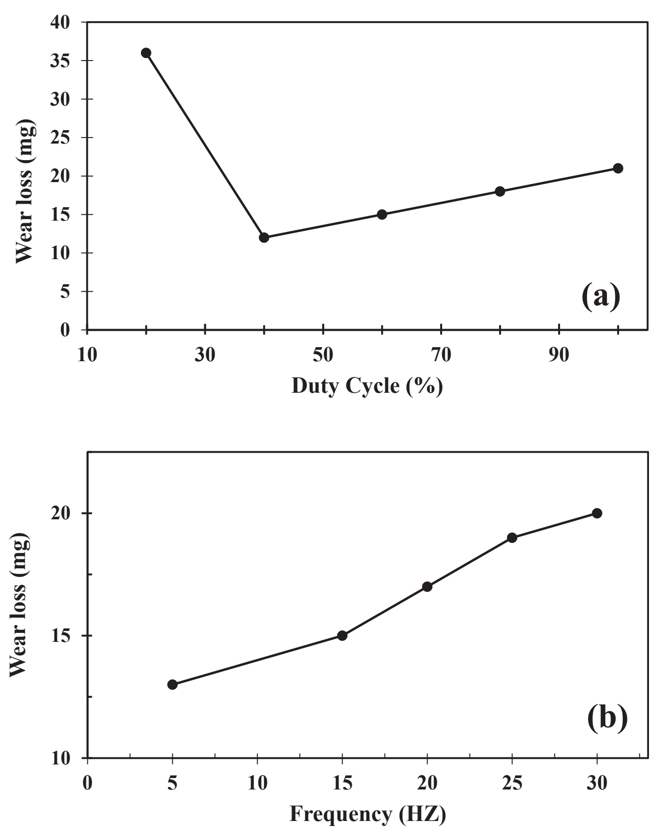

Fig. 5. Wear resistance of Cr-Al_2O_3 films electrodeposited from Cr bath containing 1 g/l alumina against: (a) duty cycle and (b) frequency.

3.2. *Assessment of optimal coating conditions to obtain maximum performance of the coatings and ranking the alternatives*

3.2.1. *Estimation of criteria weights by AHP and entropy methods*

Twelve candidates (alternatives) illustrated in Table 5 and four

Table 5
Candidate coating conditions.

Candidate No.	Duty Cycle (%)	Frequency (Hz)	Al2O3 particle concentration in bath (g/l)
C1	20	10	1
C2	40	10	1
C3	60	10	1
C4	80	10	1
C5	100	10	1
C6	40	5	1
C7	40	15	1
C8	40	20	1
C9	40	25	1
C10	40	30	1
C11	40	10	0
C12	40	10	0.5

Table 6
Calculated criteria weights.

Criteria	AHP	Entropy
Wear loss (mg)	0.51	0.26
i_{corr} (μACm^{-2})	0.31	0.19
Hardness (HV)	0.12	0.28
Current efficiency (%)	0.06	0.27

Table 7
The decision matrix.

Candidate No.	Candidate selection criteria			
	Wear loss (mg)	i_{corr} (μA Cm^{-2})	Hardness (HV)	Current Efficiency (%)
c1	36	6.87	592	11.66
c2	12	1.23	1291	26.11
c3	15	1.41	1186	23.85
c4	18	1.6	1113	20.1
c5	21	1.98	1021	14.07
c6	13	1.52	1292	26.97
c7	15	1.71	1213	25.65
c8	17	2.08	1158	24.03
c9	19	2.27	1084	21.51
c10	20	2.34	1072	19.36
c11	21	3.07	1024	15.77
c12	19	1.86	1110	22.99

criteria (wear loss, icorr, hardness and current efficiency) were considered for evaluation of the optimal conditions. The final outcome of the subjective method by using the pairwise comparisons in AHP route and the objective method in entropy technique are all gathered in Table 6. The maximum eigenvalue of the pairwise comparison matrix in AHP method was 4.023. Based on the information given in Table 3, the random consistency index (RI) is 0.9 for n = 4. Using Eq. (5), the value of (CI) was computed to be 0.007. Using Eq. (4), the consistency ratio was calculated to be 0.008. A consistency value of less than 0.1 ensures consistent comparison [23].

Table 8
The normalized decision matrix.

Candidate No.	Selection criteria			
	Wear loss (mg)	i_{corr} (μA cm^{-2})	Hardness (HV)	Current Efficiency (%)
c1	0.5265	0.7231	0.1539	0.1563
c2	0.1755	0.1295	0.3357	0.3500
c3	0.2194	0.1484	0.3084	0.3197
c4	0.2632	0.1684	0.2894	0.2694
c5	0.3071	0.2084	0.2655	0.1886
c6	0.1901	0.1600	0.3359	0.3615
c7	0.2194	0.1800	0.3154	0.3438
c8	0.2486	0.2189	0.3011	0.3221
c9	0.2779	0.2389	0.2819	0.2883
c10	0.2925	0.2463	0.2787	0.2595
c11	0.3071	0.3232	0.2663	0.2114
c12	0.2779	0.1958	0.2886	0.3082

Table 9
The best and the worst values of all criterion functions in VIKOR method.

	Wear loss (mg)	i_{corr}(μACm^{-2})	Hardness (HV)	Current Efficiency (%)
F^*	0.1755	0.1295	0.3359	0.3615
F^-	0.5265	0.7231	0.1539	0.1563

Table 10
The required data for solving Eq. (15) in VIKOR method.

S^*	0.0035	R^*	0.0034
S^-	1.0000	R^-	0.5100

3.2.2. Assessment of alternatives

By using the weighting methods, the criteria weights are

Table 11
The rank of the candidates in VIKOR method.

AHP					Entropy				
No.	S_i	R_i	Q_i	Rank	No.	S_i	R_i	Q_i	Rank
1	1.0000	0.5100	0.0000	12	1	1.0000	0.2800	0.0000	12
2	0.0035	0.0034	1.0000	1	2	0.0154	0.0151	0.9919	2
3	0.1040	0.0638	0.8899	3	3	0.1359	0.0550	0.8567	4
4	0.2053	0.1274	0.7763	6	4	0.2701	0.1212	0.6656	8
5	0.3294	0.1912	0.6511	10	5	0.4585	0.2275	0.3724	11
6	0.0371	0.0212	0.9655	2	6	0.0206	0.0108	0.9973	1
7	0.1089	0.0638	0.8875	4	7	0.1035	0.0325	0.9149	3
8	0.1874	0.1062	0.8062	5	8	0.1881	0.0542	0.8317	5
9	0.2629	0.1488	0.7263	8	9	0.2903	0.0963	0.7016	7
10	0.2985	0.1700	0.6875	9	10	0.3463	0.1342	0.6027	9
11	0.3822	0.1912	0.6246	11	11	0.4641	0.1975	0.4254	10
12	0.2302	0.1488	0.7427	7	12	0.2400	0.0759	0.7651	6

Table 12
The ideal and negative ideal solution for all criteria in TOPSIS method.

	Wear loss (mg)	i_{corr}(μACm^{-2})	Hardness (HV)	Current Efficiency (%)
V^+	0.0895	0.0402	0.0403	0.0217
V^-	0.2685	0.2242	0.0185	0.0094

Table 13
The rank of the candidates in TOPSIS method.

AHP					Entropy				
No.	S^+	S^-	Q_i	Rank	No.	S^+	S^-	Q_i	Rank
1	0.2579	0.0000	0.0000	12	1	0.1634	0.0000	0.0000	12
2	0.0007	0.2579	0.9973	1	2	0.0031	0.1624	0.9812	1
3	0.0235	0.2381	0.9101	3	3	0.0182	0.1487	0.8911	4
4	0.0470	0.2189	0.8232	5	4	0.0369	0.1348	0.7850	7
5	0.0727	0.1954	0.7288	10	5	0.0630	0.1178	0.6516	10
6	0.0120	0.2460	0.9533	2	6	0.0069	0.1574	0.9578	2
7	0.0274	0.2310	0.8938	4	7	0.0167	0.1471	0.8981	3
8	0.0467	0.2120	0.8194	6	8	0.0293	0.1345	0.8212	5
9	0.0628	0.1972	0.7586	8	9	0.0420	0.1233	0.7460	8
10	0.0704	0.1907	0.7303	9	10	0.0493	0.1179	0.7050	9
11	0.0929	0.1676	0.6483	11	11	0.0674	0.1012	0.6000	11
12	0.0565	0.2077	0.7861	7	12	0.0354	0.1316	0.7882	6

Table 14
The rank of the candidates in COPRAS method.

AHP					Entropy				
No.	S^+	S^-	Q_i	Rank	No.	S^+	S^-	Q_i	Rank
1	0.0278	0.4927	0.1131	12	1	0.0853	0.2743	0.1307	12
2	0.0613	0.1297	0.3855	1	2	0.1885	0.0702	0.3660	1
3	0.0562	0.1579	0.3224	3	3	0.1727	0.0852	0.3189	3
4	0.0509	0.1864	0.2763	5	4	0.1538	0.1004	0.2779	7
5	0.0432	0.2212	0.2332	10	5	0.1253	0.1194	0.2296	10
6	0.0620	0.1466	0.3488	2	6	0.1917	0.0798	0.3479	2
7	0.0585	0.1677	0.3091	4	7	0.1811	0.0912	0.3178	4
8	0.0555	0.1946	0.2714	6	8	0.1713	0.1062	0.2886	5
9	0.0511	0.2158	0.2459	8	9	0.1568	0.1176	0.2627	8
10	0.0490	0.2255	0.2354	9	10	0.1481	0.1228	0.2496	9
11	0.0446	0.2568	0.2083	11	11	0.1316	0.1413	0.2199	11
12	0.0531	0.2024	0.2607	7	12	0.1640	0.1095	0.2779	6

Table 15
The rank of the candidates in ELECTRE method.

AHP			Entropy		
No.	Q_i	Rank	No.	Q_i	Rank
1	−56	9	1	0	6
2	54	1	2	22	1
3	35	3	3	18	2
4	4	5	4	11	3
5	−47	8	5	−30	10
6	44	2	6	7	4
7	35	3	7	4	5
8	14	4	8	−4	7
9	−5	6	9	−13	9
10	−26	7	10	−6	8
11	−47	8	11	−13	9
12	−5	6	12	4	5

obtained. The subsequent step is sorting the alternatives based on these weights by assistance of MCDM procedure. The data, including wear loss (mg), i_{corr} (μACm^{-2}), hardness (HV) and current efficiency (%) for the alternatives are mentioned in Table 7 (decision matrix). By following the mentioned processes, the decision matrix is normalized by the usage of Eq. (6) as shown in Table 8. The ideal solution, negative ideal solution, utility and regret measures that are prerequisites for the final results in VIKOR method are listed respectively in Tables 9 and 10 and all the results for the VIKOR method by the mentioned procedure are listed in Table 11. The other methods similarly used to find the ranking of alternatives and the results gained by TOPSIS, COPRAS and ELECTRE methods respectively are visible in Tables 13–15. The ideal and negative ideal solutions that are needed in the TOPSIS method are all gathered in Table 12.

As can be seen in Fig. 6, different ranking methods generate different results and this is caused mainly by the strategy that each method uses to opt the best candidate. As an example, the strategy in the VIKOR method is that the best candidate is the one that is closest to the ideal solution but in TOPSIS method the best alternative is the one which has the shortest distance to the ideal solution and the farthest distance from the negative-ideal solution which means that it is not always close to the ideal solution. Unlike the mentioned methods, ELECTRE ranks alternatives first by pairwise comparisons of the alternatives under each criterion with the goal of elimination of less favorable alternatives from the pool of candidates. Introducing concordance and discordance will make this issue to happen. The other procedure for ranking alternatives is utilized by the COPRAS. This method will determine the significance and priority of the alternatives among the mentioned criteria and this will assist to rank the candidates.

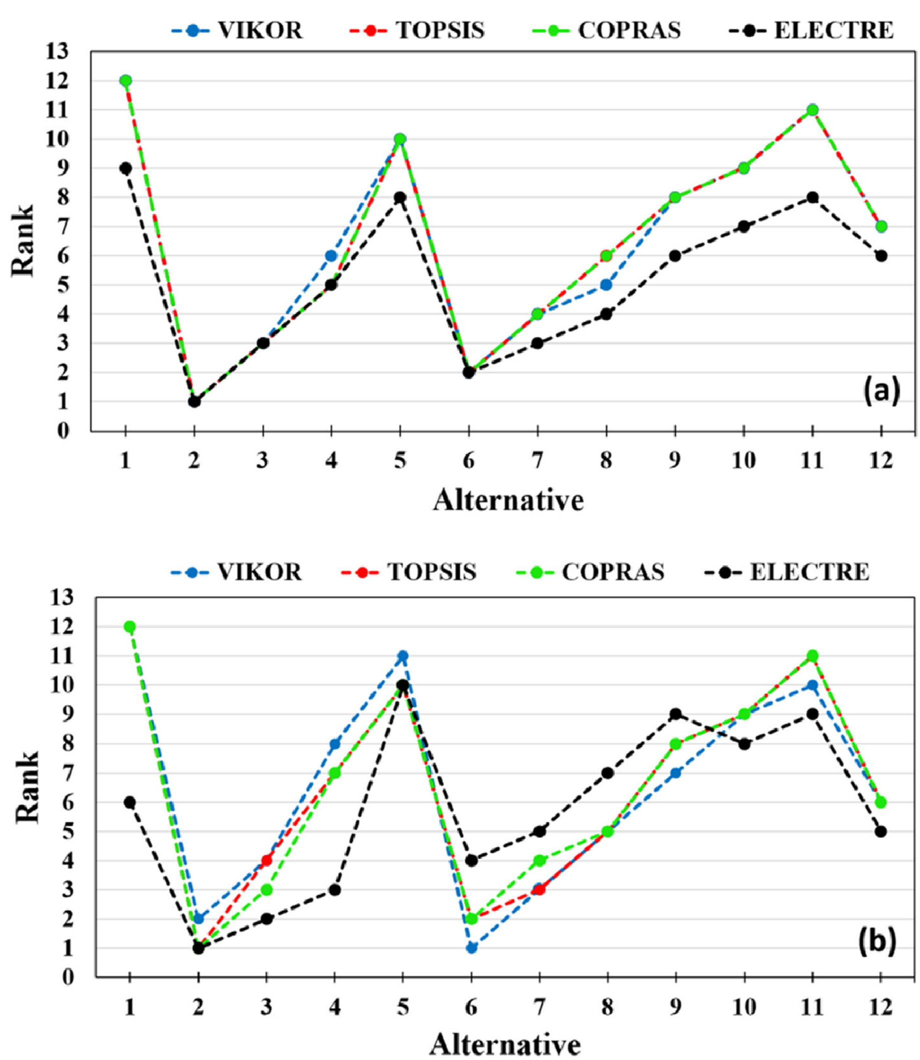

Fig. 6. Comparison of obtained rankings using different MCDM methods, (a) AHP, (b) Entropy.

Table 16
The Spearman's rank correlation coefficients of different MCDM methods.

The Utilized Method	AHP	Entropy
VIKOR-TOPSIS	0.9930	0.9790
VIKOR-COPRAS	0.9930	0.9720
VIKOR-ELECTRE	0.9947	0.6736
TOPSIS-COPRAS	1	0.9930
TOPSIS-ELECTRE	0.9877	0.7368
COPRAS-ELECTRE	0.9877	0.7614

Table 17
The Spearman's rank correlation coefficient for similar MCDM but different weighting methods.

The Utilized Method	Spearman's Coefficient
VIKOR	0.9580
TOPSIS	0.9720
COPRAS	0.9790
ELECTRE	0.7584

In this study, in order to evaluate the best coating condition, the wear loss and i_{corr} should be minimized and the hardness and current efficiency should be maximized.

Based on majority of the used methods and their results, the optimal process for electrodeposition of $Cr-Al_2O_3$ coating from Cr(III) bath on copper is alternative number 2. The best candidate among all alternatives will be the one which have the best performance for the criteria that have highest weighting factors and as it is shown in Table 7, this candidate has shown a good performance for most significant criteria. This candidate can produce a coating with good wear and corrosion resistance and high hardness and current efficiency.

As can be seen in Table 11, in some cases using the same ranking method generates different results. It is visible in Table 11 that the best candidate chosen by using AHP-VIKOR is the candidate number 2 but utilizing Entropy-VIKOR technique will opt the candidate number 6 as the best one. As it can be seen in Table 6 the main reason for this is that the utilized weighting procedures (AHP and Entropy) present different weight factors for each criterion. The candidate number 2 has the highest efficiency for two criteria, lowest wear loss and i_{corr}, and as the AHP method have allocated the highest weight factors to these two criteria, this candidate will be chosen as the best. Unlike the AHP technique, the entropy technique have allocated the highest weight factor to Hardness and Current efficiency which introduce candidate number 6 as the best alternative.

Another achievement of this study is as follows: utilization of subjective weighting methods can assist scientists to gain more similar result; though they decide to use different methods. To achieve this goal, they should use Spearman's Rank Correlation Coefficients shown in Table 16. By using a subjective weighting method, ranking of the alternatives from different methods become much closer and the Spearman coefficient tends to 1; but the Spearman coefficients obtained by the Entropy weighting technique considerably differs from 1; so the ranking of alternatives by four different MCDM methods do not have as much similarity in the Entropy method as the AHP method weighting technique, as is shown in Fig. 6.

It is visible in Fig. 7 that using different weighting methods have different impacts on the rankings and some of the MCDM methods are more affected by the used weighting procedure. The most difference between obtained results using AHP and ENTROPY methods is for ELECTRE and the lowest difference is for CORPAS method. The spearman coefficient for this comparison can be seen in Table 17.

4. Conclusions

Appropriate selection of optimal pulse parameters for $Cr-Al_2O_3$

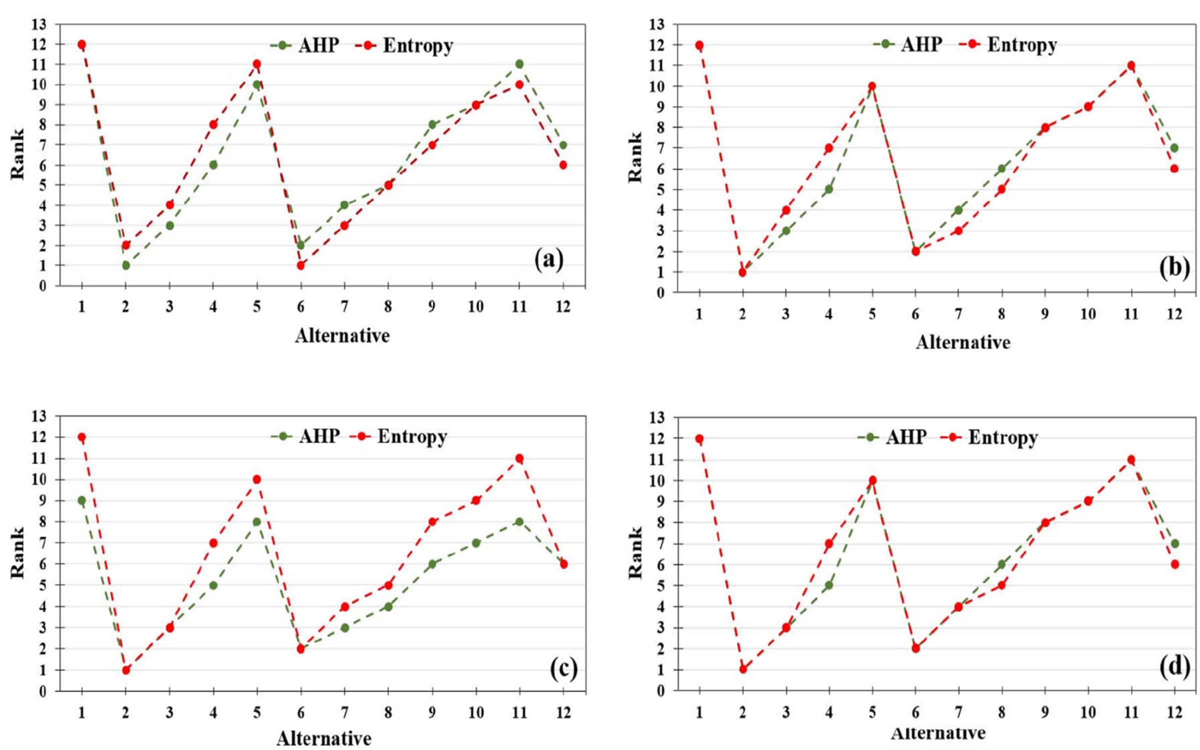

Fig. 7. Comparison of obtained rankings using different weighting methods, (a) VIKOR, (b) TOPSIS, (c) ELECTRE, (d) COPRAS.

nano-composite electrodeposition is obtained by utilization of subjective AHP approach to the coatings for best wear and corrosion resistance. Employment of subjective approach reduces the effect of selection methods and improves ranking process by a more consistent weighting procedure. The study elucidates a managerial decision making technique which includes subjective weighting routine for selection of the optimal electrodeposition parameters for most consistent results. Furthermore, selection procedures are not equally affected by the weighing method. ELECTRE has the highest and COPRAS has the lowest sensitivity to the weighing method.

Experimental discoveries of the study checked by VIKOR, ELECTRE, COPRAS and TOPSIS in combination with AHP yield the advantageous choice of the Cr–Al_2O_3 nanocomposite coating at 40% duty cycle, 10 Hz frequency and 1 g/l Nano- Al_2O_3 content as preferred alternative conditions. In addition, it is found that the influence of duty cycle on properties of the deposit is more determinant than the other parameters.

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References

[1] M. Salehi Doolabi, et al., Influence of pulse parameters on electrocodeposition of Cr–Al2O3 nanocomposite coatings from trivalent chromium bath, Int. Heat Treat. Surf. Eng. 6 (4) (2012) 178–184.
[2] M. Ashby, et al., Selection strategies for materials and processes, Mater. Des. 25 (1) (2004) 51–67.
[3] M. Chiner, Planning of expert systems for materials selection, Mater. Des. 9 (4) (1988) 195–203.
[4] H. Zafarani, A. Hassani, E. Bagherpour, Achieving a desirable combination of strength and workability in Al/SiC composites by AHP selection method, J. Alloys Compd. 589 (2014) 295–300.
[5] P. Chatterjee, V.M. Athawale, S. Chakraborty, Selection of materials using compromise ranking and outranking methods, Mater. Des. 30 (10) (2009) 4043–4053.
[6] M. Yousefpour, A. Rahimi, Characterization and selection of optimal parameters to achieve the best tribological performance of the electrodeposited Cr nanocomposite coating, Mater. Des. 54 (2014) 382–389.
[7] P. Liu, X. Zhang, Research on the supplier selection of a supply chain based on entropy weight and improved ELECTRE-III method, Int. J. Prod. Res. 49 (3) (2011) 637–646.
[8] T.L. Saaty, The Analytic Hierarchy Process, McGrew Hill, New York, 1980. International, Translated to Russian, Portuguesses and Chinese, Revised edition, Paperback (1996, 2000), Pittsburgh: RWS Publications.
[9] S.R. Maity, P. Chatterjee, S. Chakraborty, Cutting tool material selection using grey complex proportional assessment method, Mater. Des. 36 (2012) 372–378.
[10] A. Shanian, O. Savadogo, A material selection model based on the concept of multiple attribute decision making, Mater. Des. 27 (4) (2006) 329–337.
[11] H. Çalışkan, et al., Material selection for the tool holder working under hard milling conditions using different multi criteria decision making methods, Mater. Des. 45 (2013) 473–479.
[12] S. Opricovic, Multicriteria optimization of civil engineering systems, Fac. Civ. Eng. Belgrade 2 (1) (1998) 5–21.
[13] Z. Zeng, A. Liang, J. Zhang, Electrochemical corrosion behavior of chromium–phosphorus coatings electrodeposited from trivalent chromium baths, Electrochim. Acta 53 (24) (2008) 7344–7349.
[14] G. Saravanan, S. Mohan, Pulsed electrodeposition of microcrystalline chromium from trivalent Cr-DMF bath, J. Appl. Electrochem. 39 (8) (2009) 1393–1397.
[15] J. McDougall, M. El-Sharif, S. Ma, Chromium electrodeposition using a chromium (III) glycine complex, J. Appl. Electrochem. 28 (9) (1998) 929–934.
[16] H.R. Zafarani, et al., Removal of chromate ion from aqueous solutions by sponge iron, Desalination Water Treat. 52 (37–39) (2014) 7154–7162.
[17] H.R. Zafarani, et al., Green walnut shell as a new material for removal of Cr (VI) ions from aqueous solutions, Desalination Water Treat. 55 (2) (2015) 431–439.
[18] S. Surviliene, et al., Effect of MoO_2 and TiO_2 on electrodeposition and properties of chromium coating, Surf. Coat. Technol. 137 (2) (2001) 230–234.
[19] M. Salehi Doolabi, S. Khatiboleslam Sadrnezhaad, D. Salehi Doolabi, Electroplating and characterization of Cr–Al2O3 nanocomposite film from a trivalent chromium bath, Anti-Corrosion Methods Mater. 61 (4) (2014) 205–214.
[20] T.L. Saaty, How to make a decision: the analytic hierarchy process, Eur. J. Oper. Res. 48 (1) (1990) 9–26.
[21] S. Perez-Vega, et al., Analytical hierarchy processes (AHP) for the selection of solvents in early stages of pharmaceutical process development, Process Saf. Environ. Prot. 89 (4) (2011) 261–267.
[22] H. Goh, et al., Combination of TOPSIS and AHP in load shedding scheme for large pulp mill electrical system, Int. J. Electr. Power Energy Syst. 47 (2013) 198–204.
[23] M. Dağdeviren, S. Yavuz, N. Kılınç, Weapon selection using the AHP and TOPSIS methods under fuzzy environment, Expert Syst. Appl. 36 (4) (2009) 8143–8151.
[24] E. Albayrak, Y.C. Erensal, Using analytic hierarchy process (AHP) to improve human performance. An application of multiple criteria decision making problem, J. Intell. Manuf. 15 (2004) 491–503.
[25] R. Khorshidi, et al., Selection of an optimal refinement condition to achieve maximum tensile properties of Al–15% Mg 2 Si composite based on TOPSIS method, Mater. Des. 46 (2013) 442–450.
[26] C. Shannon, A Mathematical Theory of Communication, bell System technical journal 27: 379-423 and 623–656. Mathematical Rev (MathSciNet) MR10, 133e, 1948.
[27] S. Opricovic, G.-H. Tzeng, Compromise solution by MCDM methods: a comparative analysis of VIKOR and TOPSIS, Eur. J. Oper. Res. 156 (2) (2004) 445–455.
[28] P.-L. Yu, A class of solutions for group decision problems, Manag. Sci. 19 (8) (1973) 936–946.
[29] M. Zeleny, Multi Criteria Decision Making, McGraw-Hills, New York, 1982.
[30] R.N. Kackar, Off-line quality control, parameter design, and the Taguchi method, in: Quality Control, Robust Design, and the Taguchi Method, Springer, 1989, pp. 51–76.
[31] S. Opricovic, Preference stability of compromise solution in multiple decision making, in: XIth International Conference on Multiple Criteria Decision Making, Coimbra, Portugal, 1994.
[32] K.P. Yoon, C.-L. Hwang, Multiple Attribute Decision Making: an Introduction, vol. 104, Sage publications, 1995.
[33] E. Zavadskas, A. Kaklauskas, Determination of an efficient contractor by using the new method of multicriteria assessment, in: International Symposium for "The Organization and Management of Construction". Shaping Theory and Practice, 1996.
[34] B. Roy, The outranking approach and the foundations of ELECTRE methods, Theory Decis. 31 (1) (1991) 49–73.
[35] J. Figueira, V. Mousseau, B. Roy, ELECTRE Methods, in Multiple Criteria Decision Analysis: State of the Art Surveys, Springer, 2005, pp. 133–153.
[36] P. Gyftou, et al., Tribological study of Ni matrix composite coatings containing nano and micro SiC particles, Electrochim. Acta 50 (23) (2005) 4544–4550.
[37] Y. Yao, et al., Electrodeposition and mechanical and corrosion resistance properties of Ni–W/SiC nanocomposite coatings, Mater. Lett. 61 (1) (2007) 67–70.
[38] J.-L. Wang, R.-D. Xu, Y.-Z. Zhang, Influence of SiO 2 nano-particles on microstructures and properties of Ni-WP/CeO 2-SiO 2 composites prepared by pulse electrodeposition, Trans. Nonferrous Metals Soc. China 20 (5) (2010) 839–843.
[39] S. Pouladi, M. Shariat, M. Bahrololoom, Electrodeposition and characterization of Ni–Zn–P and Ni–Zn–P/nano-SiC coatings, Surf. Coat. Technol. 213 (2012) 33–40.
[40] S. Aruna, M. Muniprakash, V.W. Grips, Effect of titania particles preparation on the properties of Ni–TiO2 electrodeposited composite coatings, J. Appl. Electrochem. 43 (8) (2013) 805–815.
[41] M. Eslami, et al., Study on tribological behavior of electrodeposited Cu–Si 3 N 4 composite coatings, Mater. Des. 58 (2014) 557–569.