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Laser Cladding of MCrAlY coatings on stainless steel

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Abstract

MCrAlY alloys (where M stands for Ni,Co or both) are commonly used as overlay protective coatings in gas turbine engine components against high temperature oxidation and corrosion. The protective effect of these alloys is due to the formation of a continuous thermally stable oxide layer on the coating surface. In this work several types of MCrAlY alloys, differing in their elemental composition, have been deposited on austenitic stainless steel by means of laser cladding. The microstructure of the coatings have been characterized by SEM-EDS and XRD. As expected, elemental composition compatible with γNi/γ' Ni3Al, γNi/β-NiAl or γCo/β-(Co,Ni)Al phases are observed in hypoeutectic or hypereutectic microstructures depending on the alloy composition. The high temperature oxidation behavior of the coatings was evaluated by air furnace oxidation tests at 1100ºC for 200 h. The oxidized surface of the samples was examined by SEM-EDS and the oxides present identified by theoretical stoichiometric calculations. Results indicate the formation of a uniform Al_3O_2 protective oxide scale with NiO, CoO, Y_2O_3/$YAlO_3$ and Cr_2O_3 oxide inclusions.

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Keywords: MCrAlY; laser cladding

1. Introduction

To comply with CO_2 emission standards and increase the efficiency of electricity generation in power plants, the firing temperatures and pressures of gas turbines are steadily increasing in the last years. As a consequence, new demands are imposed in machine component materials, which must demonstrate enhanced mechanical behavior at higher temperatures while withstanding a severe oxidizing and corrosive environment. Improved alloy processing

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techniques have allowed the development of nickel based superalloys or improved austenitic steels compositions with superior mechanical properties at high temperature. However, this could only be achieved at the cost of detrimental oxidation and hot corrosion resistance thus imposing the need of coating procedures on these components.

Common examples of such protective coatings are those based on MCrAlY alloys [J. R. Davis(2000)], where M stands for Ni, Co or both. Their properties against hot oxidation and corrosion are due to the formation of a continuous thermally stable oxide layer (Al_2O_3) on the coating surface [T. Nidjam et al.(2006), G. Marginean and D. Utu(2012)]. In their formulation, Ni and/or Co act as solid solution matrix with Cr giving improved hot corrosion resistance and increased aluminum chemical activity. Small amounts of yttrium are usually included to improve the adherence of the oxidation product [F. Tancret el at.(2003)]. The use of Ni or Co based matrix gives better oxidation or corrosion resistance respectively, with balanced performance if both elements are present.

MCrAlY alloys can be applied as bond coat for thermal barrier coatings or overlay coatings. Processing techniques as plasma spray, physical vapor deposition of HVOF are the common means of application. In all cases, low porosity and good adherence may be obtained if process parameters are satisfactory optimized. As an alternative, laser cladding is used in this work aiming to obtain fully dense layers metallurgically bonded to the substrate. Other authors have already investigated the characteristics of some MCrAlY coatings by laser cladding on Ni-based superalloy substrates[C. Bezencon et al.(2003), K. Partes et al.(2008), F. Vollertsen et al.(2005), R. Vila and S. Costa Santos(2011)]. In the present study, coating deposition is performed in austenitic steel substrates. Power plant generation base on coal fire steel boilers would benefit from the use of protective coatings, as they would allow the operation at higher temperatures and therefore increase their overall efficiency.

2. Experimental

The laser cladding equipment consisted of a 2kW Nd:YAG laser (Rofin DY022) operating in continuous wave. Power feeding was performed coaxially through a YC50 cladding head by means of a Suzer-Metco Twin 10C unit. Control of the laser processing was based on a ABB 6-axix robot unit(IRB 2400). Commercially available MCrAlY alloys provided by Sulzer were used, whose nominal composition is listed in Table 1. They mainly differ in the matrix composition of the alloy, being Ni based (AMDRY 963), Co-Ni based (AMDRY 995) and Ni-Co based (AMDRY 365). Powder size is -90+45 μm for the first and second alloy and -75+38 μm for the third.

Cladding was performed on 10 mm thick austenitic stainless steel substrates (AISI 304). Three sets of test samples (composed of three coating probes for each of the MCrAlY alloys) were produced by covering 30mmx30mm areas by overlapping single laser scans at an 35-40% overlapping ratio. Processing parameters for all samples were 2200 W laser power, 15 mm/s scan velocity and 21-25 mg/mm powder feed rate. Laser was defocused to a diameter of 4 mm on the working surface. He was used as shielding and powder carrier gas to avoid oxidation of processed samples. A set of the produced samples were transversally cut, polished and chemically etched prior to optical and SEM inspection. The remaining two sets were used in the XRD analysis and oxidation tests.

Table 1. Nominal composition of commercial alloys used in the study.

(wt%)	Ni	Co	Cr	Al	Y	Other
NiCrAlY	Bal.		24.5	6	0.4	
CoNiCrAlY	32	Bal.	21	8	0.4	<1
NiCoCrAlY	Bal.	23	17	12.5	0.4	<5.0

Isothermal oxidation tests were performed at 1100ºC up to 200h in static air. The oxidized specimens were removed from furnace at different intervals, 5,10,25,50,100 and 200h, and air cooled to room temperature. The oxidation behavior of the coatings was evaluated by measuring the weight gains of the samples. The sensitivity of the balance used was 0.01 mg. The surface of oxidized specimens was inspected by SEM-EDS

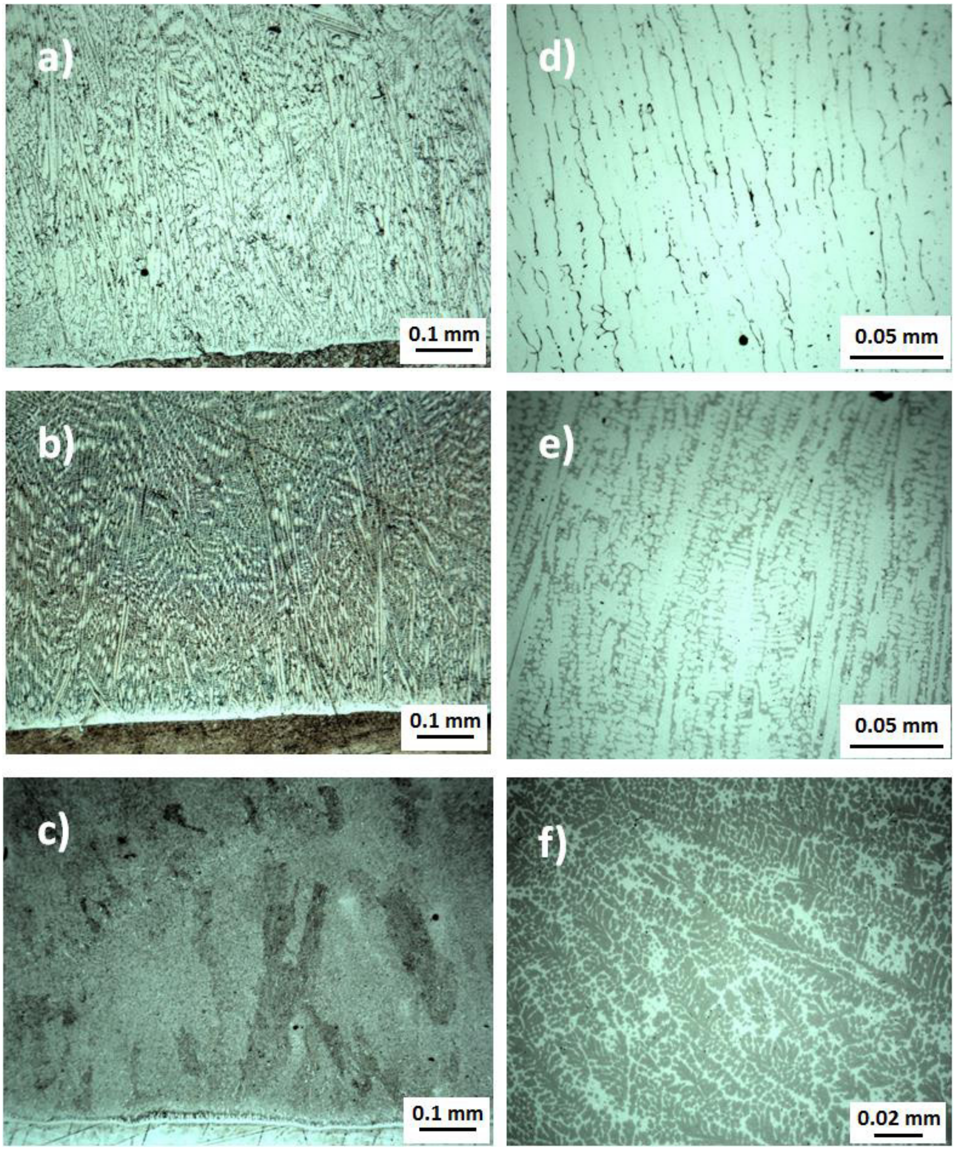

Fig. 1. Optical micrograph of coating-substrate interface and closer view of coating microstrure for (a),(d) NiCrAlY, (b),(e) CoNiCrAlY,and (c),(f) NiCrCrAlY.

3. Results

3.1. Microstructure

Laser parameters employed resulted in dense layers metallurgically bonded with the substrate with approximately 1 mm thickness. Figure 1 shows optical micrographs of the revealed microstructure of each of the alloys employed. In all cases a planar solidification front is clearly visible demonstrating the metallurgical bond with the substrate. The microstructure follows a dendritic pattern in the three cases. Dendrites are columnar in the NiCrAlY and CoNiCrAlY alloys as seen in Figure 1 d) and e).

Residual round spherical pores are visible in all samples which were addressed to shielding gas trapping during the alloy solidification. A detailed inspection of the layers revealed another type or source of porosity: interdendritic defects can be seen across the alloy microstructure [M.J.Tobar et al.(2013)]. This was understood as shrinkage interdendritic microporosity. This phenomena, well known in aluminum casting alloys, is due to a shortage in liquid eutectic during dendritic solidification. The dendrite being the first to solidify causes a metal shrinkage whose empty volume has to be compensate by the flow of interdendritic liquid, the last to solidify. Depending on the solidification rate and range (mushy zone) of the alloy the liquid flow may not cope with the cavities, thus leaving pores along the interdendritic spaces.

Samples processed under SEM-EDS inspection for elemental composition gave results shown in Table 2. All coatings show no Fe dilution, with measured composition equivalent to nominal. Individual analysis of the dendritic and interdendritic zones in the NiCrAlY alloy shows a slightly increased amount of Al in the interdendritic. This is compatible with an hypoeutectic structure made of solid solution Ni dendrites as primary phase, and Al intermetallics as secondary phase in the interdendritic. According to designed composition in this alloy, with a reduced Al content, the intermetallic should correspond to the γ' Ni3Al intermetallic phase[C. Bezencon et al.(2003), K. Partes et al.(2008), R. Vila and S. Costa Santos(2011)].

Dendrites are also of columnar type in the CoNiCrAlY case. EDS analysis also suggest an hypoeutectic solidification with Ni solid solution dendrites and intemetallic Al phases in the interdendritic. In this case, due to the increased Al amount, this secondary phases should be the monoalumnide NiAl, corresponding to γ/β type MCrAlY alloy.

Unlike the previous cases, the NiCoCrAlY alloy shows equiaxed dendrites in its structure. Composition analysis suggests an hypereutectic solidification with NiAl primary phase dendrites and Ni solid solution in the interdendritic region.

Table 2. Elemental analysis by SEM-EDS.

(wt%)	Ni	Co	Cr	Al
		NiCrAlY		
Gobal	68		26	6
Dendrite	69		26	5
Interdendrite	68		25	7
		CoNiCrAlY		
Gobal	32	38	23	7
Dendrite	30	40	23	7
Interdendrite	36	34	18	12
		NiCoCrAlY		
Gobal	45	23	18	14
Dendrite	49	21	13	17
Interdendrite	43	26	22	9

Deposited coatings were examined by XRD to assess the metallic phases present and indicated by EDS analysis. As shown in Figure 2, results confirmed the above described phase composition. Due to limited dilution with substrate, no evidence of secondary precipitates other than alloy specific ones was found.

3.2. Oxidation kinetics

No cracks or spallation on the deposited coatings was observed after oxidation at 1100ºC for 200h. Figure 3a represents the weight gain as function of time for the three coating types tested. NiCoCrAlY shows a higher weight gain than that of NiCrAlY and CoNiCrAlY. This may be undestood as a consequence of the double content of Al in

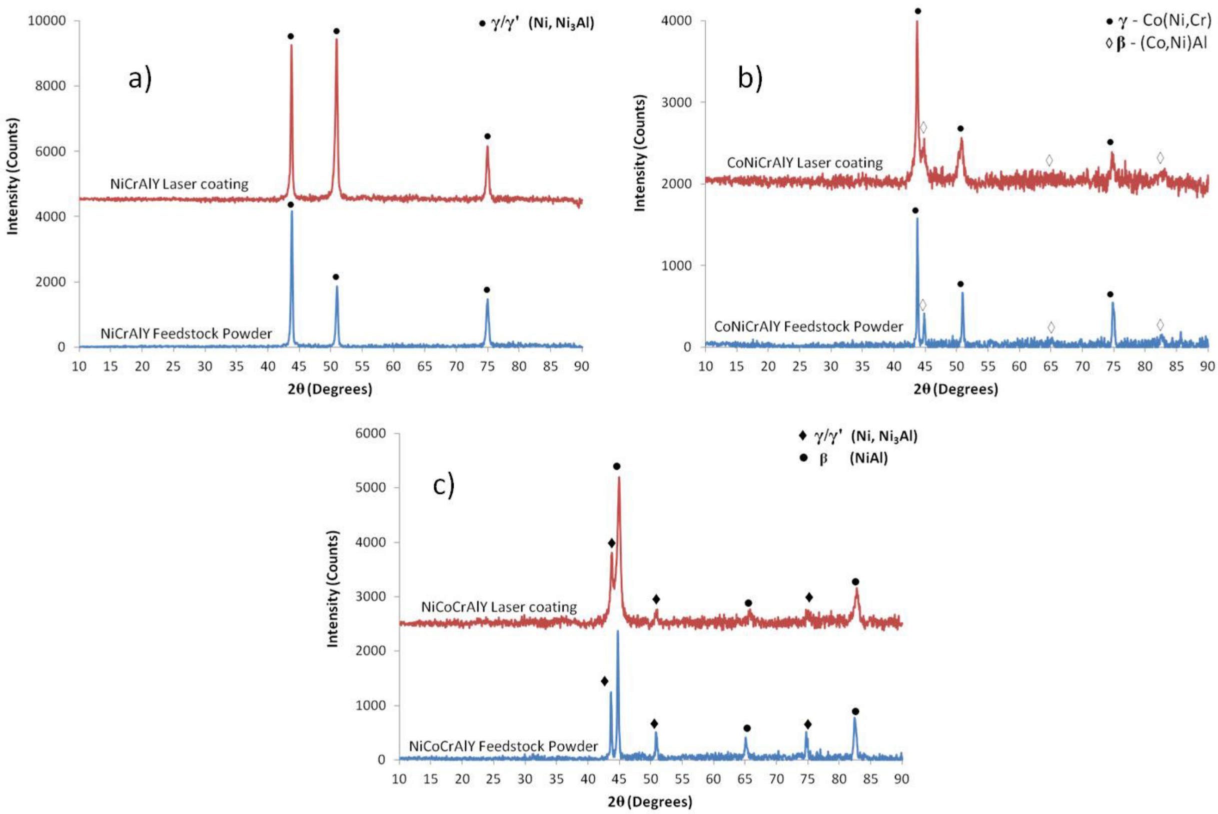

Fig. 2. XRD patterns of deposited MCrAlY alloys and comparison with respective feedstock powders (a) NiCrAlY (b) CoNiCrAlY an (c) NiCoCrAlY.

the first alloy (14%) as with respecto to the other two (6-8%), therefore increasing the rate of Al_3O_2 oxide scale formation. Oxidation test results corresponding to uncoated A304 stainless steel samples performed in the same conditions are shown in Fig 3b for comparison. Claddin of

The surface morphology of the oxidized samples was examined by SEM-EDS and results are summarized in Figure 4. The surface of the NiCoCrAlY sample (Fig. 4a) after 200h at 1100ºC shows a rather dense and homogeneous appearance with some inclusions visible as brighter objects. EDS analysis indicates a continuous Al_2O_3 oxide layer with NiO, CoO, Y_2O_3 and Cr_2O_3 oxides randomly distributed over the surface. NiO, CoO and Cr_2O_3 possibly combine to form $(Co,Ni)(Al,Cr)_2O_4$ spinel [M. Ferdinando et al.(2010)]. Oxide composition (types and weight percentage) was deduced by normalized stoichiometric calculations from EDS measurements. The analysis was performed on all samples taken from air furnace at different oxidizing intervals. This allowed to obtain the time evolution of the oxide layer components, which is shown at the right of the surface micrograph. A fast increase of the Al_2O_3 ratio is observed, presumably due to the large Al content in the alloy which inhibits the growth of Ni,Co and Cr oxides. At 200h, the Al_2O_3 represents about the 95% of the oxide layer composition.

The same oxides were found on the CoNiCrAlY surface. In this case, however, the lower content in Al results in a more heterogeneous oxide surfaceas shown in Fig 4.b). A greater amount of Ni,Cr and Y oxides is observed, which are larger in size, reaching about 50% of oxide layer composition.

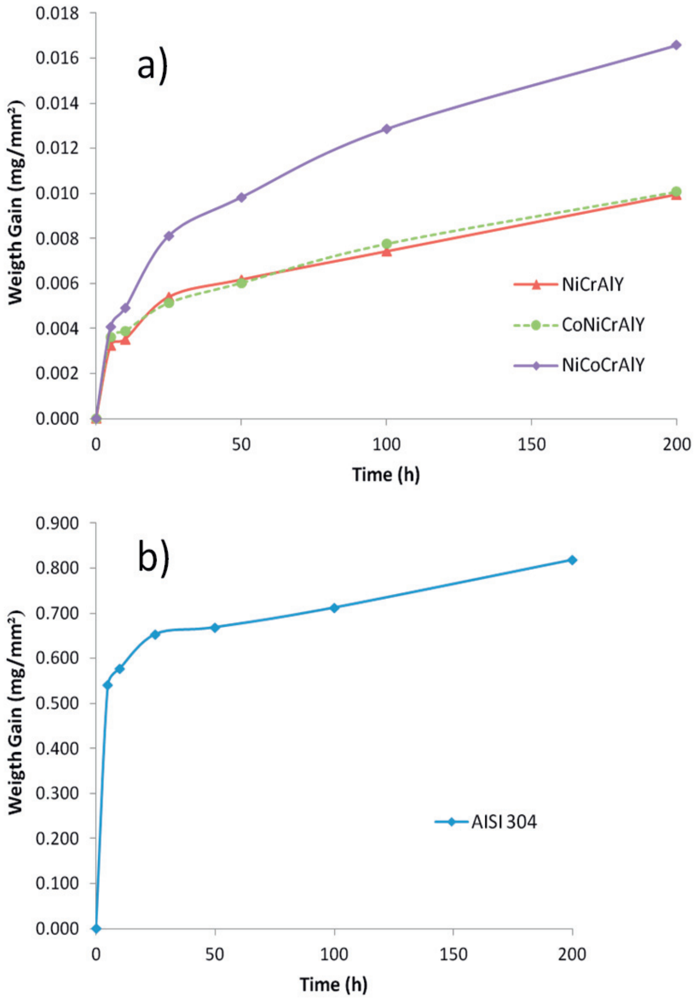

Fig. 3. Oxidation kinetics (a) three laser cladded MCrAlY coatings tested (b) Weight gain curve for AISI 304 stainless steel used as substrate. Oxidation ratio of steel is about 80 times higher than that of MCrAlY alloys as evidenced by the different scales.

4. Conclusions

Three types of commercially available MCrAlY alloys mainly differing in NiCo matrix composition and Al content were deposited by laser cladding on austenitic substrates. Dense layers with metallurgical bonding were obtained in all cases. Microstrucure composition analysis and evaluation shown patterns compatible with an

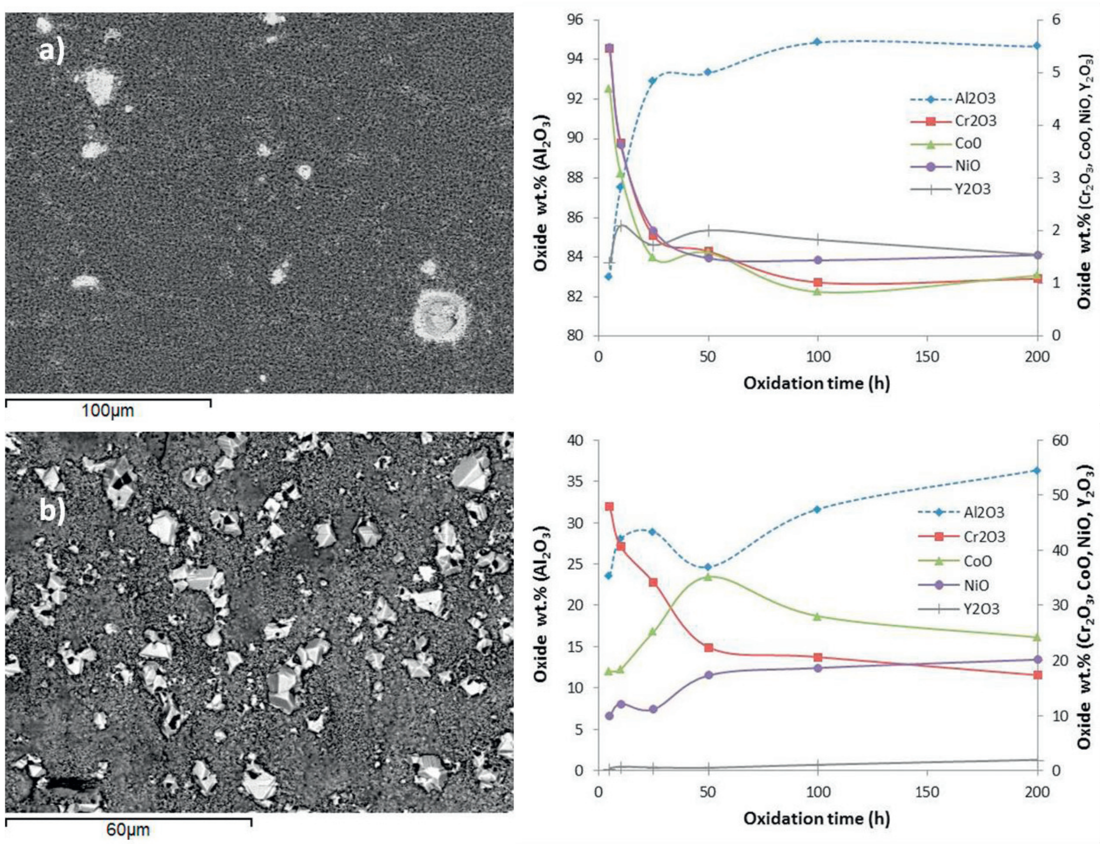

Fig. 4. (a) Surface morphology BSE Image of oxidized NiCoCrAlY after 200h at 1100ºC. On the right, time evolution of stoichiometric oxide composition (b) Equivalent figures for CoNiCrAlY alloy.

hypoeutectic γ/γ´structure the NiCrAlY alloy, γ/β hypoeutectic for the CoNiCrAlY and γ/β hypereutectic in the NiCoCrAlY

Under high temperature oxidation tests performed in air furnace at 1100ºC up to 200h, weight gain of NiCoCrAlY was significantly larger than those of Ni and CoNi alloy counterparts, and 50 times less than the weight gain of the substrate. This can be understood as a consequence of its larger Al content. Surface morphology was inspected by SEM-EDS, revealing a dense, stable and continuous Al_2O_3 oxide layer with Ni, Co, Cr and Y oxide inclusions. The percentage of these oxides is as low as 5% in the NiCoCrAlY coating, reaching about a 50% in the CoNiCrAlY one.

Results indicate the use of laser cladding technique as an alternative to plasma spray or HVOF methods, yielding fully dense coatings with metallurgical bonds to substrate. Other characteristics of the coatings as corrosion and mechanical resistance are currently under study..

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