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Investigation into Black Oxide Coating of 410 Grade Surgical Stainless Steel Using Alkaline Bath Treatment

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***Abstract*—**High reflectance of surgical instruments under bright light hinders the visual clarity during laparoscopic surgical procedures leading to loss of precision and device control and creates strain and undesired difficulties to surgeons. Majority of the surgical instruments are made of surgical grade steel. Instruments with a non reflective surface can enhance the visual clarity during precision surgeries. A conversion coating of black oxide has been successfully developed 410 grade surgical stainless steel .The characteristics of the developed coating suggests the application of this technique for developing 410 grade surgical instruments with minimal reflectance.

***Keywords*—**Conversion coatings, 410 stainless steel, black oxide, reflectance.

I. Introduction

STAINLESS steels are widely used for the manufacture of surgical instruments [1]. Reflection under bright lights from the surgical instruments made of surgical grade stainless steel creates undesired difficulties to the surgeons like loss of precision, lack of device control etc in laparoscopic surgeries [2]. The precision and device control in laparoscopic and key-hole surgeries are vital . Matte black oxide coating of surgical steels have been suggested to reduce the problems created due to the reflection of light from the surgical instruments made of surgical grade stainless steel. Black oxide is a conversion coating formed on the metal surfaces as a result of chemical reaction of the metal atoms with an oxidizing agent like air, alkaline aqueous salt solution, and molten salts. The conversion coating is a film of chemical compound formed by the reaction of the substrate in air and the properties do not vary from the main substrate [3].

Black oxide coating provides reduced light glare, dimensional stability, anti-galling property, improved lubricity, superior finish, corrosion protection etc [4]. The various black oxide processes are hot alkaline black oxide process, cold black oxide process, and molten salt black oxide process [7]. These methods have been tried for coating 300 series grade surgical stainless steel. Currently surgical equipments are manufactured from superior grade 410 stainless steels. The martensitic stainless steel is strong, hard, has good wear resistance but less resistance to corrosion [5]. In the present study all three methods suggested for conversion coating of 300 series stainless steel has been investigated on 410 grade steel by altering the various parameters like the composition of the mixture ,time and temperature. It was found that a black oxide (Ferric oxide, Fe3O4) conversion coating with good characteristics can be developed on grade 410 stainless steel using the molten salt process with a composition of 400g/L of sodium hydroxide, 320g/L sodium nitrate, and 200g/L of sodium dichromate in water at a temperature of 1390C and coating duration of 40 minutes. The reflectance, thickness and surface roughness parameters of the coating suggest its application for black oxide coating of surgical instruments made of 410 grade stainless steel so as to obtain minimal reflecting surgical surfaces.

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II. Experimental

A.Materials and Sample Preparation

Type SAE grade 410, 316L & 310, stainless steel mechanically cleaned ,degreased in alkaline solution followed by a pickling process in 20% diluted Hydrochloric acid were used as the specimens[6]. Prepared samples are shown in Fig. 1.

Fig. 1 Prepared samples ready for coating process

B. Deposition Procedure

Coating of black oxide was attempted by three methods as detailed below. For each method the coating solution was transferred to a heating container of 50 litres capacity with two heating coils with heating capacity up to 3000C .The solution was allowed to reach the required coating temperature for each method. Then the specimens were partially dipped in the high temperature solution so as to get the required coating. The specimens were taken out at intervals of 5, 15, 25, 35, 45 and 55 minutes monitored by a calibrated stopwatch.

Method 1: By treating in hot solution of sodium hydroxide, sodium nitrate and sodium nitrite in water with a composition of 700g/L of sodium hydroxide, 100g/L of sodium nitrate and 100g/L of sodium nitrite in water. A 10 litre of solution was used to completely immerse the heating coils in the heater vessel used. After weighing in the chemicals and mixing them in water, the mixture was transferred to the heating container. The mixture was maintained at a temperature of 1400C during the coating process. [7]

Method 2: Coating by treating in solution having composition of 110g/L of potassium hydroxide, 200g/L of potassium nitrate in 10 litres of water. The mixture was maintained at a temperature of 1350C during the coating process. [7]

Method 3: Using composition of 400g/L of sodium hydroxide, 320g/L sodium nitrate, and 165g/L of sodium dichromate in 10 litres of water. The mixture was heated to a temperature of 1450C during the coating process. Fig. 2 shows the actual coating process in progress.[7]

Fig. 2 Setup showing the coating process

As the preliminary samples of 410 grade on physical verification showed uniform coating only by the method 3 and that too at longer intervals, this method was chosen for further investigation to get optimal time and temperature and composition for uniform black oxide coating of 410 grade stainless steel. This was done by subjecting 410 grade samples to coating by method 3 at temperatures varying between 1150C-1500C. The process was also further explored with varying percentage of the sodium dichromate (Na3Cr3O7) (50-350g/L) while maintaining the same composition for sodium hydroxide (NaOH) and sodium nitrate (NaNO3).

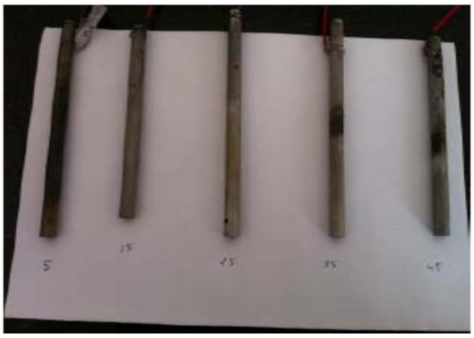
C. Surface Characterization

Measurement of reflectance : Reflectivity is a vital parameter in this work. In optics and photometry, reflectivity is the fraction of incident radiation reflected by a surface. In general it must be treated as directional property that is the function of the reflected direction, incident direction, and the incident wavelength. However it is also commonly averaged over the reflected hemisphere to give the hemispherical spectral reflectivity. When reflection occurs from thin layers of material, internal reflection effects can cause the reflectance to vary with surface thickness. Reflectance is the fraction of electromagnetic power reflected from a specific sample, while reflectivity is a property of the material itself, which could be measured on a perfect machine if the material filled half of the space [8]. The reflectance of the samples were measured with UV-VIS-NIR spectrophotometer Varian, Cary 5000 with Spectral range: 175 – 3300 nm Wave length accuracy: ± 0.1 nm (UV –Vis), ± 0.4 nm (NIR) Wave length reproducibility: 0.025 nm Limiting resolution: 0.05 nm (UV –Vis), 0.2 nm (NIR)

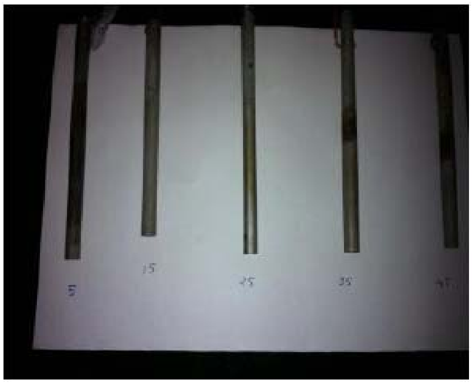
Measurement of thickness and roughness : Average thickness of the films and average roughness was measured using a Dektak 6M stylus profilometer (Veeco, USA) [9]-[11]. The stylus profiler takes measurements electromechanically by moving the sample beneath a diamond-tipped stylus. The film undergoing measurement is deposited with a region masked; this creates a step on the sample surface, and the thickness of the sample can be measured accurately by measuring the vertical motion of the stylus over the step. The profilometer measures the average thickness and roughness of the sample.

III. Results and Discussion

The results of the coating produced by the three methods on SAE grade steel samples of 310, 316 L and 410 are tabulated in Table I. On preliminary observation it was found that a good uniform dull matte black coating was formed on the grade 410 steel specimens coated by method 3 at a coating time of 45 minutes. No coating was observed on the 316 L samples. As the base interest was to coat surgical steel of 410 grade, method 3 was taken up for further investigation with changes in coating parameters. Fig. 3 shows the samples after the coating procedure. Samples in Fig. 3(c) clearly show black oxide conversion coating.



(a)



(b)

(c)

Fig. 3 Photographs of 410 grade samples after the primary coating (a) Method 1 (b) Method 2; and (c) Method 3

The coating characteristics obtained by varying the temperature of the bath under method 3 without altering the composition of the solution and time of coating are tabulated in Table II. A thin layer of conversion coating was observed on the specimen for all temperatures from 1200C to 1450C. The coating formed at a temperature of 1300C returned the lowest reflectance along with the maximum thickness and minimum roughness. Fig. 4 shows the variation of thickness, roughness and percentage reflectance of the samples for the various temperatures. Fig. 5 shows the variation in sample colour in different samples from black to brown.

TABLE I
TABULATED RESULTS OF BLACK OXIDE COATING ON VARIOUS GRADE OF STEEL BY THE THREE METHODS

Sl no	Chemical composition Chemical	quantity	Steel Grade	Coating Time	coating	Colour	Visual examination Results
			Method 1 (max temp 140^0C)				
				5	No	-	
	Sodium Hydroxide	0.700 kg		15	No	-	
			SAE 410	35	No	-	No coating was observed
1.	Sodium Nitrate	0.100 kg		35	No	-	
	Sodium Nitrite	0.100 kg		45	No	-	
			SAE 310	45	Uniform	Black	Fine uniform coating
	water	1 litre	SAE316L	45	No	-	No coating observed
			Method 2 (max temp 135^0C)				
				5	No	-	
	Potassium Hydroxide	1.100 kg		15	No	-	
			SAE 410	35	No	-	No coating observed
2.				35	No	-	
	Potassium Nitrate	0.200 kg		45	No	-	
			SAE 310	45	Uniform	Black	Fine uniform coating
	water	1 litre	SAE316L	45	No	-	No coating observed
			Method 3 (max temp 140^0C)				
				5	Traces	Black	
	Sodium Hydroxide	0.400 kg		15	Traces	Black	Black coating was observed which became more uniform with increase in coating time
	Sodium Nitrate	0.320 kg	SAE 410	35	Non uniform	Black	
3.				35	Uniform	Black	
	Sodium Dichromate	0.165 kg		45	Uniform	Black	
			SAE 310	45		Black	Uniform coating
	water	1 litre	SAE316L	45			No coating observed

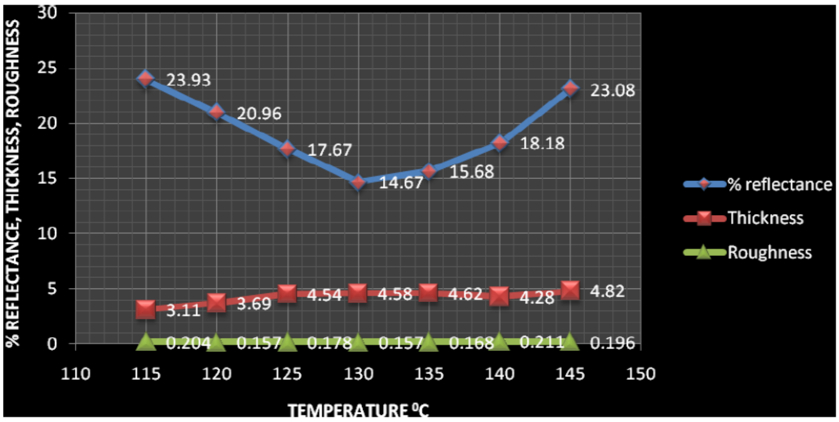


Fig. 4 Variance of Reflectance, thickness, and roughness at different temperatures

TABLE II
TABULATED RESULTS OF BLACK OXIDE COATING ON 410 GRADE SAMPLES FOR THE VARIOUS TEMPERATURES

Exp no	Temperature	Specimen	Time of exposure	Coating	Colour	% R	t	Ra
1	115^0C	1	45	None	--	23.93	3.11	0.204
3	120^0C	2	45	Traces	Black	20.96	3.69	0.157
3	125^0C	3	45	Non uniform	Black	17.67	4.54	0.178
4	*130^0C*	*4*	*45*	*Uniform*	*Black*	*14.67*	*4.58*	*0.157*
5	135^0C	5	45	Uniform	Brown black	15.68	4.62	0.168
6	140^0C	6	45	Uniform	Brown	18.18	4.28	0.211
7	145^0C	7	45	Uniform	Brown	23.08	4.82	0.196

*t- thickness of coating obtained µm; %R- average percentage of reflectance obtained in the visible region (380-750 nm); Ra- average roughness values in µm

Fig. 5 Colour variation of the coated samples

As austenitic steels have a higher reflectance than the ferritic and martensitic steels and their integrated solar reflectance of 68% is considered too much for their use in endoscopy two of the natural oxides on stainless steel, Fe2O3 and Cr2O3 have been studied as separate films, and their optical constants determined by combined transmission and reflectance measurements. It has been found that Fe3O4 and Cr2O3 gives better selectivity than Fe2O3. Hence it is concluded that the ferritic and martensitic steel base is to be preferred for developing surgical instrument because of its lower reflectance [12]. Based on this the surface conversion of SAE 410 grade steel was further investigated with dichromate leading to a surface layer of Fe2O4 and Cr2O3 which will have lower reflectivity.

TABLE III
TABULATED RESULTS OF BLACK OXIDE COATING ON 410 GRADE SAMPLE BY VARYING SODIUM DICHROMATE COMPOSITION

Exp No	Composition in kg/L ($Na_3Cr_3O_7$)	Sample	Time of coating	Boiling point	Coating	Colour	%R	t	Ra
1	0.050	8	30	125^0C	Traces	-	23.08	1.02	0.128
		9	40			Black	18.95	1.93	0.168
3	0.100	10	30	133^0C	Non Uniform	Black	17.33	1.96	0.179
		11	40			Black	18.51	1.91	0.210
3	0.150	12	30	137^0C	Uniform	Black	17.06	2.21	0.236
		13	40			Black	15.68	3.16	0.162
4	0.200	14	30	139^0C	Uniform	Black	15.73	4.69	0.140
		15	40			Black	13.45	4.83	0.152
5	0.250	16	30	144^0C	Uniform	Black	15.29	4.47	0.195
		17	40			Brown	17.67	4.54	0.178
6	0.300	18	30	150^0C	Uniform	Brown	19.73	4.13	0.152
		19	40			Brown	21.16	3.39	0.139
7	0.350	20	30	153^0C	Uniform	Brown	23.76	5.83	0.137
		21	40			Brown	23.93	4.91	0.204

* t- thickness of coating obtained µm; %R- average of percentage reflectance obtained in visible region (380-750nm); Ra- average roughness values in µm

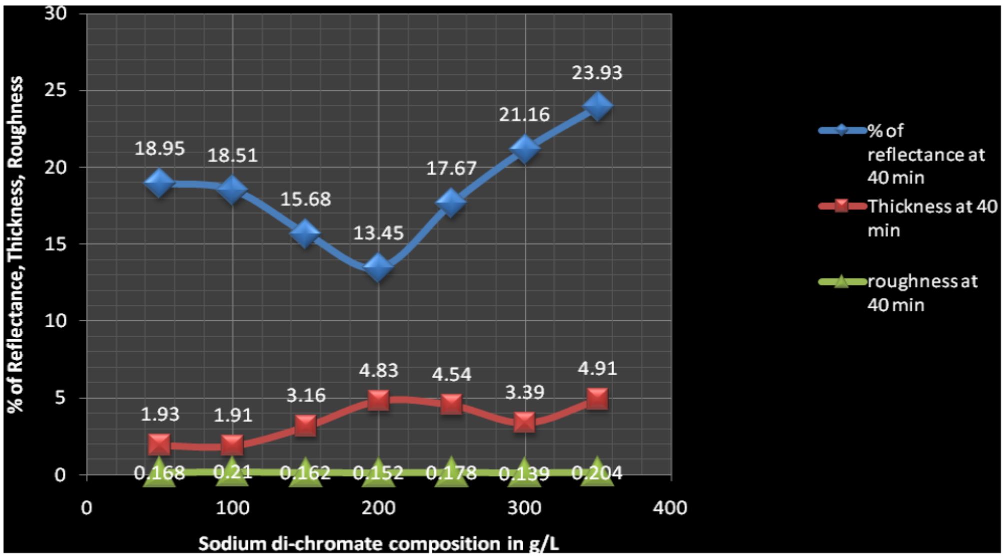


Fig. 6 Variation of % of reflectance, thickness and roughness with change in sodium dichromate composition

Since di-chromate composition is detrimental in a lower reflective coating the 410 grade samples were subjected to coating process by method 3 by varying the dichromate composition and the results are tabulated in Table III. Fig. 6 shows the variation of thickness, roughness and percentage reflectance of the samples by varying the dichromate composition. It is seen that the coating done using composition of 400 g/L of sodium hydroxide, 320 g/L sodium nitrate, and 200 g/L of sodium dichromate in 10 litres of water with a coating temperature of 1390C and coating duration of 40 minutes gave a uniform black coating with the lowest reflectance of 13.45%, thickness of 4.83 μm and a low roughness of 0.152 μm and is shown in Fig. 7 (a).The other samples in figure show lesser coating characteristics.

(a) (b) (c)

Fig. 7 Coated samples by varying sodium dichromate composition

IV.Conclusion

Conversion Black oxide coating was successfully done on grade 410 stainless steel using hot alkaline process with alkaline solution consisting of sodium nitrate, sodium hydroxide and sodium dichromate. Analysis of the coated surfaces were further made based on temperature changes, time of coating, change in composition of solution and sodium di-chromate ratio to get the coating with maximum thickness and lowest reflectance and having average roughness at the lower range. The best coating was obtained with a solution of 400 g/L of sodium hydroxide, 320g/L of sodium nitrate, 200g/L of sodium Di-chromate in water at an alkaline bath temperature of 1390C and an exposure time of 40 minutes. The minimum average percentage of reflectance in visible region obtained was 13.45% and the thickness of the coating was 4.83μm. The average roughness value is 0.152 μm. The reflectance value obtained is far less compared to base 410 grade Stainless steel samples and suggests the usage of the coating procedure for producing low reflective surgical instruments for laparoscopic and endoscopic application.

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