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Corrosion and hardness characteristics of metalized ABS plastics prepared by FDM rapid prototyping process

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Abstract

An attempt has been made in this work to develop nickel chromium coatings with enhanced corrosion and hardness properties on ABS plastics prepared by FDM-RP process. The increase of corrosion resistance of Ni-Cr electrodeposited coatings in sea water medium claimed that these coated plastics can find as substitute for metal parts used in automobile components. Hardness values measured by Vickers hardness tested validated the improved mechanical properties. The presence of micro roughness and improved tensile strength values signify that the coatings have firmly absorbed on ABS plastics. The morphology of Ni-Cr coatings was found uniform and analyzed using SEM images.

Keywords Ni-Cr coatings, FDM-RP, corrosion resistance, tensile, SEM

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Introduction

In the field of surface engineering, Ni-Cr coatings are widely employed for wear and corrosion resistance in piston rings made of mild steel. Nickel and Chromium coatings are the important electrodeposited metals and they are produced by electrodeposition/pulse electrodeposition on metals[1-2]. In recent years. the investigations on the metallization of ABS plastics are gaining much importance owing to their practical application in automobile components[3-6]. This is due to the fact that ABS plastics are having good tensile strength and cushioning effect when it is subject to severe impact loads. Electroless nickel coated ABS injection moldings have been reported for their higher corrosion resistance in aggressive media[7-8]. However, metallization of ABS plastics prepared through RP process is still at entry level. The presence of honey comb structure of ABS obtained by RP method is claiming that metallization on it will improve the mechanical properties considerably better than the injection molded plastics.

This gives an idea for identifying a suitable corrosion resistant coating to reduce the damage of automobile vehicles when high impact load is applied. The developed coatings is expected to increase hardness and tensile strength. The performance of coatings is to be screened by mass gain studies, Vickers hardness test, Tensile strength, corrosion resistant measurement by potentiodynamic polarization and AC impedance methods. The uniformity of the surface is a desirable factor for improvement on mechanical properties for metalized ABS which will be determined by micro structural analysis using SEM images.

Experimental Procedure

The bath developed in the present study consisted of the following ingredients.

I. $NiSO_4.6H_2O$ = 120 g/l

$NiCl_2$ = 25 g/l

Boric acid = 60 g/l

Cetyl Tri Methyl Ammonium Bromide (CTAB) = 3 g/l

Ammonium Sulphate = 5 g/l

Sulfamerizine (Brightner) = 0.5 mg/l

Bath parameters:

pH = 4.3

Current density = 45 mA/cm^2

Plating time = 90 min.

Anode =Ni plates of size 100 x 300 mm

Cathode = ABS plastics coated with electrodeposited copper on EN.

II. $CrCl_3.6H_2O$ = 90 g/l

Sodium formate = 50 g/l

Gly oxylic acid = 7 g/l

Potasium chloride = 72 g/l

CTAB = 1 g/l

Sulfamerizine (Brightner) = 1 mg/l

Bath parameters:

pH = 3

Current density = 100 mA/cm^2

Plating time = 5 min.

Anode =Lead plates of size 100 x 300 mm

Cathode = Nickel plated ABS plastics coated with electrodeposited copper on EN.

The autocatalytic deposition of nickel with 10 microns thickness has been carried out on ABS plastics as described earlier[9]. The electrodeposition of copper was performed on EN coated ABS as reported elsewhere[10].

Evaluation of high strength coatings through different techniques

Mass-gain method

ABS plastics prepared by RP process with size 20 x 50 x 2 mm^3 were used in the plating bath. They were mechanically polished with fine grit paper, washed with distill water and then degreasing was carried out by tri choloro ethylene to remove finger prints and oily substances. It is again washed and etched in 2% HCl and 1% H_2O_2 solution. Then the plastics were sensitized and activated by adopting the

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procedure as reported earlier[11]. The initial mass of ABS plastic was weighed using electronic weighing machine. Then the plastics were subjected to EN plating(10 μm) and electrodeposition of copper(2 μm), nickel and chromium(38 μm). The rate of deposition was calculated using the following formula:

$$\text{The rate of deposition } (\mu m/h) = \frac{W \times 10^4}{D\,A\,T}$$

Where,

W – Weight of the deposit (g)

D – density of the deposit (g/cm^3)

T – plating duration (h)

A – Surface area of the specimen (cm^2)

Micro hardness measurements

Micro hardness measurements for all the as metalized ABS (20 x 50 x 2 mm^3) were measured using Vicker's harness tester as per ASTM E-384 with a load of 100 g. A diamond shaped indentation was created on each coated plastics at eight different locations and the mean of hardness was calculated from the diagonal of indendation on Vicker's scale using the formula.

$$V.H.N = (1854 \times load) / d^2$$

where d = diagonal of the indentor

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Corrosion resistance measurements

The potentiodynamic polarization and impedance studies were performed on metalized ABS plastics with the Ni-Cr coated area of 10 mm^2 exposed surface (test electrode) in 3.5% NaCl, 40 mm^2 of platinum electrode (counter electrode) and saturated calomel as reference electrode in three electrode cell assembly.

Potentiodynamic polarization method

A constant quantity of 250 ml of 3.5% NaCl (sea water) solution was taken in a 250 ml beaker. The test electrode, reference electrode and the counter electrode were positioned in the electro chemical workstation (Sinsil Model 604E, USA) and the readings were recorded by shifting the potential ± 300 mV from OCP at a scan rate 10 $mV.second^{-1}$ for the metalized ABS.

The corrosion rate factors like E_{corr} and I_{corr}, were recorded. The reduction in E_{corr} and I_{corr} values indicated that the coatings are having good corrosion resistance than those reported earlier[12-13].

Impedance measurement

AC impedance was carried out in the frequency range of 100 kHz to 0.01 Hz under potentiostatic conditions using 3.5% NaCl as corrosive environment for Ni-Cr. The impedance measurements were performed on metalized plastics at room temperature. The electrical equivalent circuit[14] used which is equivalent to Randell's investigations for the corroding system is appended below:

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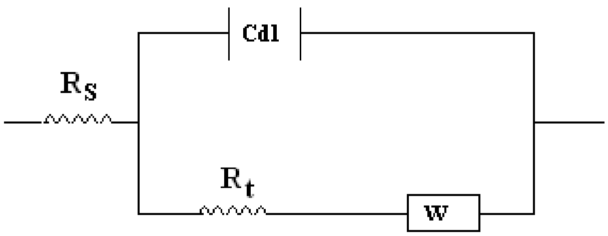

R_S – Solution resistance

R_t – Charge transfer resistance

W – Warburg impedance

C_{dl} – Double layer capacitance

The cell impedance consisted of real part (Z') Vs imaginary part (Z''). A plot of real part (Z') Vs imaginary part (Z'') gave a distorted semicircle which indicated the presence of highly resistive surface. The experimental plots maping was carried out for calculating charge transfer resistance(R_t) by considering the components of circuits[15] as reported in Warburg impedance analysis. The double layer capacitance can be determined from the frequency at which Z'' is maximum from the relation

$$C_{dl} = \frac{1}{2\pi Z''_{max} R_t}$$

Tensile strength measurements

This measurement was carried out using Instron 8801 as per ASTM D638 at a strain rate of 2 mm/min.

JCSE The Journal of Corrosion Science and Engineering
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Scanning electron microscopic studies (SEM)

The micro structural images of Ni-Cr coated ABS plastics were studied using SEM analyzer. The coated test electrodes were prepared for size 10 x 10 mm^2 and placed firmly on crusible to be examined for SEM images. The SEM images were portrayed by using VEGA3 TESCAN model with an acceleration voltage range of 3,000 V and with the magnification range of 1kx.

Results and Discussions

Mass gain studies

The results of Ni-Cr coatings on ABS plastics obtained by mass gain method and eddy current tests are given in Table 1. It has been noticed that the incorporation Cr improves brightness besides micro hardness values. The addition chromium into nickel matrix significantly improved the tensile strength because of its higher ductility. The rate of deposition for Ni-Cr was calculated as 50μm at the plating duration of 90 minutes.

Micro hardness measurements

The hardness of the electrodeposited Ni-Cr coatings determined by Vicker's hardness tester is presented in Table 2. The increased hardness of Ni alloy coatings could be due to the combined effect of hard coatings with soft copper layers formed on EN coatings.

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Corrosion resistance studies

Potentiodynamic polarization studies

The corrosion resistance experiments were performed for hard coatings on ABS plastics has been done by employing current-voltage measurements using polarization studies. The coated surface was exposed to sea water medium for 5 hours and OCP was noted. This study was carried out by changing potentials ± 300 mV from OCP vs $Hg/Hg_2Cl_2/KCl$(Satd.). The corresponding corrosion potential and corrosion current were measured for the polarized coatings.

E_{corr} values for Ni-Cr alloy coatings were noted as -362 mV. Also, I_{corr} values have been shifted to $501x10^{-8}$ A which is the lowest I_{corr} values for Ni-Cr coatings. The results are given in table 3.

Electrochemical Impedance Spectroscopy (EIS) studies

The calculated impedance values of Ni-Cr coated ABS in 3.5% sea water medium are given in the table 4. It is evident from table 4 that the R_t values are enhanced where as C_{dl} values decreased. It has been noticed that Nyquist plot has not shown perfect semi-circle and best fitted curve was drawn by changing the equivalent circuits as indicated by Randell's. This could be the reason for a highly resistive surface. The decreased C_{dl} values have been claimed for Warburg's impedance. It is evident that Ni-Cr hard coatings on ABS plastics prepared by FDM RP method can be used for automobile machine parts as an alternate to metal frames/fittings.

Tensile strength measurements

The tensile strength of hard surfaces coated on ABS plastics which was electrodeposited by copper on EN. It has been observed that the tensile fracture on

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the coated ABS plastics was 0.8 mm at 790 N loads. It is validated that Ni-Cr coatings offer high mechanical properties.

Scanning Electron Microscopic studies

Figure 3 indicates the micro structural images of Ni-Cr coatings prepared from nickel electroplating bath. It is visualized that globular structures along with spherical particles aggregation confirm the existence of nickel and chromium on ABS matrix. The appearance of black patches might be due to the formation of oxide layers i.e. Cr_2O_3. The formation of pin holes in micro structure indicating the hydrogen evaluation which has to avoided to nullify hydrogen embrittlement.

In comparison with Ni-Cr coated micro structural images, the presence of layered polystyrene group (Figure 4) of rapid prototyped plastics. The appearance of black patches could be due to the removal of polymeric film from ABS matrix by etching process and the later has played a dominant role for making effective adherence of coatings on ABS plastics.

Conclusion

An attempt has been made successfully to develop hard coatings based on Ni-Cr on FDM rapid prototyped ABS plastics coated with copper on EN. The hard coatings exhibited excellent hardness, corrosion resistance and tensile strength. SEM images confirmed the existence of Ni-Cr in ABS polymer matrix. This investigation was found useful to develop an alternate coating materials for automobile parts replacing metals.

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Table 1 The results of mass gain studies and eddy current test obtained for Ni-Cr coatings on Cu electroplated ABS plastics coated with EN

S.No.	Deposition timings (sec.)	Thickness (µm)		Inference
		Weight gain method	Eddy current test	
1	180	50	51	Bright with uniformity

Table 2 Micro hardness values for Ni-Cr coatings on Cu electroplated ABS plastics coated with EN

S.No	Coatings	Hardness (V.H.N) Load:100g
1.	Ni-Cr coatings on ABS	995
2.	ABS coated with electrodeposited Cu on EN	550
3.	ABS plastic	70

Table 3 Potentiodynamic polarization studies of Ni-Cr coatings on Cu electroplated ABS plastics coated with EN

Nature of deposit	E_{corr} (mV vs SCE)	I_{corr} (x 10^{-8} A. cm^{-2})
Ni-Cr coatings on ABS	-362	501

Table 4 Impedance values of Ni-Cr coatings on Cu electroplated ABS plastics coated with EN

Nature of deposit	R_t (Ohm.cm^2)	C_{dl} (μF. cm^{-2})
Ni-Cr coatings on ABS	990	0.357

Legends for figure

1. Potential current curves for Ni-Cr coatings on ABS plastics in sea water medium
2. Nyquist plots for Ni-Cr coatings on ABS plastics in sea water medium
3. Load-Extension curve for Ni-Cr coatings on ABS plastic surfaces.
4. SEM image of Ni-Cr coated ABS plastics
5. SEM image of uncoated ABS plastics
6. EDAX for Ni-Cr coated ABS plastics

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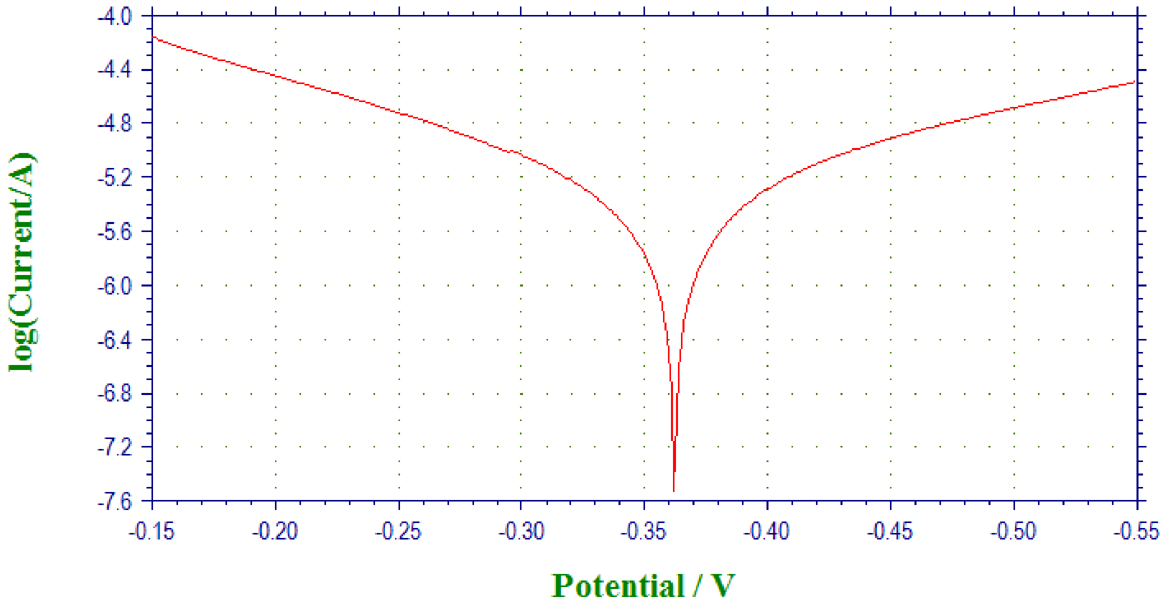

Figure 1

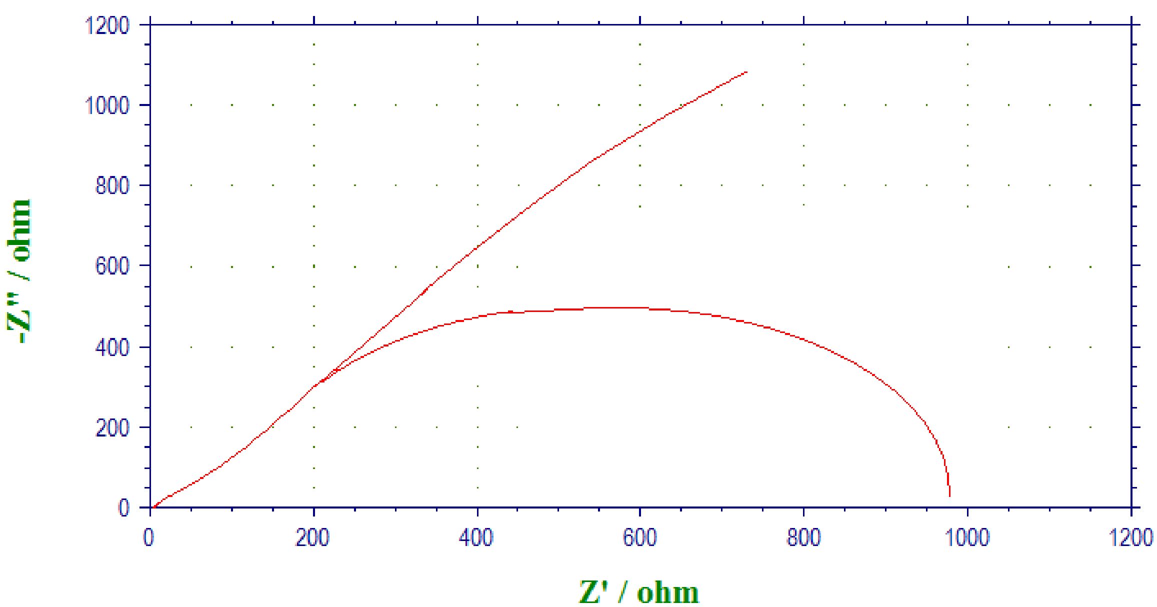

Figure 2

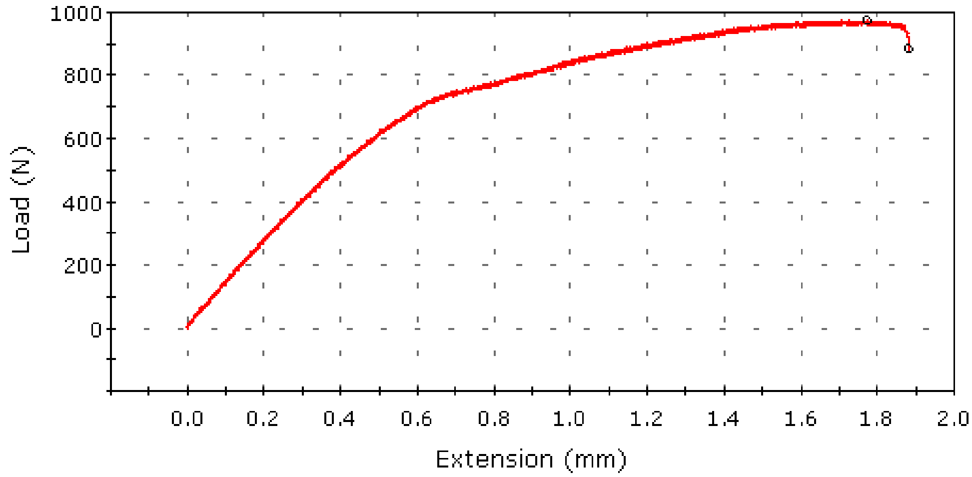

Figure 3

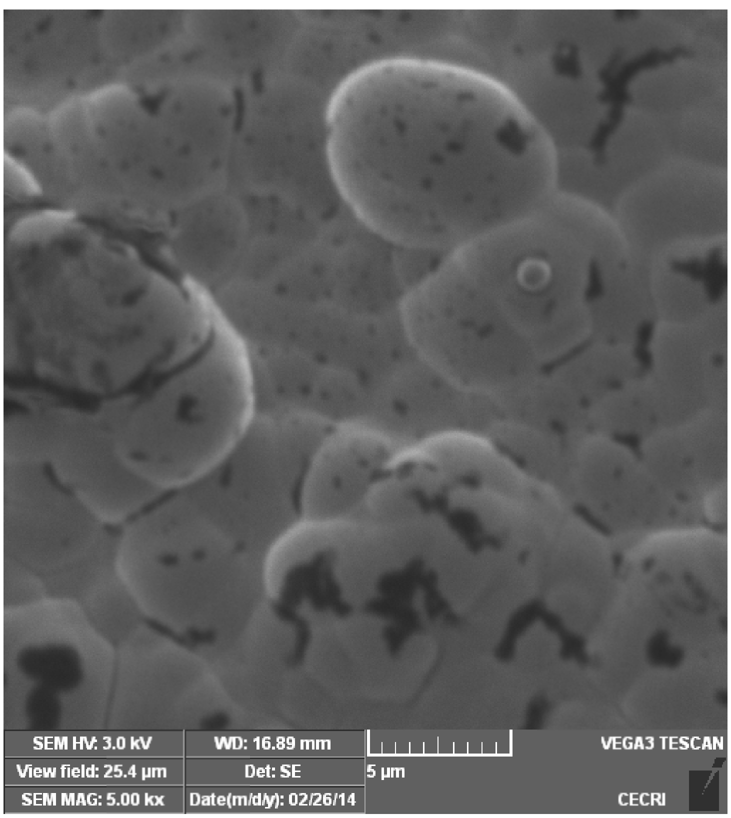

Figure 4

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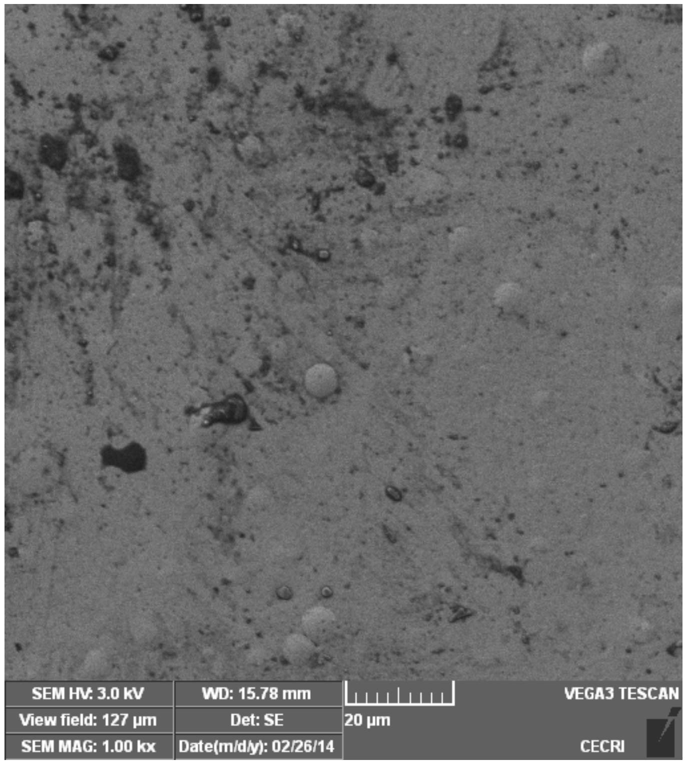

Figure 5

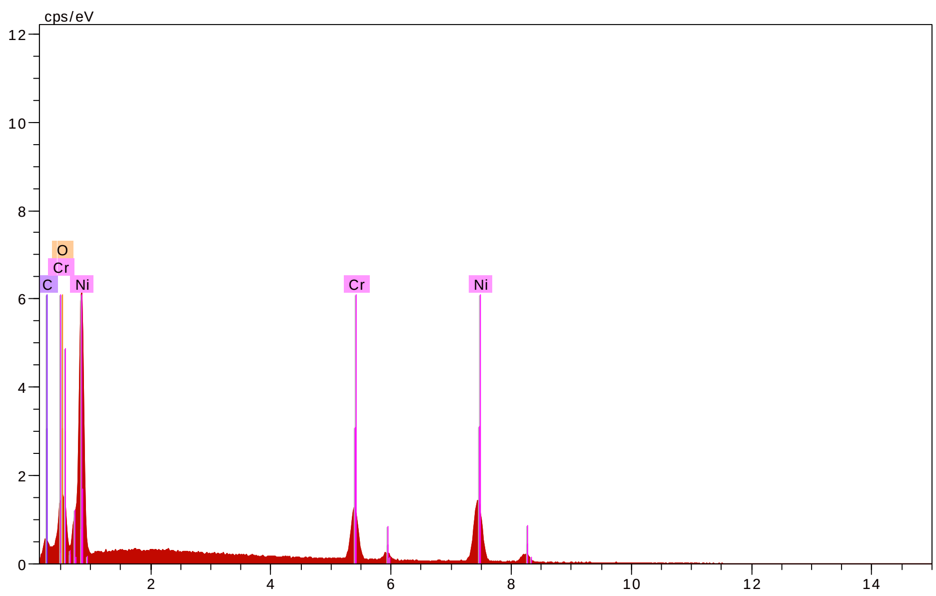

Figure 6