

HIGH-TEMPERATURE OXIDATION-RESISTANT NiCr/Al DUPLEX COATING ON CARBON STEEL SUBSTRATE

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Received: 17 December 2018; Accepted for publication: 2 December 2019

Abstract. In this study, high temperature oxidation-resistant NiCr/Al duplex coatings on carbon steel substrate have been fabricated by electrical wire arc-spraying process. The oxidation resistance properties of NiCr/Al duplex coating system have been evaluated at 800 °C during retention times of 1.5, 3.0, 4.5 and 6.0 hours. The morphology and chemical composition of their cross-sectional structures were investigated using scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS). Micro-hardness and X-ray diffraction (XRD) measurements on the cross-sectional structure of the NiCr/Al coating were also taken place. After the oxidation test, SEM/EDS data indicated the diffusion of aluminum into the NiCr coating whereas XRD patterns revealed the appearance of new phases (Al_3Ni_2 and Al_2O_3). In addition, an increase in micro-hardness (upto 518 - 842 HV) was obtained after oxidation test. These obtained findings indicated that NiCr/Al coating had higher oxidation resistance than NiCr coating. The results suggested that the NiCr/Al duplex coating can be a good candidate for applying to high temperature working parts such as cement plant and waste treatment plant, etc.

Keywords: thermal spray; NiCr/Al duplex coating; oxidation resistance.

Classification number: 2.9.1, 2.9.4.

1. INTRODUCTION

In fact, many machines and equipment must operate in severe conditions such as corrosion and abrasion, especially corrosion at high temperature. The formation of oxide layers during the oxidation and corrosion of metal can lead to the degradation of the properties of component materials. A solution is to manufacture an anticorrosive (anti-oxidant) coating at high temperature on their surface before operating or recovering worn parts during working. Thermal spray technology may meet the above requirements [1-2]. NiCr alloy coating is applied for anti-corrosion at high temperature because Ni is resistant to abrasion and Cr is resistant to abrasion

with good thermal resistance [3-7]. Al is a popular, lightweight and cheap metal, often forms hard thin oxide film on the surface and has good resistance against corrosion. In previous studies, the Al coating on NiCr alloy is studied mainly focusing on mechanical properties and corrosion resistance [7-11]. Kazuo Ishikawa *et al.* [7, 8] studied a duplex coating composed of aluminum on uncoated 80Ni-20Cr alloy. In these studies, the coating was manufactured by a Sulzer METCO 12E flame spray gun and coating materials were metal wires. Results showed that NiCr/Al duplex coating has better resistance against corrosion than SS400 steel and single component coatings in a hot, near neutral aqueous environment. In the studies in [10, 11], the authors studied structure and properties of Al coating on Ni-15Cr alloy substrate at 1050 °C during retention time of 5 hours. Results of analyzing X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron probe micro-analyzer (EPMA) indicated that Al is diffused into Ni-15Cr alloy in depth of 20 – 30 μm to form NiAl intermetallic phases such as γ -Ni₃Al, β -NiAl and a mixture of β -NiAl + α Cr phases and Cr₂Al phase.

The recent years, our group studied the effect of heat treatment on the properties of NiCr coating. The NiCr coating was annealed at temperature in a range of 400 ÷ 1000 °C [12]. The obtained results showed that with increase of the annealing temperature, the coating's porosity has a tendency to decrease while the weight loss of the coating after dry wear tests according to the ASTM G99 standard and its microhardness tends to increase. In the present work, the NiCr coating and NiCr/Al duplex coating were deposited on carbon steel substrate by electric wire arc-spraying technique. The oxidation resistance property of these coatings at 800 °C was studied. The microstructure, microhardness, chemical composition and phase composition of the coating after oxidation testing are also presented and discussed in this report.

2. MATERIALS AND METHODS

2.1. Materials and preparation of samples

There are two types of specimens: Type 1 includes NiCr coating specimens without Al and NiCr/Al specimens; and type 2 includes comparative specimens: uncoated carbon steel and SUS304 stainless steel. The specimens have size of 50 × 50 × 5 mm. Chemical compositions of carbon steel were checked on PDA-7000 (Shimadzu) optical emission spectrometer equipment (given in Table 1).

Table 1. Chemical compositions of carbon steel.

Elements	C	Si	Mn	P	S	Cu	Ni	Cr	Mo
Average content (%)	0.180	0.103	0.581	0.017	0.011	0.002	0.011	0.016	0.035
Elements	Ti	V	Al	W	Co	Nb	Pb	Mg	Fe
Average content (%)	0.006	0.006	0.010	0.005	0.003	-	0.008	0.010	98.99

NiCr alloy wire (79.39 % Ni; 18.16 % Cr; 0.9 % Si; 0.26 % Ti; 0.73 % Mn; 0.56 % Fe) and aluminum wire (99.5 % Al) with a diameter of 2 mm have been used to spray on carbon steel substrate. The chemical compositions of NiCr alloy wire and aluminum wire are provided by

Metallisation Limited. Prior to the spraying, the surfaces of carbon steel substrates were degreased with acetone and then grit blasted on SPEEDO PBM – 100 abrasive blast machine by aluminum oxide Al_2O_3 with particle size of 0.8 – 1.2 mm. Then the steel substrate sprayed with NiCr alloy coating in thickness of 200 - 250 μm , followed by an aluminum coating in thickness of 120 - 150 μm using OSU-HESSLER 300A arc-spray equipment. Time between two sprayings should not exceed 20 minutes to avoid surface oxidation. Thickness of the coating was measured by Minitest 600 of ElektroPhysik.

2.2. Oxidation resistance test

Oxidation resistance of NiCr and NiCr/Al coating specimens and comparative specimens were tested at 800 °C for retention times of 1.5, 3.0, 4.5 and 6.0 hours. Test equipment is resistance furnace SX2-10-12 with maximum heating temperature of 1200 °C; output of 10 kW; temperature lift rate is 50 °C/min. The test was conducted for 3 specimens and its result was average value of 3 measurement times. Before oxidation test, NiCr and NiCr/ Al coating specimens and comparative specimens were dried at 120 °C for 6.0 hours, then photographed on their surface by digital camera Canon IXUS 180 and weighted by Precisa 5-digit balance XR 205SM-DR. The total surface area (S) and initial weight (M_0) of these specimens were evaluated. The coating specimens and comparative specimens were heated in the furnace with directly air contact on all sides. Thus, the oxidation continuously occurred during the heating and retention process.

After certain retention times, the specimens were cooled with the furnace and then weighted for the second time to take value M_1 . The difference $M = M_1 - M_0$ is incremental weight and quotient M/S is average value of the weight growth rate by time. The more incremental the quotient M/S of the specimens is, the more such specimens are oxidized. Figure 1 presents the temperature diagram of the oxidation test.

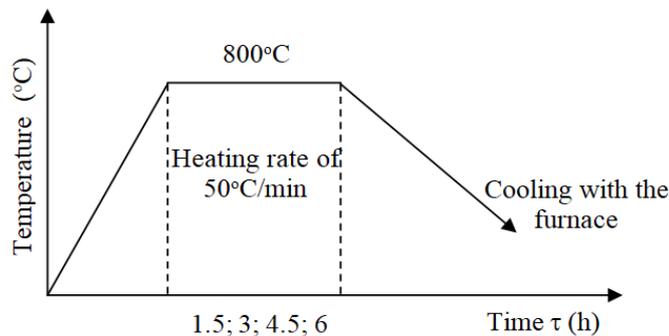


Figure 1. Temperature diagram of oxidation test.

2.3. Coating characterization methods

The cross-sectional structure and chemical composition of coatings have been analyzed using a scanning electron microscopy coupled with energy dispersive spectroscopy (SEM – EDS, JEOL JSM – 6510 LV). Furthermore, the micro-hardness of the coating was determined by using AVK-CO/Mitutoyo equipment (10 points on cross-section under a weight load of 300 g in 15 s with 50 μm distance of the indentations). To identify the possible phases that present in the coating after oxidation test, X-ray diffraction (XRD, SIEMENS D5005X-RAY instrument) has been used at temperature of 25 °C, with 2θ angle scanning from 10° to 60° at 0.03 °/s of step scan.

3. RESULTS AND DISCUSSION

3.1. Anti-oxidation of the coatings

Figure 2 shows the specimen surface before and after oxidation test at 800 °C for 1.5, 3.0, 4.5 and 6.0 hours. Results indicate that the surface of the NiCr and NiCr/Al coated specimens is rather intact and has no rust points after test for 1.5 hours at 800 °C; SUS304 steel specimen after test for 1.5 hours has yellow and red rust points on the surface; the surface of the uncoated carbon steel comparative specimen only after test for 1.5 hours is strongly oxidized, blistered and come off. The oxidation process continues after incremental time. After 6 hours of oxidation test, SUS304 steel specimen has its thin film peeled off on the surface; uncoated carbon steel specimen is strongly oxidized and has a thick dark red ferric oxide layer on the surface; NiCr and NiCr/Al coated specimens have no rust and NiCr/Al coating has more smooth surface and brighter color.

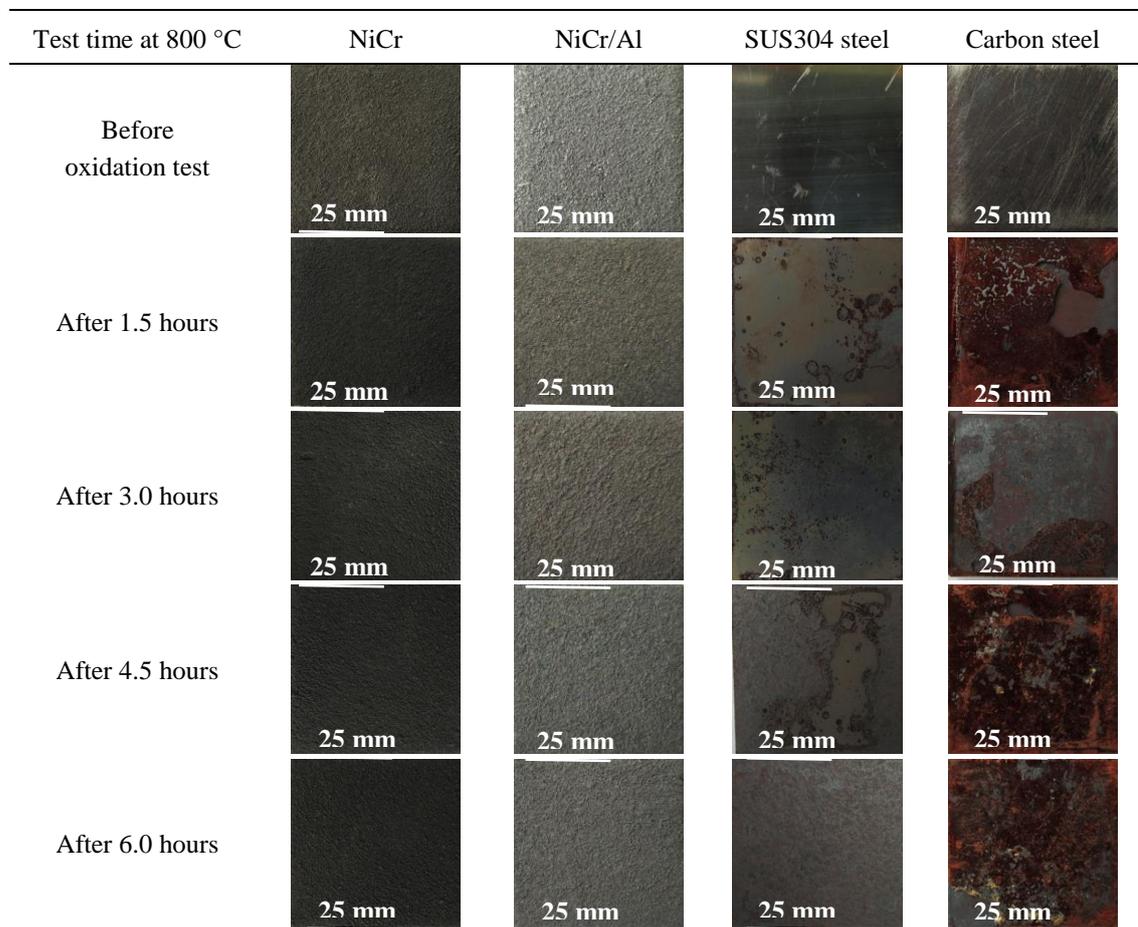


Figure 2. Surface observations before and after oxidation test after 1.5, 3.0, 4.5 and 6.0 hours at 800 °C.

This can be explained as follows: in an environment with oxygen at high temperature, the surfaces of the uncoated carbon steel specimen were constantly oxidized and formed red oxides.

SUS304 steel specimen has a protective oxide film on the surface. However, this oxide film is very thin, so after a long oxidation time, the surface of SUS304 steel is still peeling. For the coated carbon steel specimen, the NiCr and NiCr/Al coatings protect the steel substrate from direct contact with oxygen in the air, so the surface of these specimen do not appear red rust and not peeling.

Figure 3 shows weight gain of oxidation tests at 800 °C, for 1.5, 3.0, 4.5 and 6.0 hours. Based on results of weight gain upon oxidation test at 800 °C, the longer the heating time is, the more weight gains, but weight gain at times is different, *i.e.* weight gain for 4.5 hours and 6.0 hours is 0.00075 g/cm² for NiCr coating specimen and 0.00047 g/cm² for NiCr/Al coating specimen respectively, 0.00028 g/cm² less than NiCr coating specimen. This may be explained as follows: In initial test, for 1.5 – 3.0 hours, the specimens are continuously oxidized; weight gain of the specimen is continuous by time; oxide films formed on the surface prevent oxygen from contacting the substrate surface to reduce oxidation process. Al₂O₃ film formed on the surface of NiCr/Al coating specimen is rather sustainable to prevent from next oxidation process and reduce oxidation and weight. For SUS304 steel specimen, its weight gain is rather low because it has rather sustainable Cr oxide film and smooth surface. For the uncoated carbon steel comparative specimen, its oxidation process by time and weight gain occur continuously; for 4.5 hours, thick ferric oxide coating is formed on the surface, the oxidation process is reduced but its weight gain is still high and the highest among the test specimens. The oxidation test process of NiCr and NiCr/ Al coating specimens were conducted at 800 °C during retention times of 1.5, 3.0, 4.5 and 6.0 hours. The next studies only focus on studying test specimens with the maximum duration of 6 hours.

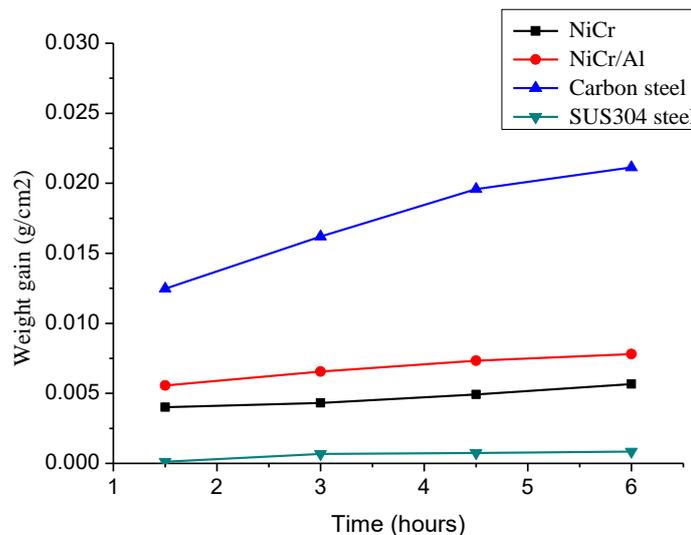


Figure 3. Weight gain of the coating upon oxidation test after 1.5, 3.0, 4.5 and 6.0 hours at 800 °C.

3.2. Microstructure study

Figure 4 shows the microstructure of NiCr and NiCr/Al coating specimens after oxidation test at 800 °C during retention time of 6 hours. Figure 4a shows the microstructure of NiCr coating specimens, from the left to the right are: the steel substrate, NiCr coating and epoxy coating consecutively. Visual observation of the microstructure shows that there is a rather clear but very tight interface between the coating and the steel substrate. The NiCr coating has

laminated structure; the coatings are overlapped; there are black areas which may be porous holes, the interface among the coatings. The NiCr coating is about 300 - 350 μm in thickness. After oxidation test, the NiCr coating is still quite intact and tight, suggesting that the NiCr coating has a role of preventing oxygen direct contact with the steel substrate. It therefore protected the steel from oxidation. Figure 4b is the microstructure of NiCr/Al coating, from the left to the right is: NiCr coating, Al coating and epoxy coating. The NiCr/Al coating is about 400 - 450 μm in thickness. The oxidation test occurs at temperature of 800 $^{\circ}\text{C}$ – much higher than melting point of Al (660 $^{\circ}\text{C}$), thus it favors the melted Al to spread and fill into the porous holes of the NiCr coating. Therefore, after the oxidation test, NiCr coating has lower porosity; the interfaces among the coatings, between the coatings and the steel substrate are more seamless, so that increasing the ability to protect the steel substrate from oxidation.

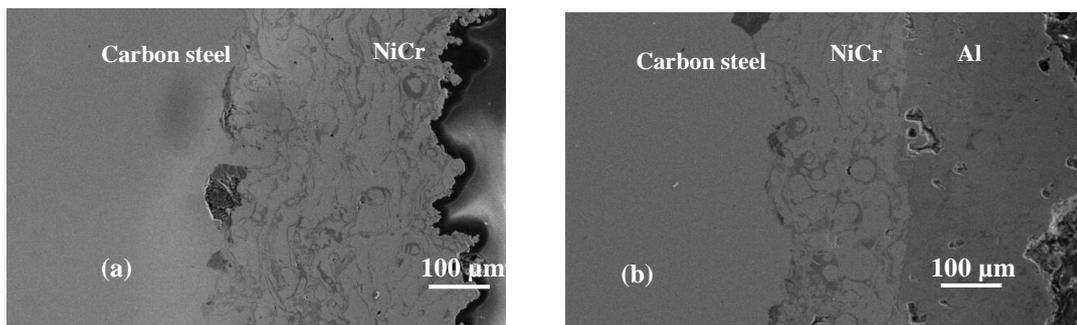


Figure 4. Microstructures after 6 hours oxidation test at 800 $^{\circ}\text{C}$ of (a) NiCr and (b) NiCr/Al coating specimens.

3.3. Microhardness of the coatings

Microhardness was measured on the cross-sectional structure of the NiCr/Al coating before and after oxidation test. The microhardness of the specimens was continuously measured from the outer coating to the inner steel substrate; distance between the measuring indentation was 50 μm . All microhardness measurements were performed three times and the results are calculated as an average value.

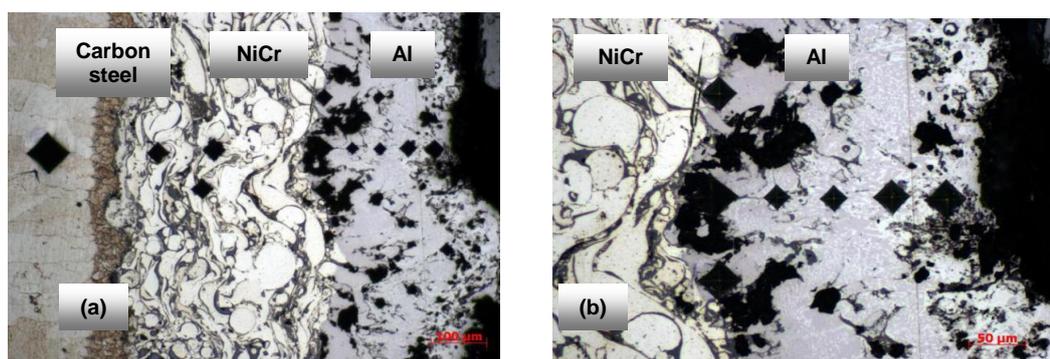


Figure 5. Cross-sectional structure after 6 hours oxidation test at 800 $^{\circ}\text{C}$ of the NiCr/Al coating with microhardness measuring traces. Magnification: $\times 200$ (a); $\times 500$ (b).

Table 2. Microhardness on the cross-sectional structure of NiCr/Al coating.

Positions of microhardness measurement	Microhardness average value, HV 0.3	
	NiCr/Al	NiCr/Al
	Before oxidation test	After oxidation test
Near the outer surface	50	388
~50 μm from the surface	55	476
~100 μm from the surface	55	842
~ 150 μm from the surface	58	518
~ 200 μm from the surface	180	430
~400 μm from the surface (NiCr coating)	287	295
~420 μm from the surface (NiCr coating)	286	337
~ 500 μm from the surface (Carbon steel substrate)	189	180

Figures 5a and 5b are the cross-sectional microstructure of the NiCr/Al coating before and after oxidation test at 800 °C for 6 hours with microhardness measuring traces from the outer surface to the inner steel substrate. Microhardness values on the cross-section of the NiCr/Al coatings are shown in Table 2. Additionally, results of microhardness measurement indicate that forming new phases significantly increases hardness on the coating surface against hardness of the NiCr alloy coating and the steel substrate. High hardness on the coating surface would increase wear resistance of the coating.

3.4. Chemical composition of the coating

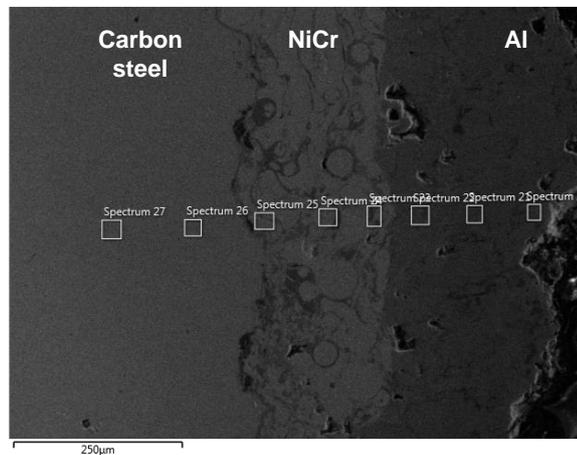


Figure 6. NiCr/Al coating specimen after oxidation test after 6 hours at 800 °C.

Chemical composition of the coating was studied on the cross-section of the coating and measured in 8 regions from the outer coating to the steel substrate. Figure 6 shows SEM-EDS photo for NiCr/Al coated specimen after oxidation test at 800 °C for 6 hours. Chemical compositions in the analysis regions of the NiCr/Al coating are presented in Table 3. At the area near surface of the coating (region #20) and the interface between Al coating and NiCr coating (regions #22 and #23), Al element content is rather high but there are elements of Ni and Cr. It

indicates that after oxidation test at 800 °C, Al was diffused into the NiCr coating. At the interface between NiCr coating and the steel substrate (region #25), besides Ni and Cr elements, there is also the presence of Fe element with a content of 8.13 %. This result shows that the NiCr coating and the steel substrate interacted with each other. Thus, the chemical compositions obtained by EDS data are similar to previous results and conform to the literature [9, 10]. These results forecast an appearance of the phases on a basis of the chemical compositions in the studied region and the phase diagram. To ensure the conclusion on the new phases after oxidation test, we continue to study intermetallic phases by X-ray diffraction method as shown later on.

Table 3. Chemical compositions (% mass) of NiCr/Al specimen after oxidation test.

Region (Near the outer surface)	C	O	Al	Cr	Ni	Si	Fe	N	Mn	Cu	Total %
#20 (20 μm)	26.85	9.83	37.95	3.58	19.14	0.95	1.70				100
#21 (100 μm)	4.93	6.62	58.79	6.92	20.97	0.45	0.41	0.91			100
#22 (180 μm)	4.01	9.15	52.37	7.70	25.79	0.66	0.30				100
#23 (250 μm)	5.47	11.73	39.04	10.91	31.18	1.03	0.47	0.17			100
#24 (320 μm)	4.69	13.95	0.49	22.24	54.15	1.97	0.92	1.60			100
#25 (400 μm)	3.89	11.64	0.87	14.63	58.53	0.93	8.13	1.38			100
#26 (500 μm)	4.73	0.24		0.36		0.23	94.45				100
#27 (620 μm)	3.01	0.43				0.26	95.55		0.49	0.26	100

3.5. XRD study

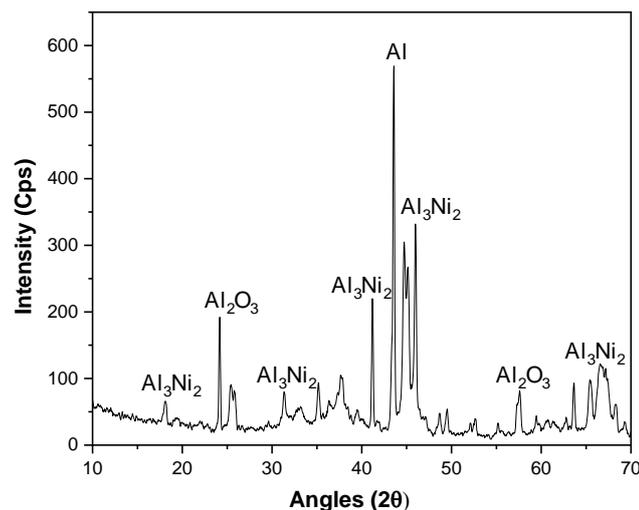


Figure 7. XRD pattern of NiCr/Al coating after 6 hours oxidation test at 800 °C.

Study on phases by X-ray diffraction method (XRD) of NiCr/Al coating specimen after oxidation test at 800 °C for 6 hours was conducted on the cross-section of the coating. Analysis results are shown on Figure 7. Analysis results indicate that on the cross-section of the coating, besides aluminum (Al) crystal phase, there are intermetallic crystal phases of Al_3Ni_2 and Al_2O_3 with relatively high intensity at scanning angles 2θ in range of 10 to 60°. This proves that the coating after oxidation test has a high quantity of the Al coating on the surface interacting NiCr alloy coating to form Al_3Ni_2 new phase. Results of analyzing chemical compositions by EDS method and analyzing phases by XRD method are rather the same to the study results in the references [13-15]. The coatings after oxidation test have low porosity and incremental microhardness. After the oxidation test, Al_3Ni_2 intermetallic phase formed on the coating surface with relatively high intensity has higher microhardness of the coating system than the initial NiCr alloy coating.

4. CONCLUSION

The NiCr coating and NiCr/Al duplex coating were prepared on carbon steel substrate by electric wire arc-spraying technique. The oxidation resistance properties of these coatings at 800 °C were characterized. The obtained results showed that the NiCr/Al duplex coating had higher oxidation resistance than NiCr coating and SUS304 and carbon steels. Weight gain of the NiCr/Al coating upon oxidation test is less than the NiCr coating. After oxidation test, aluminum was diffused into the NiCr coating. The formation of new phases (Al_3Ni_2 and Al_2O_3) could be resulted in an increase of coating microhardness upto 518 - 842 HV. The NiCr/Al coating had lower porosity and of more dense (at the interface) than NiCr coating. The results indicated that the NiCr/Al duplex coating can be a solution to improve tools used in high-temperature environments such as cement plant and waste treatment plant, etc.

Acknowledgments: This work is financially supported by the Institute for Tropical Technology, Vietnam Academy of Science and Technology.

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