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Long-term Annealing of NiCrAlY LENS Coating on 316L Steel

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Abstract

This article presents the results of a research on the behavior of NiCrAlY coating obtained by the LENS method on austenitic stainless steel type 316L under long-term annealing conditions at 1000°C for 25, 100 and 250 hours. The morphology of the NiCrAlY layer as a function of annealing time and temperature was characterized. The chemical composition and distribution of alloying elements were evaluated using scanning microscopy and micro-area chemical composition analysis. It was revealed that NiCrAlY coatings deposited by LENS method are characterized by good metallurgical quality. The long-term annealing of the NiCrAlY coating led to microstructural changes in the form of the disappearance of the original dendritic structure and the formation of a solid solution of nickel with chromium and a small amount of aluminum, as well as chromium α-Cr precipitates and Ni-Y-type phases. The effect of increasing iron concentration in the coating due to diffusion-to-core processes was also found

Keywords: NiCrAlY, LENS, Additive manufacturing, Long-term annealing, Microstructural stability

1. Introduction

MCrAlY oxidation resistant coatings are manufactured by a many standard technologies such as different variants of thermal spraying processes such as: atmospheric plasma spraying, vacuum plasma spraying, low-pressure plasma spraying, high-velocity oxy-fuel or high-velocity air-fuel. As a results the good quality coatings with high adhesion are deposited, when the process parameters are correctly optimized. The most important artefacts negatively influenced on the quality of coatings are mainly pores and cracks. Even a low porosity level may strongly be influenced on the oxidation behaviour of MCrAlY type of because pores and cracks (especially in the form of continuous net) can permit the diffusion of aggressive atmosphere through the coatings zone. These phenomena strongly decrease the oxidation and corrosion resistance of whole coating system. Due to presences of pores and cracks in the coatings, laser remelting processes are usually used to improve the metallurgical of coatings [1-6].

LENS (Laser Engineered Net Shaping) is a laser-based additive manufacturing technique, which involves melting with a laser beam a stream of material particles blown by an inert gas depositing these particles onto a base material. It was developed in 1997 by Sandia Corporation, to this day a high development of this technique is observed. It belongs to the group of operations known as laser layering or laser cladding, which owes its name to the layer of metal formed by welding processes. LENS has great capabilities, which are currently most widely used in coating manufacturing processes, but it also makes it possible to regenerate existing parts by overmolding and to create completely new three-dimensional products with similar shapes to the final ones, minimizing the need for machining. Currently, these processes are possible for such material groups as steels, cast irons, titanium alloys, aluminum, nickel and some ceramics, e.g. Al_2O_3, ZrO_2. LENS is not the only term for the same process. In publications, one can find other nomenclature, but with the same meaning, i.e. DMD (Direct Metal Deposition), LAM (Laser Additive Manufacturing) and LC (Laser Cladding), which is basically just laser surfacing. The translation of the given name LENS by Sandia Corporation in Polish language itself varies. LENS is referred to as "laser fabrication of final shape and dimension," "laser-controlled mesh shaping," or more simply "LENS laser additive technique" (not to be confused with the different but similar SLM technique) [7].

Devices for obtaining coatings by the LENS method are equipped with a focusing lens head, nozzles dispensing powder material, a shielding gas supply, a movable worktable, and a laser. Powder delivery is provided by a carrier gas and a pneumatic vibration system [8]. Material particles enter through nozzles focused on a single point, meanwhile the laser beam passes through a head with a lens that focuses the beam in the same area. Particles blown through an atmosphere of inert gas (usually argon) encounter the high-power laser beam and are over-melted while still in flight on the base material. Full melting occurs on the surface of this material, forming a molten metal pool, until finally, after cooling, a layer of surfacing is formed. For subsequent layers, the whole process is repeated, and the head is positioned at the starting point with the help of a moving table. In the case of manufacturing a three-dimensional component, these operations occur until a fully formed three-dimensional solid is obtained [7].

The resulting coating by laser deposition, whose thickness is estimated at 100÷2000 μm, is metallurgically bonded to the base material. The coating thus bonded consists of three zones: the surfacing stitch (outer zone), the fusion zone and the heat affected zone (inner zones). The structure of the coating is significantly influenced by thermal phenomena occurring during the coating manufacturing process using the LENS method. Characteristic for this method is a high temperature gradient formed as a result of rapid heat transfer through the produced layer of the surfacing, the cooling rate of which is determined by the thermal properties of the substrate. Such phenomena introduce thermal stresses into the coating, which can cause cracks and can induce structural changes, i.e. initiate directional grain growth. In addition, the high temperatures resulting from laser exposure also make it difficult to produce a coating with low roughness [7]. However, among the main advantages in favor of this technology is the possibility of obtaining a dense and continuous coating on parts with complex geometries, as well as providing better protection under high-temperature oxidation conditions, enabled by a low proportion of pores and very good adhesion of the coating to the substrate [8].

Presented article is the continuation of research described in [8], where the structural analysis of NiCrAlY coatings in as-clad state were described in the details.

2. Procedure of experiment

Conventional austenitic stainless steel 316L was used as the substrate material for coating depositions in the form of rectangular sheets, with a size 40 × 40 mm and a thickness of 2 mm. Commercial Ni-22Cr-10Al-1Y powder (Amdry 962) was used as a coating material in the direct laser deposition method. The coating was manufactured via a laser cladding set-up using a LENS MR-7 (OPTOMEC, Albuquerque, NM, USA) system. Microstructural observations were carried out using a Nikon Eclipse MA2000 light microscope. For more detailed analysis of microstructural artefacts, the scanning electron microscopy (SEM) Hitachi S-3400N was also used. The SEM system was equipped with an EDS (energy-dispersive X-ray spectrometer by Thermo Noran System Six). The phases composition analysis was analyzed by XRD method (X-ray diffraction by X'Pert3 Powder diffraction analysis system).

The analyzed materials in the form of 316L steel specimens with NiCrAlY coating were subjected to long-term annealing at 1000°C. Structural evaluation of the coatings was carried out after 25, 100 and 250 hours of testing.

3. Results and discussion

Figure 1 shows the microstructure of the NiCrAlY coating in the as-clad state, along with the visible zone of the surfacing and the zone of fusion into the base material. In the surfacing zone, the boundaries of the weld stitches can be observed. The surfacing zone is characterized by a dendritic structure typical for laser process deposition of coatings. The structure of the fused zone maintains continuity with the base material, which indicates the very good quality of the bond between the coating and the substrate. In addition, the presence of columnar structures with a growth direction perpendicular to the substrate indicates an epitaxial growth process in the initial stages of coating crystallization. No cracks or pores were found in the structure of the surfaced layer.

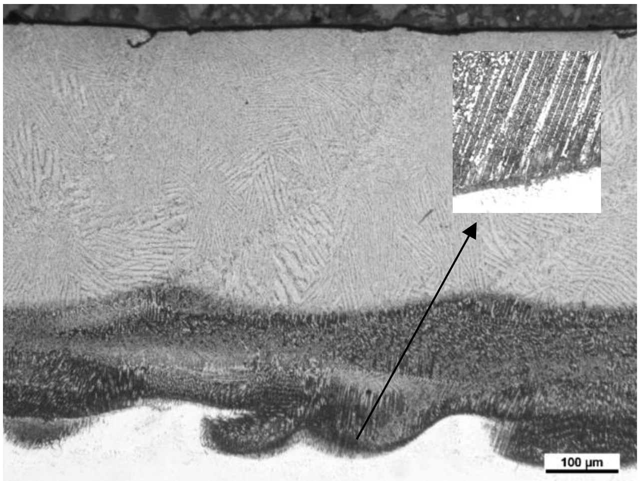
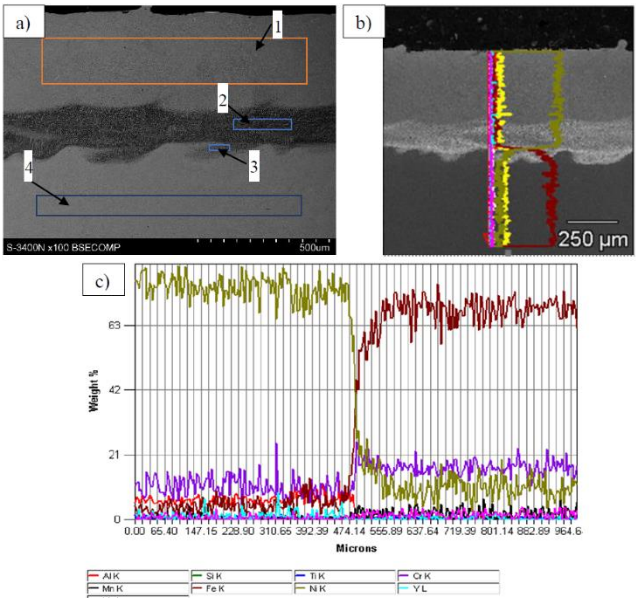


Fig. 1. Microstructure of NiCrAlY coating is as-clad state on 316L alloy

Linear and point analysis of the chemical composition in the area of the NiCrAlY coating and the fusion zone is shown in Figure 2. It indicates a clear separation boundary between the fusion zone and the substrate material. Within the outer zone of the surfacing, the powder components used for deposition of the coating and iron from the substrate material were found (at a level of 3 to 6 wt%). This indicates diffusion processes from the core. At the same time, no increased nickel and chromium content was found in the substrate material, suggesting the absence of to core-diffusion phenomena.

Research results of the NiCrAlY coating after annealing tests at 1000°C with a holding time of 25 hours are shown in Figures 3 and 4. The effect of annealing is the processes occurring in the structure of the coating related to changes in the dendritic microstructure including the formation of different types of precipitates.



	Ni	Fe	Cr	Al	Y	Mn	Mo	Si
1	77.9±0.9	3.8±0.3	11.3±0.2	6.3±0.1	0.8±0.1	-	-	-
2	76.4±1.0	6.4±0.3	8.0±0.2	7.9±0.1	1.3±0.2	-	-	-
3	54.5±0.9	23.6±0.5	13.4±0.2	6.4±0.1	0.8±0.1	0.7±0.2	0.7±0.1	-
4	10.1±0.6	68.7±0.7	17.3±0.2	-	-	1.8±0.2	1.8±0.1	0.3±0.1

Fig. 2. The chemical composition of as-clad NiCrAlY coating on 316L steel (in wt %)

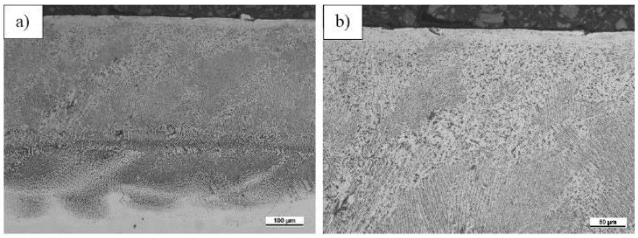
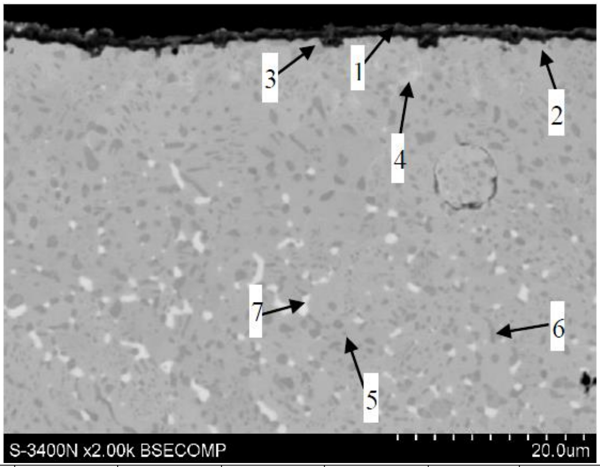


Fig. 3. Microstructure of NiCrAlY coating on 316L alloy after annealing at 1000°C/25h

Detailed results related to the evaluation of the chemical composition in the micro-areas are shown in Figure 4. The disappearance of the dendritic structure and the effect of the formation of segregations of different types, occurring, among other things, in the form of bands, are visible. A point analysis of the chemical composition indicates a strong segregation effect associated with the formation of three different structural areas: (1) a matrix marked by points 2 and 5, in which the chromium and aluminium content is close to the composition of the average coating in the as-clad state; (2) darker precipitates depleted in aluminium and nickel, with very high chromium content (areas 3 and 6); (3) light precipitates with high yttrium content and minimal chromium (areas 4 and 7). This indicates the presence of the following phases: (1) nickel solid solution, (2) α-Cr precipitates and (3) Ni-Y type precipitates, most probably Ni_5Y type (analogous to the as-clad condition).



	Ni	Cr	Al	Y	Fe	Ca
1	19.0±1.6	21.9±0.8	47.6±0.4	10.7±0.6	-	0.8±0.1
2	80.3±0.8	12.0±0.1	5.6±0.1	1.3±0.1	0.8±0.1	-
3	18.8±0.8	79.0±0.5	1.2±0.1	-	-	-
4	61.6±0.9	9.1±0.2	4.3±0.1	24.3±0.3	0.8±0.1	-
5	77.2±0.8	15.4±0.2	5.7±0.1	-	1.6±0.1	-
6	8.8±0.8	89.4±0.7	0.5±0.0	-	1.3±0.2	-
7	74.8±0.8	4.8±0.1	2.8±0.1	16.8±0.2	0.9±0.1	-

Fig. 4. Microstructure of NiCrAlY coating on 316L alloy after annealing at 1000°C/25h – details of chemical compositions in micro-areas

An important observation is the relatively homogeneous distribution of iron in the areas to which the phases were assigned. In all cases, the iron content is about 1 wt %. The analysis in point 1 concerns the oxidized zone and is not the subject of this article. Directly below the oxidized zone area is located an area dominated by nickel solid solution and α-Cr precipitates. Yttrium-rich separations were not found in this zone. They are located in an area about 15 µm below the top surface of the sample. Tests of the NiCrAlY coating after annealing tests at 1000°C with a holding time of 100 hours are shown in Figs 5 and 6.

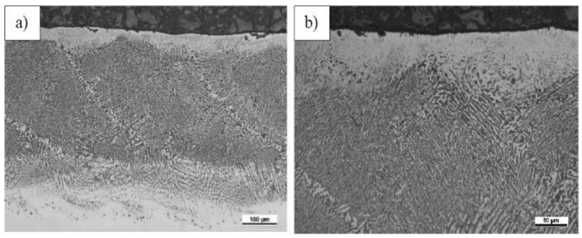
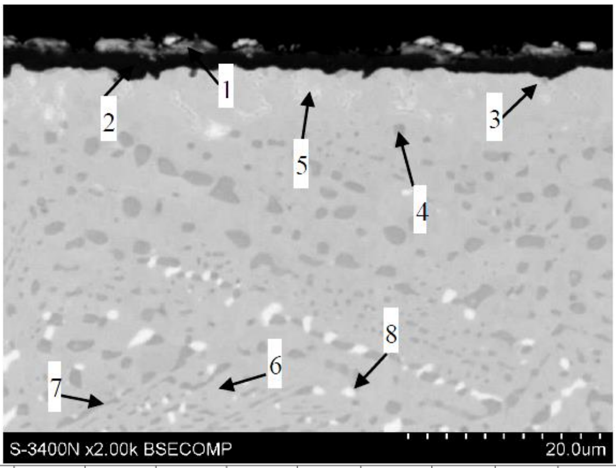


Fig. 5. Microstructure of NiCrAlY coating on 316L alloy after annealing at 1000°C/100h

Evaluation of the structure at the level of light microscopy research shows only the presence of banded precipitates. In addition, an area of different morphology directly located below the oxide layer is visible, indicating a dealumination effect due to the formation of Al_2O_3-rich oxide scale with a small amount of Cr_2O_3 z. It was also found that the area of the fusion zone undergoes diffusion "atrophy."



	Ni	Cr	Al	Y	Fe	Mo	Mn	Cu	Na
1	10.8±0.7	1.8±0.3	12.9±0.1	21.7±0.4	1.6±0.2	45.2±0.6	1.2±0.2	3.1±0.5	1.6±0.1
2	-	5.9±0.6	94.1±0.7	-	-	-	-	-	-
3	66.6±0.7	26.4±0.3	2.6±0.1	1.5±0.1	2.9±0.2	-	-	-	-
4	11.7±0.8	87.9±0.7	0.4±0.1	-	-	-	-	-	-
5	53.2±0.8	22.5±0.2	2.0±0.1	19.7±0.2	2.5±0.1	-	-	-	-
6	82.1±0.8	10.0±0.1	6.1±0.1	-	1.7±0.1	-	-	-	-
7	14.7±0.8	83.0±0.7	0.8±0.0	-	1.5±0.2	-	-	-	-
8	75.0±0.8	3.8±0.1	3.0±0.1	17.4±0.2	0.9±0.1	-	-	-	`-

Fig. 6. Microstructure of NiCrAlY coating on 316L alloy after annealing at 1000°C/100h – details of chemical compositions in micro-areas

From a microstructural point of view, analogous types of precipitates were identified as described for the samples after 25 hours of annealing. The main difference resulting from the longer annealing time is the smaller number of precipitates with a much larger dimension, which is the result of their coalescence and diffusive growth. Compared to tests of the sample after 25 hours, it was found that the iron content increased, to locally about 3 wt %. Iron was also found in oxidation products on the outer surface. Tests of the NiCrAlY coating after annealing tests at 1000°C with an endurance time of 100 hours are shown in Figures 7 and 8. In the case analyzed, the subsurface zone, which is the result of depletion in aluminium, was clearly characterized (see point 4 in Fig. 8).

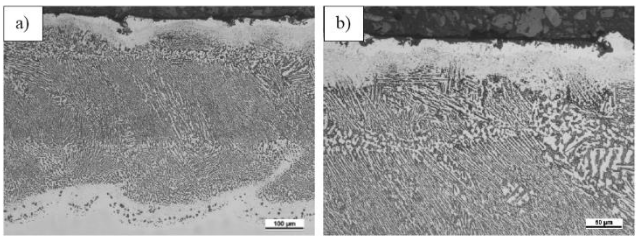
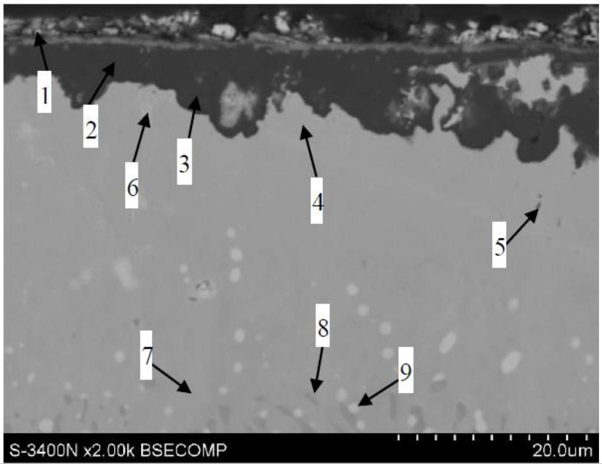


Fig. 7. Microstructure of NiCrAlY coating on 316L alloy after annealing at 1000°C/100h

The depleted area under the oxide layer and a section of the zone with precipitates are shown in Figure 8. Analogously as before, Ni-Y precipitates can be identified in this case, but with increased chromium content (points 6 and 9), and chromium precipitates with increased nickel (point 8). The chromium content of the nickel solid solution did not change significantly.



	Ni	Cr	Al.	Y	Fe	Mo	Ca	Cl
1	11.5±1.0	5.0±0.4	9.2±0.1	43.6±0.6	1.9±0.3	28.1±0.7	0.8±0.1	-
2	11.3±1.2	6.8±0.5	33.0±0.3	44.3±0.7	2.4±0.4	2.3±0.4	-	-
3	-	-	100.0±0.8	-	-	-	-	-
4	65.4±0.8	29.7±0.2	1.6±0.1	-	3.3±0.1	-	-	-
5	62.9±0.7	27.0±0.2	7.1±0.1	-	2.6±0.2	-	-	0.4±0.1
6	44.1±0.9	21.1±0.4	1.1±0.1	31.5±0.3	2.2±0.4	-	-	-
7	68.0±0.7	25.2±0.3	2.8±0.1	-	4.0±0.3	-	-	-
8	27.8±0.9	68.5±0.6	1.4±0.1	-	2.2±0.2	-	-	-
9	70.7±0.7	10.7±0.1	3.6±0.1	13.7±0.2	1.3±0.1	-	-	-

Fig. 8. Microstructure of NiCrAlY coating on 316L alloy after annealing at 1000°C/250h – details of chemical compositions in micro-areas

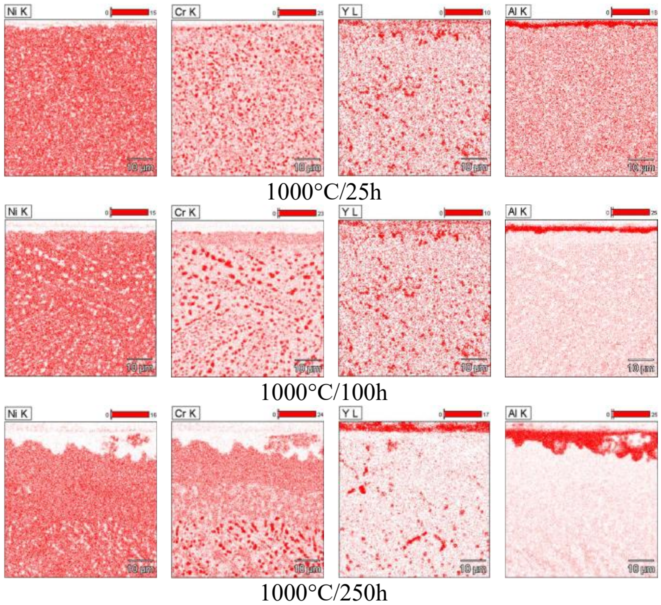


Fig. 9. Microstructure of NiCrAlY coating on 316L alloy after annealing at 1000°C/10-250h – alloying elements distributions

Points 6 and 4 corresponding to the nickel solid solution indicate an obvious aluminum loss effect due to the formation of an

Al_2O_3-type oxide layer. At the same time, there was no chromium depletion effect. Iron content increased locally to 4 wt %.

Figure 9 shows the surface distributions of alloying elements in the NiCrAlY coating. Clearly visible are chromium-rich (α-Cr), and Ni-Y type separations, the matrix being formed by a solid solution of nickel with chromium and a small amount of aluminum. The effects of the depletion of the suboxide zone in aluminum are also evident, as well as the effects of the growth of the precipitates depending on the annealing time.

One of the most important aspects related to the main subject if this article is iron outward diffusion form substrate material to LENS coating. Fe has been used as the addition in Ni-Cr-Al system capable of stabilizing the β-NiAl phase [9]. The long-term performance of MCrAlY coatings is directly connected to the β phase stability. However, only few studies have been focused on the effect of Fe addition as a minor element (<10 wt%) in MCrAlX during high temperature oxidation.

Presented in [10] results showed that high Fe addition in the MCrAlX coating had no significant effect on oxidation, however, a great impact on coating-substrate interdiffusion and coating degradation was observed. Fe addition promotes the formation of a discontinuous σ phase layer at the coating/substrate interface, which retards Al diffusion in the IN792 substrate. CALPHAD calculations showed that high Fe addition in the MCrAlX coating increased the β phase fraction and stabilized the β phase by extending the $\beta+\gamma$ phase region. Besides, high Fe addition in the MCrAlX coating modifies Cr diffusion and alters local phase equilibrium at the coating/substrate interface. These two factors suppress inner-β depletion of high Fe containing coating. Grain coarsening of the coating can be observed during oxidation, it was retarded by high Fe addition.

4. Conclusions

The LENS method produced a good metallurgical quality NiCrAlY-type heat-resistant coating on 316L austenitic steel. There were no significant metallurgical defects that could negatively affect the coating's performance.

Long-term annealing of the NiCrAlY coating led to microstructural changes in the NiCrAlY layer in the form of the disappearance of the original dendritic structure and the formation of a structure containing a solution of solid nickel with chromium and a small amount of aluminum, as well as chromium precipitates and Ni-Y-type phases.

Extending the annealing time to 250 hours led to diffusion growth of the precipitates, depletion of the near-surface zone in aluminum and disappearance of the fusion zone. The phase composition of the precipitates did not change.

The effect of increasing iron concentration in the coating because of diffusion-to-core processes was found. No significant effects of the diffusion-to-core process were found.

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