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Duplex Coating Of Black Ceramic Coating For Copper And Stainless Steel Substrate

[Jamaliah Idris, Noor Sabariah Mahat, Mohammad Mahdi Taheri]

***Abstract*— Black ceramic coating has become the important process of metal finishes in solar thermal application. Considerable effort has been expended on developing coatings and absorber materials having high conversion efficiency. This study focused on applying the black ceramic coating using an electroplating process on two types of substrate, which is copper and stainless steel. Black chromium is the best formulation for coating and it is a common use of thermal solar application. The optical properties such as high absorptance, low emittance and metallurgical properties of the combination of black ceramic coating on both substrates are tested and analyzed. It is found that the optical properties of the copper substrate give high absorption, $\alpha > 0.95$ and low emittance, $\mathcal{E} < 0.013$. Besides that, stainless steel can be the alternative substrate for solar application because it is cheaper than copper. The value of absorptance and emittance for stainless steel is $\alpha > 0.91$ and $\mathcal{E} < 0.1$.**

***Keywords*— Duplex Coating; Black Ceramic Coating; Electroplating; Solar Thermal Application.**

I. Introduction

The duplex coating is a two layer of coating. Duplex coating is a term used to refer when two or more coating systems are used on all types of metal. The best properties of duplex coating are created from the combination of black ceramic coating. Black ceramic coating is a black color effect of the ceramic coating and it is a selective coating for many applications such as in solar thermal, automotive, aerospace and others. This study is focused on solar thermal application (solar collector) were specialist on hot water system [1].

The solar thermal collector that allows the energy coming from the sun to be taken advantage of for the purpose of saving are widely known. An ideal solar selective absorber coating must have high solar absorptance and low emittance. Solar selective black chrome coating is widely used for decorative as well as function application because of their durability and excellent optical properties [2].

Solar thermal heat systems are installed to convert solar radiation into heat in order to produce domestic hot water, heating swimming pool and to cover the demand for consumer. The physical principle of energy conversion of solar thermal is absorption, emission, reflection, and transmission [3]. In this study, the black ceramic coating on copper and stainless steel substrate was prepared by electroplating process in order to investigate their optical properties.

II. Experimental Procedure

A. *Sample preparation*

The substrate materials of copper and stainless steel is selected. Both of the substrate were selected because it wants to study different effect of duplex coating and the cost of both substrates. In electroplating process, the specimens to be used were cut into a size of 20mm x 130mm x 1mm for cathode and 35mm x 150mm x 1mm for anode [4,5].

The different materials copper and stainless steel will need a different pretreatment process prior to the electroplating of the black chromium and black nickel. This is because the materials have different properties which will need their own pretreatment process. The pretreatment process for stainless steel is the stainless steel plate must be washed with acetone, ethanol, a concentrated NaOH solution and finally rinsing with distilled water. Fail to do this step, the coating will damage. While, the pretreatment of copper plate were referred to ASTM B 281-88; the copper plates were first cleaned using soap or white spirit with cloth to remove any contact oil, grease and strain, followed by rinsing with water. After that, they were electrocleaned to produce the chemically clean surface required for electroplating. The activation process was carried out by contact 10 Vol% sulfuric acid for 15 to 20 second for oxide removal. Following activation the plates were thoroughly rinsed in distilled water to remove all trace of sulfate ions [6,7].

The new electroplating solution was synthesized for improvement in electroplating condition. The bath formulation used in this work was shown in Table 1 and Table 2.

Table 1: Hexavalent black chromium plating baths (Bath A (Wong 2005), B)

Chemicals	Bath A	Bath B
Chromic acid, CrO_3 (g/L)	250	250
Hexafluorosilic acid, H_2SiF_6 (ml)	0.5	0.5
Barium Carbonate, BaC03 (g/L)	10	10
Sodium nitrate, $NaN0_3$ (g/L)	5	3
Boric Acid, H_3B0_3 (g/L)	10	12
Urea, CH_4N_20 (g/L)	3	-

Jamaliah Idris*, Noor Sabariah Mahat, Mohammad Mahdi Taheri
Faculty of Mechanical Engineering/ Universiti Teknologi Malaysia
Malaysia

Table 2: Electrochemical deposition of black nickel (M. Lira-Cantu' et al., 2005)

Chemicals	(Bath C) Bright Nickel	(Bath D) Black Nickel
Nickel sulfate	300 g/L	-
Nickel chloride	35 g/L	75 g/L
Sodium chloride	-	30 g/L

B. *Hull Cell Test*

The hull cell used in electroplating is to determine the possible range of plating condition such as bath temperature, optimum color of the coat and current density used for electroplating. A number of copper and stainless steel plate were tested by using the hull cell with current range from 5 -8 Ampere, plating time of 5 minutes. It's found that, when the constant plating time the temperature of bath increase with the increase in the applied current. The optimum current density for the plating bath for this electroplating experiment is 25-40A/dm2. After that, the tests were followed by a simple electroplating process to produce the black ceramic coating [6,7].

C. *Electroplating Process*

The result of a single layer electroplating process for copper and stainless steel substrate were shown in Table 3 and Table 4. The electroplating was done continuously and the temperature of the bath was increased. Totally all bath formulations are showing the type of black color as shown in Table 3. The coating appearance of formulation bath A and B give the dull black tone. Furthermore, the bath formulations of C and D had a light black coating on the lower current applied. Then when the high current applied to this specimen the coating color becomes bright deep black.

This electroplating also was done with continuous process. Table 4 indicates that the stainless steel specimen coating displays a deep bright black for the formulation A. Besides that for the formulation B, as sample YB1 applied with lower current the color shows deep bright coating and after increased the current supplied the color change to dull black. The color of the coating for sample YC1 and YD1 using formulation C and D show grayish black tone when low current was applied. However, when the high current is applied for the Sample YC2 and YD2 the color change to bright black. Overall, the

Table 3: Single layer electroplating for Copper substrate
* Bath temperature: 27°C * plating time: 5 minutes

Bath formulation	Specimen	Current Applied (A)	Bath temperature After plating (°C)	Coating Appearance
A	YA1	8	30	Deep bright black
	YA2	10	32	Deep bright black
B	YB1	8	29	Deep bright black
	YB3	10	31	Dull black
C	YC1	8	30	Grayish black
	YC2	10	31	Bright black
D	YD1	8	29	Grayish black
	YD2	10	31	Bright black

Table 4: Single layer electroplating for Stainless Steel substrate
* Bath temperature: 27°C * plating time: 5 minutes

Bath formulation	Specimen	Current Applied (A)	Bath temperature After plating (°C)	Coating Appearance
A	XA1	8	30	Dull black
	XA2	10	32	Dull black
B	XB1	8	29.5	Dull black
	XB3	10	31	Dull black
C	XC1	8	30	Light black
	XC2	10	32.5	Bright black
D	XD1	8	29	Light black
	XD2	10	31.5	Bright deep black

first layer coating presents the black color and for the best optical property double layer performs.

Another layer was coated onto the specimen in order to make a duplex coating, and then the sample was re-cleaned and followed the step of electroplating. The second baths for all formulations were prepared as shown in Table 5. The coating appearance of the duplex ceramic coating for all specimens shows the deep black and dull black color. At the constant current applied bath temperatures after plating are increasing.

III. Result and Discussion

A. *Optical Properties*

The coated specimen is then observed for optical properties using UV-VIS-IR Spectroscopy to determine the value of absorptance and spectral emittance. The results for duplex ceramic coated are shown in Table 6.

The absorptance values obtained are rather high between two types of substrate copper and stainless steel. The range of absorptance value for copper substrate is 0.8946 to 0.9572. While the absorption value of stainless steel quiet low, which is in the range of 0.8048 to 0.9156. The best and the highest value for absorption are achieved by formulating A and B which is the black chromium formulation coating. The highest value based on copper substrate is XBA where a is 0.9572, followed by XAB (0.9563), and XDA (0.9448).

The range of emittance value for copper substrate is 0.0131to 0.1013 and the stainless steel substrate is 0.0943 to 0.1770. The specimens who are lowest value for the emittance for the copper substrate is XBA where e = 0.0131 and for the stainless steel substrate, the lowest value is 0.0470.

The formulation of black chromium gives the better result of high absorptance and low emittance which stated by Mo'nica Lira-Cantu (2004). Meanwhile, the black nickel is also best composition and it suitable to undercoat or the first layer of the coating.

From the findings, all the coated specimens have good selectivity of optical properties where the ratio is in the range of 9.29 to 35.29 for copper substrate. The selected ratio of the stainless steel is 4.55 to 19.41. Stated by Malhotra and

Table 5: Duplex Black ceramic coating electroplating

*Bath temperature: 27°C *plating time: 5-10 minutes

Specimen	Second Bath formulation	Current Applied (A)	Bath temperature After plating (°C)	Coating Appearance
XAB	B	10	30	Deep black
XAC	C	10	31	Dull black
XBA	A	10	29	Deep black
XBD	D	10	31	Dull black
XCA	A	10	29.5	Deep black
XCD	B	10	30	Deep black
XDA	A	10	30	Deep black
XDB	B	10	30	Deep black
YAB	B	10	30.5	Deep black
YAC	c	10	31	Dull black
YBA	A	10	29	Deep black
YBD	D	10	31	Dull black
YCA	A	10	29.5	Deep black
YCB	B	10	30	Deep black
YDA	A	10	30	Deep black
YDB	B	10	30.5	Deep black

Choptra (1985), specimen with high selectivity is not being efficient as those with higher absorptance.

Therefore, the high absorptance value is greater priority than low emittance. In the next experiment, six specimens of best form the optical property were selected. There are three specimens from copper substrate and three specimen form stainless steel substrate.

The specimen was selected for further testing; physical and metallurgical. The specimens were selected based on the criteria of best coating appearance (smooth and black coating) and optical property with higher value of absorptance, α and low emittance, Ɛ. The sample chosen were shown in Table 7 and Fig. 1

Table 6: Optical property of duplex ceramic coated

Sample	Absorptanc(α)	Emittance (ε)	α/ε
XAB	0.9563	0.0271	35.29
XAC	0.8964	0.0724	12.38
XBA	0.9572	0.0131	73.07
XBD	0.9162	0.0478	19.17
XCA	0.9448	0.0327	13.70
XCD	0.9434	0.0609	15.49
XDA	0.9437	0.0468	20.16
XDB	0.9409	0.1013	9.29
YAB	0.9156	0.0990	9.25
YAC	0.8048	0.1770	4.55
YBA	0.9124	0.0470	19.41
YBD	0.8253	0.1251	6.60
YCA	0.8907	0.1341	6.64
YCB	0.8879	0.1442	6.16
YDA	0.9134	0.0943	9.69
YDB	0.8776	0.1450	6.05

Table 7: The best 6 specimen from copper and stainless steel substrate

Specimen	Absorptance, α	Emittance, Ɛ	Coating appearance
XAB	0.9563	0.0271	35.29
XBA	0.9572	0.0131	73.07
XDA	0.9448	0.0327	13.70
YAB	0.9156	0.0990	9.25
YBA	0.9124	0.0470	19.41
YDA	0.9134	0.0943	9.69

Fig. 1: The best 6 substrates (copper and stainless steel)

B. *Metallurgical Property*

Metallurgical Property was obtained using Scanning Electron Microscope (SEM) and image analyzer. The surface microstructure of sample and coating thickness were observed and analyzed. The surface microstructure of the specimen was observed through a Scanning Electron Microscope (SEM) with higher degree of magnification. The magnification was use is 1000X. From this magnification shows the microstructure and at the same time show the micro-cracks at the black ceramic coated samples. The SEM results are shown in Fig. 2 (A-F).

The analysis of SEM shows the surface microstructure of the coated specimens. Some of the specimens showed the fine surface and some of them shown the micro-cracks surface. The crack characteristics of the specimen are summaries and the results show in Table 8.

The surface morphology of XAB is the best surface because this specimen has leased or no crack. It followed by specimen YBA which is the crack is thin and the area of the crack is large. There have no difference between both substrates from this rating crack because the substrate gives high and low value of the rating crack between each other. From this surface morphology result, the combination formula A and B is the best combination to produce the better surface morphology.

The coating thickness of the plated specimens was determined using the image analyzer. The values of coating thickness obtained are tabulated in Table 9. The table shows the coating thickness of black ceramic coating obtained from micrograph capture by Image Analyzer. It can be observed that the mean of duplex layer is visible but not is very clear. Specimen XAB had a coating thickness of 3.21 µm, while the specimen XBA coating thickness is 3.457 µm. For the specimen XDA who has the single layer of nickel coating are the thinner which is 2.716 µm. For the sample from stainless steel substrate, YBA has the highest thickness meaning of coating with 3.963 µm. It is followed by sample YAB have the 3.580 µm mean coating thickness.

The sample of stainless steel and copper substrate coated with black nickel has less value of mean of duplex coating thickness which is 2.469 µm and 2.716 µm, correspondingly.

It also observed that the coating thickness on the substrate are not uniform, the thickness at the middle of the specimen are much thinner than at the edges. The truly mention from Grainger (1989) and can be concluded that the plating thickness is not uniform, where the thickest layer occurs at the edges, even though the same current are applied in the formulation bath on the surface.

C. *Weighted Property Methods*

Selection of the best duplex black ceramic coating and the different substrates are using weighted property methods. The most important criteria in selecting a solar thermal application were set according the absorptance, spectral emittance, crack rating and adhesion. Using the weighted property method, the best specimen is selected based on the most suitable coating for solar thermal application. The five properties are assigned as the following symbol. (PI: Absorbtance; P2: Spectral Emittance; P3: Crack rating; P4: Adhesion; P5: Cost ($/kg))

The all five properties requirement are ranked according the weight properties methods and the determination of the relative importance of properties are shown in Table 10. Absorptance and spectral emittance are the major criteria for solar thermal application compared with other properties. It is because good surface coating and sufficient bonding between black ceramic coatings result to high absorptance and low emittance on the substrate materials. Meanwhile, the crack must be minimized by using adhesion with higher strength.

Table 8: Surface Morphology of specimens

Specimen	Surface Morphology	Crack Rating*
XAB	Least, no crack	6
XBA	Thinner crack with large area	4
XDA	More and more large crack	2
YAB	More and fine crack	3
YBA	Thinner and fine crack	5
YDA	Large crack	1

*Rating crack 1 to 6: 6-least amount of crack; 1-most crack

Table 9: The coating thickness of black ceramic coating

Sample	Mean of duplex coating thickness (µm)
XAB	3.210
XBA	3.457
XDA	2.716
YAB	3.580
YBA	3.963
YDA	2.469

For the given property shown in Table 11, the scaling factor value (β) for Corrospending materials is:

maximum value (absorptance and crack ranting)

β = (numerical values of property / maximum value in the list)*100

minimum value (emittance, relative cost)

*β = (lowers value in the list / numerical values of property)*100*

scaling factor, β for the maximum value (emittance)

βXAB = (0.9563 / 0.9572)*100 = 99.91

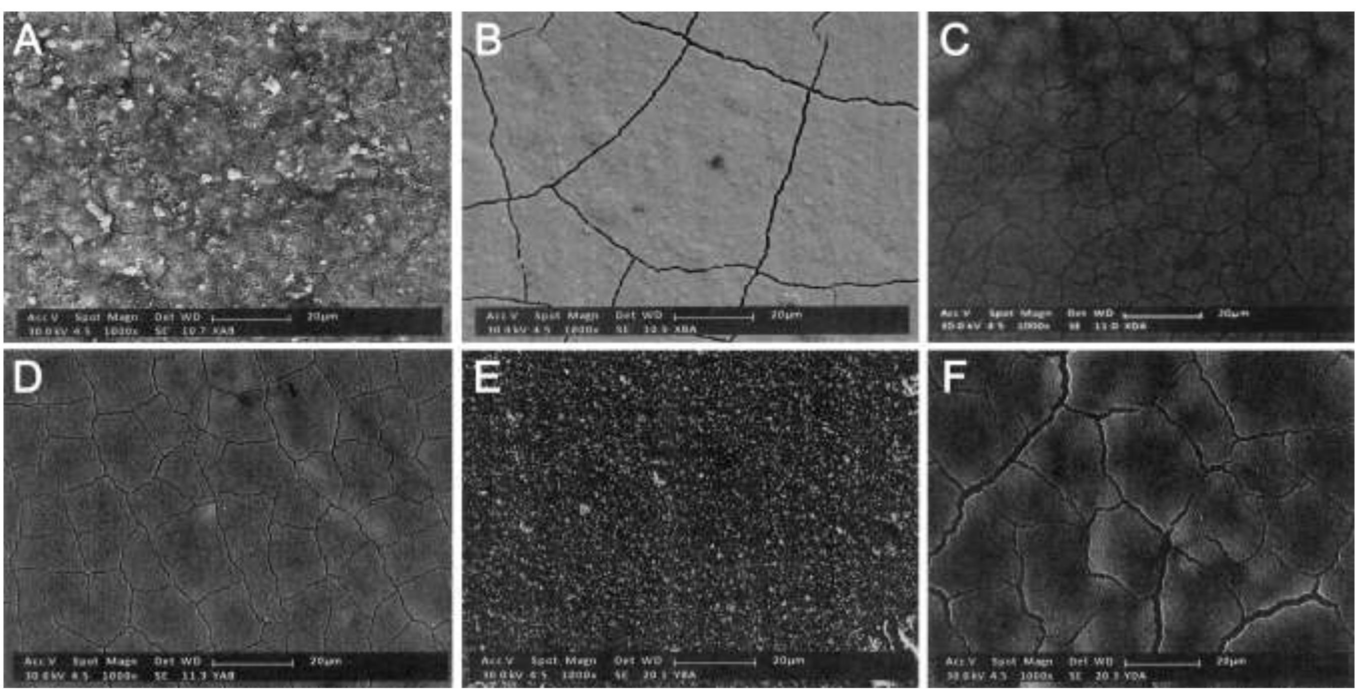

Fig.2. Surface Morphology of specimens by SEM A) XAB for copper substrate. B) XBA for copper substrate. C) XDA for copper substrate. D) YAB for stainless steel substrate. E) YBA for stainless steel substrate. F) YDA for stainless steel substrate.

Table 10: Relative importance of properties

Property	Number of positive decisions N = n/(n-l)/2										Positive Decisions	Relative Emphasis Coefficients
	1	2	3	4	5	6	7	8	9	10		α
PI	1	0	1	1							3	0.3
P2	0				1	1	1				3	0.3
P3		1			0			0	0		1	0.1
P4			0			0		1		1	2	0.2
P5				0			0		1	0	1	0.1
	Total number of positive decisions										10	1.0

Table 11: Property of coated samples

Specimen	Absorptance	Emittance	Crack Rating	Adhesion	Relative Cost (weigh)
XAB	0.9563	0.0271	6	Good	5.6
XBA	0.9572	0.0131	4	Good	5.6
XDA	0.9448	0.0327	2	Good	5.6
YAB	0.9156	0.0990	3	Good	2.6
YBA	0.9124	0.0470	5	Good	2.6
YDA	0.9134	0.0943	1	Good	2.6

Table 12: Properties of materials expressed as β

Specimen	Absorptance	Emittance Rating	Crack	Adhesion	Relative Cost (weight)
AB	99.91	48.34	100	100	46.43
XBA	100	100	66.67	100	46.43
XDA	98.70	40.06	33.33	100	46.43
YAB	95.65	13.23	50	100	100
YBA	95.32	27.87	83.33	100	100
YDA	95.42	13.89	16.67	100	100

scaling factor, β for the minimum value (emittance)

$\beta XAB = (0.0131/0.0271)*100 = 48.34$

The properties of specimen express as value of p are listed in Table 12. The Materials performance index (y) is calculated by using "$\gamma = \sum \alpha\beta$" formula.

$\gamma XAB = 0.3(99.91)+ 0.3(48.34)+ 0. 1(100)+ 0.2(100)+ 0.1 (46.43) = 79.118$

Materials performance index can be seen in Table 13. It is obviously indicated in Table 14 that the best duplex ceramic coating is due to combination of formula B and formulation A. Besides that, the best substrate in this study is copper. The bath formulation is suitable for all substrates and gives the high absorption and low emittance.

IV. Conclusion

From this study, it can be concluded that the copper is the best type of material used as the substrate compared with stainless steel for solar thermal application. The suitable of black ceramic coating is the black chromium. It is because the black chromium has higher value of solar absorption than the black ceramic coating. The coating sample from black chromium on the copper substrate has the highest value of absorption, $\alpha > 0.95$ and the low emittance, $\varepsilon < 0.1$ is the best selection of solar thermal application. However, this material is expensive compared with other materials which will lead to high cost of the solar thermal produced using the copper substrate.

The alternative to reduce the cost of this application is by using the stainless steel as the substrate. The absorption and emittance value of stainless steel (α>0.91 and ε<0.1) are closely similar to copper when use the black chromium coating. Even though the black nickel coating is also suitable used as the coating as it has a high ratio of optical property, but it has a lower ratio compared with black chromium coating. In brief, the formulation of BA for black ceramic coating is the most suitable bath formulation of copper and stainless steel substrate.

Several recommendations are made after completion of this thesis. Since this study focuses to determine the better optical properties (absorption and emittance) for the two types of substrate. First, plating parameter such as bath temperature, distance between the cathode -anode, plating time and current density must be suitable for the new bath formulation of black ceramic coating. Besides that, a new bath must be replaced for each specimen layer coating in order to produce a high ratio of optical property of solar thermal application.

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