CHARACTERIZATION AND COMPARISON OF SOLAR SELECTIVE COATINGS BETWEEN NI-AL AND NI-CO ON ALUMINUM SUBSTRATE

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ABSTRACT:

An ideal solar absorber surface coating must have good optical properties like high solar absorptance with minimum solar emittance. Development of new coating is fabricated by embedding metallic particles composed of a nickel-aluminium (NiAl) alloy into the black paint as well as solar selective black nickel-cobalt (NiCo) electroplating on aluminium alloys with nickel undercoat is done. Characterization of such solar selective surface coatings are done and compared with commercial black paint. A new and affordable solar selective surface coating having higher solar absorption efficiency with low in-frared emittance compared to the commercial black paint coating used in most ordinary solar water heating systems has been developed. Characterization of coating includes Optical properties studies of coatings, Surface morphology and XRD studies, and solar water heater performance with new coatings.

KEYWORDS: Solar absorptance, solar emittance, solar selective coatings, NiAl, NiCo surface morphology, XRD.

1. INTRODUCTION:

Easy and efficient way to utilize solar energy is the direct conversion of sun rays to thermal energy (heat) for various applications such as solar cookers, air conditioning, water pumping and water heating. Due to affordable cost of solar water heating system, it can be used by many households in the Middle East. In this region average daily solar radiation is around 5.5 Kw.h/$m^2$and around 300 days in a year are sunny. Many researchers have focused on how to improve already existing solar water heating system by minimizing the thermal loss by providing the insulating material around the storage tank. Also, by providing the better solar selective coating on the solar collector surface efficiency can be improved with some previous research. The recent study on solar water heater shows that, the materials which are having good thermal conductivity like copper, aluminium or stainless steel when used for tubing purpose in solar water heaters act as a weak absorber for solar radiations. So, solar selective coatings are necessary to get best results in solar water heater system. In order to have efficient solar water heater system, solar selective coatings must have good spectral properties. An Ideal solar selective coating have very high absorptance coefficient over wavelength range of solar radiations and nearer to infrared range (spectrum from 0.3μm to 2.0μm) and very low emittance coefficient for long wavelength radiations (spectrum from 2.0μm to 20μm). Although black coating materials have high solar absorptance, they also suffer from the high infrared emissivity. Generally, solar selective coatings frequently applied in combinations of different materials. For example, materials having high solar absorptivity are blended with materials having low emissitivity as an underlayler coating. There exists a few solar selective paints with good efficiency such as Solokte (solec, USA), Solarect-Z (Slovenia) and Thurmalox (Dampney.USA). Most of these paints have to be brought from their original modifiers and can not be used by the many people around the world due to their high import and tax costs. Other alternatives materials are studied such as black cobalt, black nickel – cobalt, black copper-nickel alloys, black nickel and copper-magnesium films (Ehab AlShamaileh, 2010).

Scanning electron microscopic studies showed that the particles in the coatings are of dentritic structure. The high degree of solar absorptance is related to the irregular dentritic structure and surface roughness of the coatings (A.R.Shashikala, *et al*, 2007).

Solar selective black chrome coatings are widely used for decorative as well as functional applications because of their durability and excellent optical properties. Though black chrome coatings provide excellent properties, the use of toxic hexavalent chromium and requirement of high current densities are the major drawbacks in producing these coatings (J.K. Dennis, *et al*, 2003).

Several alternatives to black chrome plating like black nickel, black nickel–cobalt, black brass, and black cobalt have been studied by several investigators (S.Jhon, *et al, 1997*), (N. Karuppiah, *et al, 2000), (*Purnima Richharia, 1996), (Enrique Viveros, 1998). Recently, metallic and non-metallic nanoparticles have been applied in solar- energy applications by the researchers like absorbing films consisting of nickel nanoparticles embedded in dielectric matrix of alumina Al2O3

(Bostrom T, *et al, 2008)*. Carbon nano-particles in NiO, ZnO, SiO matrices (Katumba, G, *et al, 2008)*. But these selective coatings have not been experimentally tested on solar heaters. The surface morphology of black nickel, black nickel-cobalt coatings and its relationship with optical properties have been studied on zincated substrates (N.C. Mehra, *et al* ,1989).

2. MODIFIED/NEW SOLAR SELECTIVE COATINGS:

NiAl coating on Al substrate. Individually, nickel and aluminium have interesting thermal and spectral selective properties. Also, nickel shows good corrosion resistance and when nickel particles are added to other coating materials it will improve their heat resistance and durability. Nickel exhibits high solar absorptivity. Aluminium has high reflectivity in the infrared region of the spectrum from 0.3µm to 2.0µm which exhibits low thermal emissions produced by infrared radiant emission from the collector to the ambient air. Therefore, it makes a lot of sense to try a new coating formula based on NiAl.

a) REQUIREMENTS OF MATERIALS:

Black paint (cellulose nitrate resin, Duco), Acetone (Duco), nickel–aluminium alloy (50:50, Vineeth Precious Catalysts P.Ltd), hydrochloric acid, sodium chloride and two solar water heaters.

Fig.1 Photograph of required material.

b) NIAL COATING PROCESS:

An electric mixer shown in fig 2.is used to mix the paint with the Ni-Al particles to produce homogeneous mixture of coating. A coating mixture produced by various percentages of NiAl alloy particles and the black paint. This mixture is then diluted with acetone of 50 ml in order to have uniform layer of paint with the help of brush painting on base metal of aluminium (alloy 6061). The painted layer of black paint (unmodified) and NiAl alloy powder is blended with black paint (modified paint) in various percentages of compositions has a paint layer thickness of 10µm on aluminium plate.

Fig.2 Photograph of Paint Mixer

In below, Table 1. Shows different compositions made of the coatings to be tested.

Table 1: Different compositions for samples

Sample	Black-paint %	Ni-Al %	Acetone (ml)
1	100	0	50
2	97	3	50
3	94	6	50
4	91	9	50

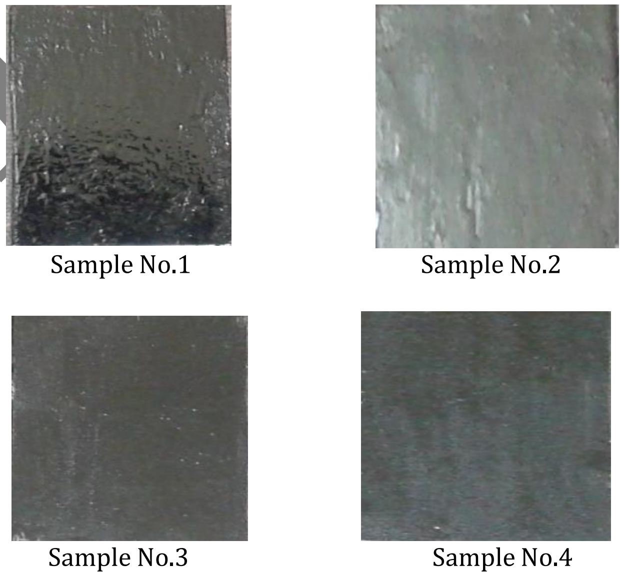


Fig.3 Photograph of Samples of NiAl coating.

c) OUTDOOR EXPERIMENT:

An experiment is conducted on five 15mm aluminium tubes filled with stationary water and fitted with a thermometer to compare the different compositions' absorbance to sunlight. The first tube was painted with commercial black paint and the other three were painted with the various compositions of the modified paint shown in Table 1 (samples 2–4). The temperature was monitored over a period of 1 day. The preliminary results of testing shows that, as the Ni-Al% by mass in black paint increases, the solar heat absorbance also increases. By visual inspection of prepared sample, it is seen that there is no any facial crack on samples to be prepeared.there is no any visual defects present in the samples.Hence, out of samples 2, 3 and 4, the optimum composition of 6% Ni-Al by mass is selected for further testing of solar water heater system. The performance study of solar water heater is done by degreasing the aluminium pipes used in solar water heater by using acetone and further tubes are etched with help of diluted hydrochloric acid (HCL) followed by washing of tubes with pure water. The sand paper in fine grit is also used for good paint adherence treatment on tubes. After this sequence of operations, aluminium tubes are painted to give thin uniform homogeneous layer by brush painting. Painted tubes are left to dry in air for 48 hours away from dust. A photograph of the experimental setup is shown in Fig. 4. It consists of two identical simple SWHSs where each is made of a flat plate collector and a storage tank.

Fig.4 A Photograph of Experimental Setup

All temperature measurements are done by using mercury-filled thermometers. The probes were immersed inside the tubes and sealed at the inlets and the outlets of the collectors. The temperature inside and outside of tubes and the ambient air temperature are measured. All temperatures are recorded every hour from sunshine to sunset (e.g. 8 am to 7 pm in the summer). The measurements were carried out regularly from May 2016 and April 2016.

Observations for flat plate collector in May 2016 and April 2016 are given in below table.

Table 2 Observations for flat plate collector in May-2016.

Time	Inlet water temperature in ^0C	Temp. In collector with unmodified paint (^0C)	Temp. In collector with modified paint (^0C)
7.00 A.M	23	26.0	26.0
8.00 A.M	23	26.0	26.1
10.00 A.M	23	37.5	37.9
12.00 Noon	23	52.5	53.2
2.00 P.M	23	60.0	63.0
3.00 P.M	23	60.5	64.0
4.00 P.M	23	59.5	62.0
6.00 P.M	23	41.0	41.5
7.00 P.M	23	32.5	32.8

Table 3 Observations for flat plate collector in April-2016.

Time	Inlet water temperature in ^0C	Temp. In collector with Unmodified Paint (^0C)	Temp. In collector with Modified
8.00 A.M	20	31.5	31.5
10.00 A.M	20	37.5	39.0
12.00 Noon	20	42.5	46.0
2.00 P.M	20	44.0	48.0
4.00 P.M	20	43.5	47.0
6.00 P.M	20	40.0	41.0
7.00 P.M	20	31.5	32.0

Performance evaluation of solar flat plate collector can be done by calculating efficiency, which can be calculated by,

η = Useful Heat Gain (Qw) / Heat supplied (Qs) (1)

Amount of useful heat gain can be calculated by considering water temperature at the inlet and outlet of tubes, and taking into account the water flow rate and its specific heat,

Qw = m × Cp × ΔT (2)

Total heat supplied to the collector is depends upon solar intensity (It) and collector area (Ac) is given by,

QS = It × Ac (3)

Table 4 Efficiency of flat plate collector in May-2016.

Time	Inlet water temperature in ^0C	Efficiency in % of collector with unmodified paint (°C)	Efficiency in % of collector with modified paint (°C)
7.00 A.M	23	6.2	6.2
8.00 A.M	23	6.2	6.5
10.00 A.M	23	30.383	31.21
12.00 Noon	23	61.80	63.27
2.00 P.M	23	77.52	83.80
3.00 P.M	23	78.57	85
4.00 P.M	23	76.47	81.71
6.00 P.M	23	37.71	38.76
7.00 P.M	23	19.90	20.53

Table 5 Efficiency of flat plate collector in April-2016

Time	Inlet water temperature in ^0C	Efficiency in % of collector with unmodified paint (°C)	Efficiency in % of collector with modified paint (°C)
8.00 A.M	20	24	24
10.00 A.M	20	36.66	39.80
12.00 Noon	20	47.14	54.47
2.00 P.M	20	50.28	58.66
4.00 P.M	20	49.23	56.57
6.00 P.M	20	41.90	44.00
7.00 P.M	20	24.09	25.14

d) LABORATORY MEASUREMENTS:

i) Surface morphological studies for the different coating samples of NiAl (10µm) carried out with scanning electron microscope (SEM) on SPPU-JEOL .

ii) X-ray diffraction (XRD) patterns of the NiAl coatings are obtained by SPPU-JEOL .

NiCo coating on Al substrate.

a) REQUIRED MATERIALS:

Aluminium alloy 6061 (Al-97.9, Mg-1.0, Si-0.6, Cu-0.25, Cr-0.25%) specimens of the size 100×50×2mm are processed for black nickel–cobalt plating at Nexus Engineers (R.R.Enterprises) chikkali, Pune.

b) NICO COATING PROCESS:

As per the following sequence of operations:

i) Solvent degreasing in trichloroethylene using ultrasonic bath for 5–10 min at room temperature.

ii) Alkaline cleaning in a solution containing sodium carbonate 20–25 g/L, sodium meta silicate 8–12 g/L and tri sodium orthophosphate, at 65°C for 3–4 min followed by water rinsing.

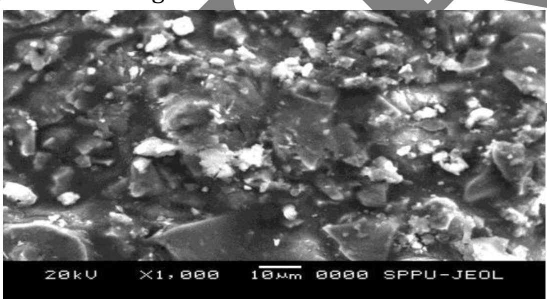


Fig.6a) Micrographs of surface of the black paint.

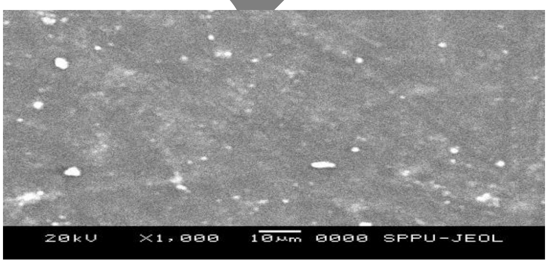


Fig.6b) Micrographs Ni-Al modified coating on Al substrate

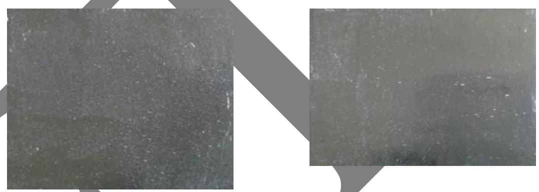
iii) Chemical polishing in a solution containing orthophosphoric acid 80%, nitric acid 3.5% and copper 0.01% for 20–25 s at 90 1C followed by hot water rinse.

iv) De-smutting in an acid solution containing 10 ml/L sulfuric acid, 12 ml/L hydrofluoric acid and 25 ml/L nitric acid for 2–3 min at room temperature followed by water rinsing and air drying.

v) Nickel plating using watts bath.

vi) Black nickel cobalt plating in a solution containing cobalt sulphate, nickel sulphate, ammonium acetate and sodium thiocyanate at 28–30°C.

c) IMAGES OF ELECTROPLATING OF BLACK NI-CO ON ALUMINIUM ALLOY 6061:



Sample No.1 Sample No.2

Fig.5 Photograph of Samples of black Ni-Co.

d) LABORATORY MEASUREMENTS

i) Surface morphological studies were carried out with scanning electron microscope SPPU-JEOL.

ii) X-ray diffraction (XRD) patterns of the coatings were obtained by Philips SPPU-JEOL.

iii) UV-VIS Spectrophotometer used for absorbance and Transmission Studies of NiCo samples conducted in Shivaji University, Kolhapur.

3. RESULT AND DISCUSSIONS:

FOR NIAL COATING

a) SURFACE MORPHOLOGY (SEM) AND XRD STUDIES:

Below fig.6 represents micrographs of surface of the black paint shown in fig. (a) And the Ni-Al alloy modified coating on aluminium surface shown in fig. (b).For the SEM testing component size of 5mm×5mm is required for both paint. The uniform dispersion of the Ni-Al particles is a major factor in the enhancement of the solar absorptivity and the reduction of thermal losses.

X-ray diffraction (XRD) pattern of black paint coating on aluminum sample is shown in fig.7. Testing of XRD is done on a specimen size of 1mm×1mm at Department of Physics, in SPPU.

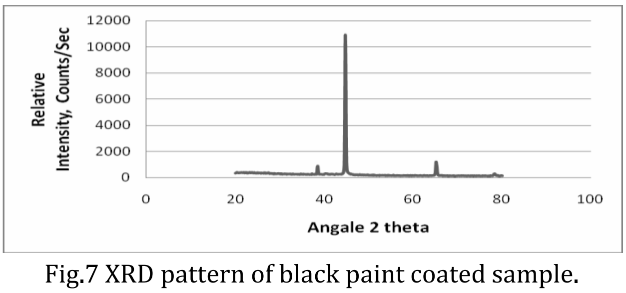


Fig.7 XRD pattern of black paint coated sample.

X-ray diffraction (XRD) pattern of Ni-Al coating on aluminum sample is shown in fig.8, clears that the modified coating contains Ni and Al with no oxide detected.

Fig.8 XRD pattern of Ni-Al coated samples.

b) SOLAR COLLECTOR TEMPERATURE AND EFFICIENCY STUDIES:

From below fig.9&10, it is clear that the NiAl-modified paint always gave higher temperature for the water inside the collector compared to commercial black paint.

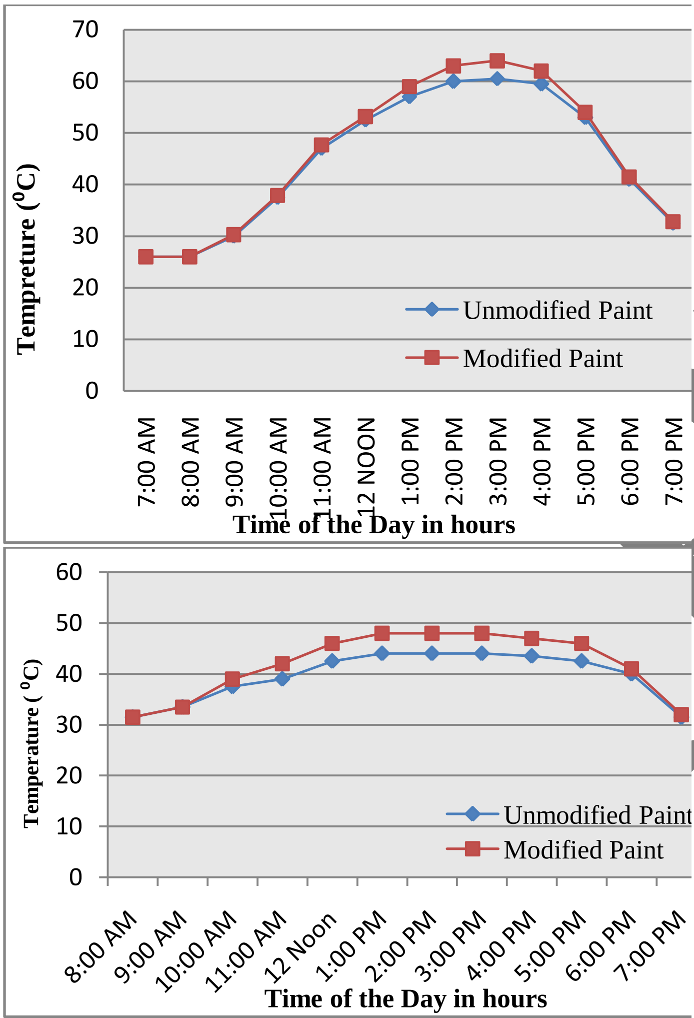
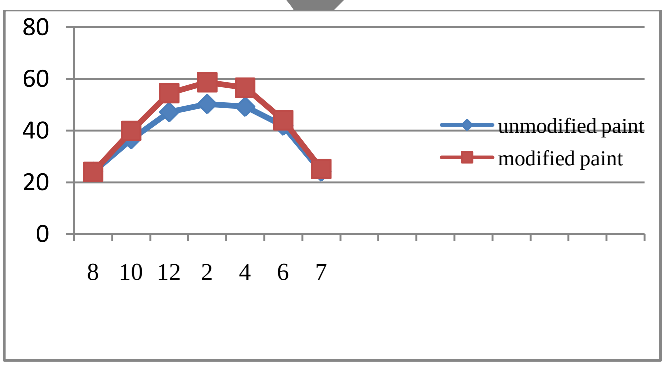


Fig.9 Temperature curve for modified and unmodified paint on solar collector in May-2016 & April-2016



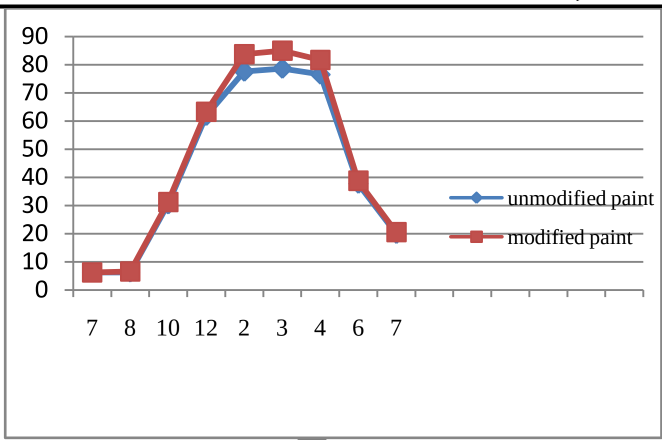
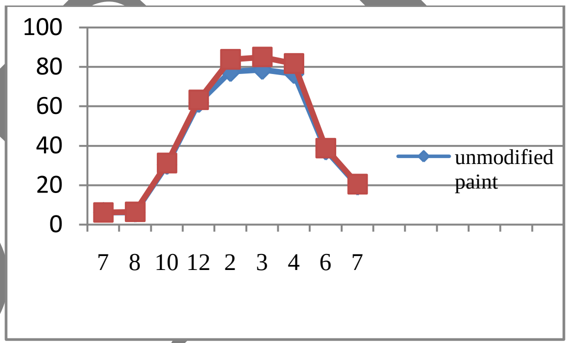


Fig.10Efficiency vs time grap for modified and unmodified paint on solar collector in May-2016 & April-2016.

FOR NICO COATING

A) EFFECT OF NICKEL UNDERCOAT THICKNESS ON OPTICAL PROPERTIES OF BLACK NI–CO COATINGS



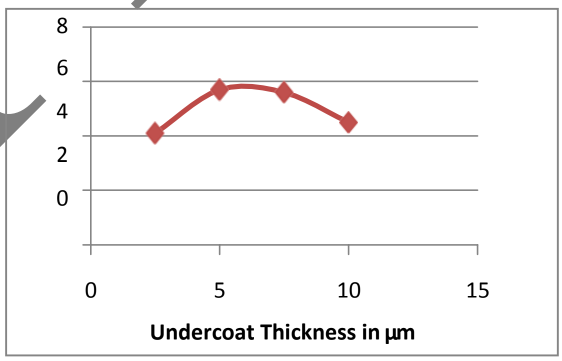


Fig.11 Effect of under coat thickness on the optical properties (ratio of absorptivity to the emissivity).

Fig.11. shows that the influence of the thickness of nickel undercoat on the optical properties of the black nickel cobalt(NiCo)coatings.

The nickel undercoat thickness was varied from 2.5 to 10 µm. Lower nickel undercoat thickness resulted in a gray colored black nickel cobalt coating with low absorptance to emittance ratio. At 5.0–7.5 µm undercoat thickness a good black Ni–Co coating with high absorptance to emittance ratio (5.57) is obtained on UV-VIS Spectrophotometer at shivaji university, Kolhapur. Further there will decrease in absorptance to emittance ratio with increase in undercoat thickness.

ii) Surface morphology and XRD studies

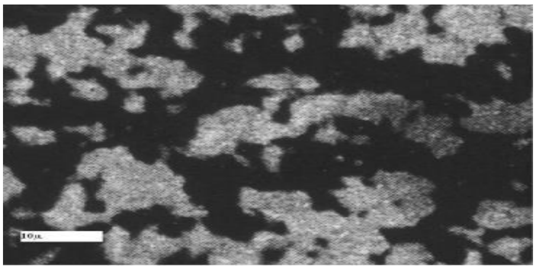


Fig.12 Micrographs of black nickel cobalt coating on nickel plated aluminum alloy 6061.

Fig.12.shows the surface morphology of black nickel–cobalt coatings on nickel-plated aluminum substrates. Surface morphology of the coatings affects the solar absorptance of the coatings. The enhancement of solar absorptance may occur either by an array of fine particles causing intrinsic adsorption or by reducing the front surface reflections from an absorber surface. The particles have irregular needle like shape shown in fig.12, also the grains are compact, have more uniform structure in nickel-plated substrate. The irregular and needle like structure facilitates trapping of radiation so that the solar energy is absorbed by the black coating to a greater extent.

X-ray diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials. It provides information on crystal structure, phase, preferred crystal orientation (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects.

The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint of the periodic atomic arrangements in a given material. XRD pattern of the black nickel cobalt coating (25–50 nm) with nickel undercoat is given in fig.13.

X-ray diffraction (XRD) is a versatile, non-destructive analytical technique that reveals detailed information about the chemical composition, crystallographic structure and physical properties of materials. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays diffracted at specific angles from each set of lattice planes in a sample.

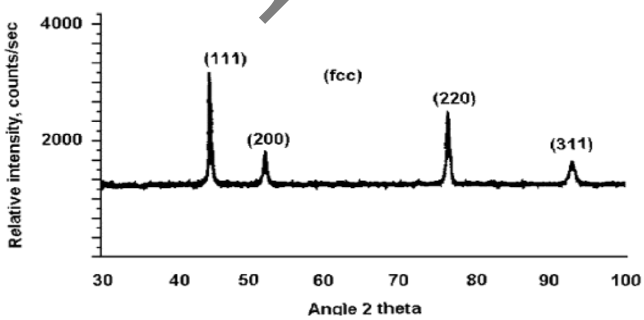


Fig.13 XRD pattern of black nickel cobalt coating.

XRD pattern in Fig.13 shows the presence of FCC structure with major intensity Ni (1 1 1) peak and very small intensity Ni–Co peaks.

4. CONCLUSIONS

This paper concludes,

1) The new coating, comprising NiAl alloy particles, shows that the solar water heater system collect thermal energy more efficiently than ordinary black paint.

2) An outdoor experimental study of flat plate collector shows that, the new system having NiAl coating always produce warmer water.

3) Black nickel cobalt electroplating on aluminium alloys process provides high solar absorptance (0.95) and low thermal emittance (0.10), which is suitable for solar selective applications.

4) SEM and XRD studies showed that, the particles in the coatings are of dentritic structure. The high degree of solar absorptance is related to the irregular dentritic structure and surface roughness of the coatings with no oxides present which help to increase corrosion resistance.

5) Characterizations done in this paper shows that, NiAl and NiCo coatings have more efficient than ordinary black paint used in solar water heating systems.

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