Properties of low-pressure cold-sprayed coatings for repairing of casting defects

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Low-pressure cold spraying (LPCS) is a coating technique, in which a portable cold spray system, e.g., DYMET 304K system is used to prepare technical coatings. Usually, compressed air is used as the process gas. The LPCS process is an appropriate method for spraying of metallic-ceramic composite powder materials, e.g., Cu, Ni, Zn, Al with additions of Al_2O_3 particles in the powder blends. The main functions of the hard ceramic particles are cleaning the nozzle, activating the sprayed surface and peening the coating structure. This method has advantages for example in the field of repairing and restoration applications. For that, repairing casting defects and voids is one interesting application of the process. For these purposes, zinc-based composite materials are recommended for restoration and repairing of corrosion and mechanical damages. In this study, $Zn+Al+Al_2O_3$, $Zn+Cu+Al_2O_3$ and $Zn+Ni+Al_2O_3$ composite materials were investigated. Zinc and aluminum give corrosion resistance by cathodic protection whereas copper and nickel will provide also more mechanical resistance. Coating properties, such as microstructures, open-cell potential behavior and mechanical properties (hardness and adhesion strength) were investigated. The coatings have relatively dense coating structures and for corrosion resistance, zinc gives a cathodic protection for other materials in these composite coatings. Furthermore, mechanical properties are sufficient due to the relatively high hardness and adhesion to the Fe52 steel base material. These coatings have high potential in their use as repair materials for macroscopic casting defects.

1 Introduction

Cold spraying as a thermal spray process is based on the use of low process temperatures and high particle velocities. Particles are accelerated to high velocity by drag forces [1]. Powder particles impact to the sprayed surface with high kinetic energy and deform on the impacts in a solid state. This is high advantage to the formation of coating structure with low porosity level and oxygen content (no melting of powder particles). [2,3] During the impacts, powder particles deform plastically and adhere to the sprayed surface, building-up the coating. Due to the deformation mechanism, coating materials should be or contain ductile, deformable material, e.g., metal powders. In addition to the metals and metal alloys, composite powder mixtures are shown their suitability to use in cold spraying [1,2,4-8].

Low-pressure cold spray (LPCS) process uses low pressure (pressure max. 9 bar (DYMET)) of process gas which is usually compressed air. Furthermore, powder is fed radially. [2,3,5] Typically, the LPCS process is a method for spraying soft metallic powder with an addition of hard ceramic particles as powder mixtures, forming a composite coating structures for various applications. One advantage of the LPCS system is that equipment is portable which in turn enables using a LPCS system for *on-site* coating. LPCS method can be used in the field of repairing and restoration and flexible applications due to the portability [1,5,7,9], e.g., in automotive and aerospace industries. Furthermore, LPCS process is a relevant spray process for soft metals (Al, Zn and Sn) which in turn can be used in restoration of engine blocks, castings, molds and dies. Portability is also an advantage in localized corrosion protection (on weldments), decorative coating production and metal joining. [5,7,8]

This study focuses on a structural characterization of LPCS composite coatings which have high possibilities to be used in repairing applications, e.g., for casting defects. Coating materials are typically $Zn+Al+Al_2O_3$, $Zn+Cu+Al_2O_3$ and $Zn+Ni+Al_2O_3$. Additionally, mechanical properties of the coatings and casting defects repaired using these composite materials are evaluated, reflecting their high potential to use as technical coatings.

2 Experimental

Coatings were manufactured at Tampere University of Technology, Department of Materials Science using DYMET 403K low-pressure cold spray equipment (OCPS, Obninsk, Russia). DYMET 403K was installed in a x-y manipulator (traverse speed 6 m/min) for spraying the coating samples. In addition to these experiments, DYMET 403K was installed in an industrial robot (5 m/min) for spraying the samples for bond strength measurements. A round nozzle was used. Fe52 steel substrates were grit-blasted (36 Mesh, Al_2O_3 grits) prior to spraying. Spraying parameters were as following: compressed air was used as a process gas, pressure 6 bar, flow rate of air 260 l/min, powder feed 5 (from level of 1-8), beam distance 1 mm, spray distance 10 mm, preheating temperature: 440°C ($Al+Zn+Al_2O_3$) and 540°C ($Cu+Zn+Al_2O_3$ and $Ni+Zn+Al_2O_3$) and amount of layers: 7 ($Al+Zn+Al_2O_3$), 4 ($Cu+Zn+Al_2O_3$) and 6 ($Ni+Zn+Al_2O_3$) layers. Repaired casting defects were sprayed manually (hand-held spraying). The preheating temperature of compressed air was 650°C and the rest of spraying parameters were like the same as above.

Three different composite powders ($Zn+Al+Al_2O_3$, $Zn+Cu+Al_2O_3$ and $Zn+Ni+Al_2O_3$) were tested in order to evaluate their potential for reparation and restoration of defects in various components. There are many repair possibilities for composite coating materials, e.g., fixing holes, repairing mechanical damages, and filling cracks [10].

However, generally at least one component in the composite powder mixtures should be plastically deformable (ductile, e.g., metallic material), making it possible to build-up a coating structure [2]. In this study, powders used were 50%(Al+Al_2O_3(K-10-01))+50%(Zn+Al_2O_3(K-00-11)), Zn+Al+Al_2O_3(K-20-11), Cu+Zn+ Al_2O_3(K-01-11), Ni+Zn+Al_2O_3(K-714) supplied by TWIN Trading Company (Moscow, Russia). Morphologies of the powders are as following: Al and Zn particles are spherical, Cu and Ni particles are dendritic and Al_2O_3 particles are blocky in their shapes, Fig. 1.

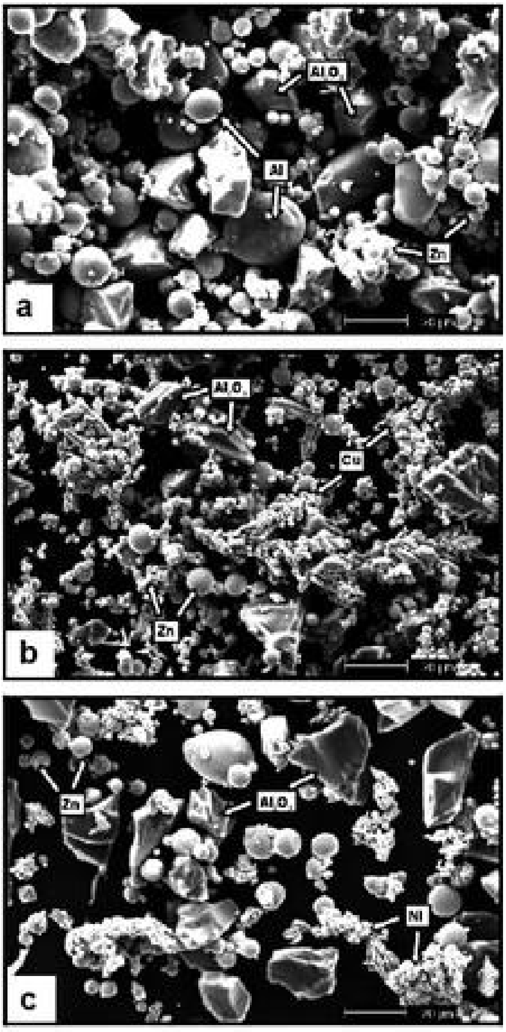

Fig. 1. Morphologies of powders a) Zn+Al+Al_2O_3, b) Zn+Cu+Al_2O_3 and c) Zn+Ni+Al_2O_3. SEM (SE) images.

Powder morphologies and coating structures were characterized using a Philips XL30 scanning electron microscope (SEM) whereas casting defect repairs were analyzed using a Zeiss ULTRAplus field-emission scanning electron microscope (FESEM). Compositions were calculated from SEM (BSE) images as an average of five measurements by using image analysis (Image Tool). The electrochemical cell used in the open-cell potential measurements consisted of a tube, of diameter 20 mm and volume 12 ml, glued on the surface of the coating specimen. A 3.5 wt.% NaCl solution was put in to the tubes for nine-day measurements. Open-cell potential measurements were done with a Fluke 79 III true RMS multimeter. A silver/silver chloride (Ag/AgCl) electrode was used as a reference electrode.

Vickers hardness ($HV_{0.3}$) was measured as an average of ten measurements with a Matsuzawa MMT-X7 hardness tester. Bond strength values were determined according to the standard EN582 using a tensile pull test (Instron 1185, mechanical testing machine). Three measurements were carried out to calculate the average values of bond strengths.

3 Results and discussions

LPCS Zn+Al+Al_2O_3, Zn+Cu+ Al_2O_3 and Zn+Ni+Al_2O_3 coatings on Fe52 steel plates and in the repaired casting defects were analyzed in order to get a general view of coating properties and in addition to that, structures of the coatings in the specific components. Microstructures, compositions, corrosion behavior and mechanical properties were performed.

3.1 Microstructure of LPCS coatings

LPCS Zn+Al+Al_2O_3, Zn+Cu+Al_2O_3 and Zn+Ni+Al_2O_3 coatings have relatively dense internal structures, Fig. 2. Coating thicknesses of LPCS Zn+Al+Al_2O_3, Zn+Cu+Al_2O_3 and Zn+Ni+Al_2O_3 coatings were 330 µm, 350 µm and 300 µm, respectively. Porosity is negligible and no pores are detected inside the structures. This indicates a high level of plastic deformation of the particles and thus, highly deformed and dense coating structures. In addition, Al_2O_3 particles arisen from initial powder compositions (Fig. 1) are also detected inside the coating structures. These hard particles have three main functions: they i) keep the nozzle clean, ii) activate the sprayed surface and iii) hammer (by shot peening) the metallic structure of the coating [4]. Generally speaking, these functions assist the formation of high quality coatings manufactured from composite powder feedstock using the cold spray process.

The compositions of the coatings are analyzed by using image analysis, Table 1. It should be noticed that Zn+Al+Al_2O_3 coating is prepared from the powder mixture of 50(Zn+Al_2O_3)+50(Al+Al_2O_3), explaining the higher amount of Al_2O_3 particles inside the coating structure compared with Zn+Cu+Al_2O_3 and Zn+Ni+Al_2O_3 coatings. Common for all these coatings is that amount of Zn is ~25% and other metallic material (Al, Cu or Ni) is ~65%. Additionally, particles are rather equally distributed in all coating structures (Fig. 2).

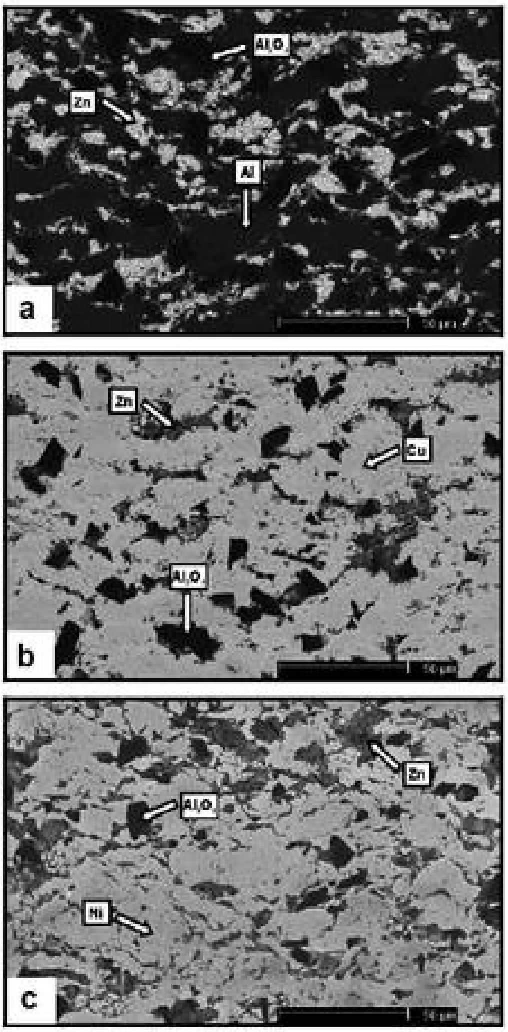

Fig. 2. Microstructures of LPCS a) Zn+Al+Al_2O_3, b) Zn+Cu+ Al_2O_3 and c) Zn+Ni+ Al_2O_3 coatings. SEM (BSE) images.

Table 1. Compositions (%±Std.dev.) of LPCS coatings measured by using image analysis.

Coating	Zn	Al	Al_2O_3
Zn+Al+Al_2O_3	27%±2.2	59%±3.5	14%±2.7
Coating	**Zn**	**Cu**	**Al_2O_3**
Zn+Cu+Al_2O_3	20%±0.9	73%±1.3	7%±1.0
Coating	**Zn**	**Ni**	**Al_2O_3**
Zn+Ni+Al_2O_3	26%±1.6	66%±1.5	8%±1.5

As is known, all these powder materials are very suitable for cold spraying [2,3] and therefore, they also have high potential to be used as composite materials. This makes it possible to connect desired properties of both materials and therefore, improve the properties of composite coating itself. Generally speaking, zinc and aluminum give corrosion resistance (cathodic protection) whereas copper and nickel provide more mechanical resistance.

3.2 Denseness of LPCS coatings

Coatings gave the cathodic protection over Fe52 substrate material due to the sacrificial behavior of Zn in the composite coatings. This is reached in the open-cell potential behavior of the coatings compared with substrate (Fe52) and reference materials (Cu bulk, electrolytically prepared Ni and flame-sprayed Zn coatings), Fig. 3. Microstructural characterization showed relatively dense coating structures without noticeable pores (Fig. 2) and in addition to that, open-cell potential behavior proves the corrosion protection of these coating materials.

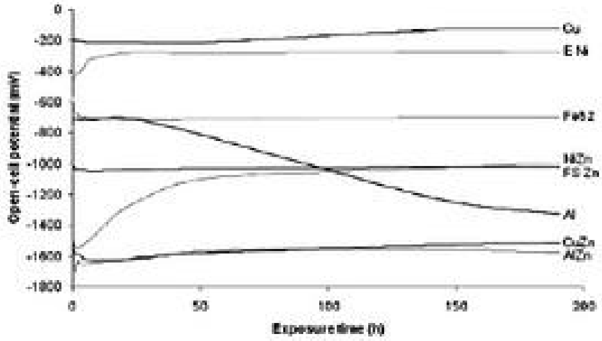

Fig. 3. Open-cell potential behavior of LPCS Zn+Al+Al_2O_3 (AlZn), Zn+Cu+Al_2O_3 (CuZn) and Zn+Ni+Al_2O_3 (NiZn) coatings, Cu, Al and Fe52 bulk materials and electrolytically prepared Ni (E Ni) and flame-sprayed Zn (FS Zn) coatings as references in 3.5% NaCl solution. Ag/AgCl reference electrode.

3.3 Mechanical properties of LPCS coatings

LPCS composite coatings have dense structures due to high level of plastic deformation. Furthermore, mechanical properties were investigated in order to get more information about coating quality. Relatively high hardness and good bond strength reflect highly deformed coating structures and good adherence between coatings and substrates, Table 2. Hardness measurements were gained from metallic part of the structures in order to evaluate the deformation of metallic particles (the function of Al_2O_3 particles is only to assist the formation and deformation of metallic part of the coatings).

Table 2. Hardnesses ($HV_{0.3}$±Std.dev.) and bond strengths (MPa±Std.dev.) of LPCS coatings.

Coating	Hardness ±Std.dev. ($HV_{0.3}$)	Bond strength ±Std.dev. (MPa)
Al+Zn+Al_2O_3	88±2.4	32.4±4.4
Cu+Zn+Al_2O_3	140±10.0	29.1±4.8
Ni+Zn+Al_2O_3	133±5.9	42.3±3.9

As materials, hardnesses of bulk materials from the softest to the hardest are as following: Zn 43 $HV_{0.3}$ [4], Al 72 $HV_{0.3}$ [11], Cu 87 $HV_{0.3}$ [11] and Ni 111 $HV_{0.3}$ [4] measured in our previous studies. LPCS

$Zn+Cu+Al_2O_3$ coating is mostly deformed indicated by high hardness values. Higher level of plastic deformation of Cu particles compared with Ni particles was also detected in our previous study [4]. However, it should be noticed that as composite mixture coating $Cu+Zn+Al_2O_3$ and $Ni+Zn+Al_2O_3$ coatings had higher hardness and bond strength than $Cu+Al_2O_3$ and $Ni+Al_2O_3$ due to the deformation, indicating higher coating quality. Soft Zn particles assist other particles to stick and structures become tighter and more work-hardened. All hardness values are higher that corresponding bulk materials, reflecting work hardening occurs during particle impacts.

3.4 Repaired casting defects

In addition to the evaluation of coating properties, three different casting defects were repaired using LPCS process and these composite materials. Reportedly, LPCS coatings are the effective method for filling voids and defects [5,7,8]. In this study, defects were first engraved, then filled manually by hand-held spraying and finally ground to a flat surface, Figs. 4, 6 and 8. Then, samples were cut and the cross-sections (small images inside Figs. 4, 6 and 8) were polished and characterized using FESEM, Figs. 5, 7 and 9. First, casting defect was repaired with LPCS $Zn+Al+Al_2O_3$ coating, Fig. 4.

Fig. 4. Repaired casting defect by using LPCS $Zn+Al+Al_2O_3$ coating. Digital camera image.

Defect (or hole) was filled with coating material and layered structure is observed in the repaired part, Fig. 5. An interface between coating and substrate is shown with white arrows and layered structure with black arrows. Inside the coating, darker areas consist of Al and Al_2O_3 particles whereas lighter parts are composed of Zn and Al_2O_3 particles. First, Zn particles are adhered to the hole edges and then, Al particles are stuck to the Zn layer, Fig. 5b. Interestingly, this so-called layer formation is build-up fairly randomly which in turn, might be caused by a different impact angle of the impacted particles in the different part of the coating (defect interface vs. middle point of the coating). In addition, Zn particles might be in the softer state due to the thermal softening while the highest preheating temperature is used and thus, first adhere to the substrate surface.

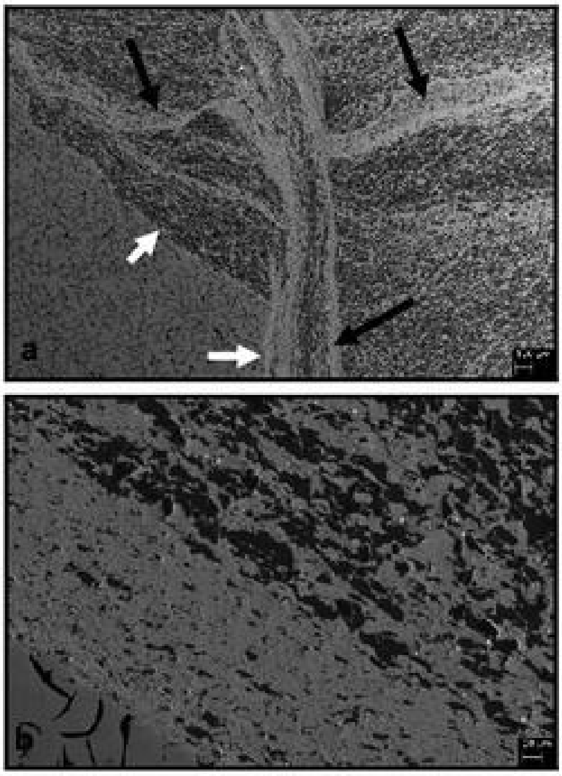

Fig. 5. LPCS $Zn+Al+Al_2O_3$ coating. Cross-section of repaired part a) general (black arrows shows layered structure and white arrows coating-substrate interface) and b) detailed view. FESEM images.

Another example of repaired casting defect is filled with LPCS $Zn+Cu+Al_2O_3$ coating, Fig. 6. More detailed structure of the repaired casting defect also showed similar layered structures. However, the layered structure is not so obvious in this case than it was with the LPCS $Zn+Al+Al_2O_3$ coating (Fig. 5). Cu and Zn particles were more evenly distributed than Zn and Al particles. This can be explained with dendritic particle morphology (fine primary particle size, a few microns) of Cu powder particles. An interface between coating and substrate (Fig. 7a, white arrow) seems to be faultless and particles are tightly bonded to the substrate surface and to other particles (Fig. 7b). Black particles are Al_2O_3 particles arisen from an initial powder mixture.

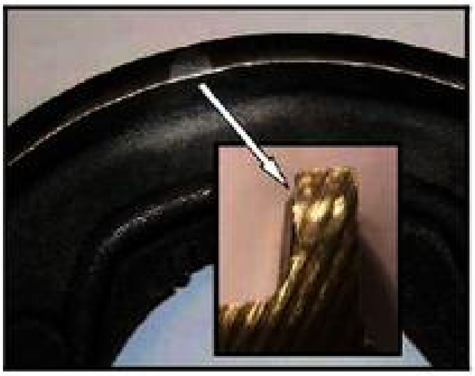

Fig. 6. Repaired casting defect by using LPCS $Zn+Cu+Al_2O_3$ coating. Digital camera image.

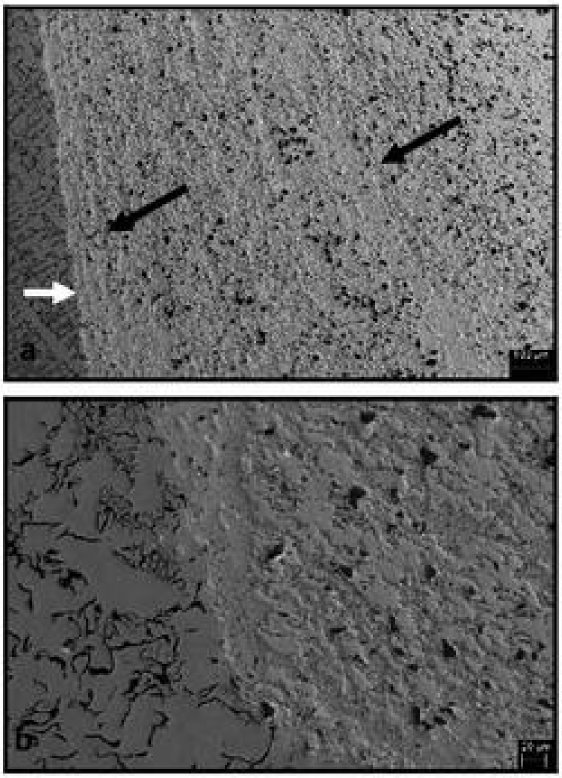

Fig. 7. LPCS Zn+Cu+Al_2O_3 coating. Cross-section of repaired part a) general (black arrows shows layered structure and white arrow coating-substrate interface) and b) detailed view. FESEM images.

Similarly, third casting defect was repaired by using LPCS Zn+Ni+Al_2O_3 coating, Fig. 8. Like in the other cases, also here defect was filled very compactly, indicating the suitability of this composite coating for repairing application. Furthermore, repaired coating consisted of layers (layered structure), Fig. 9a (black arrows). Darker part of the coating contains Zn and Al_2O_3 particles and lighter gray area Ni and Al_2O_3 particles. Good bonding between particles and the faultless interface between coating and substrate is also detected in this coating, Fig. 9b.

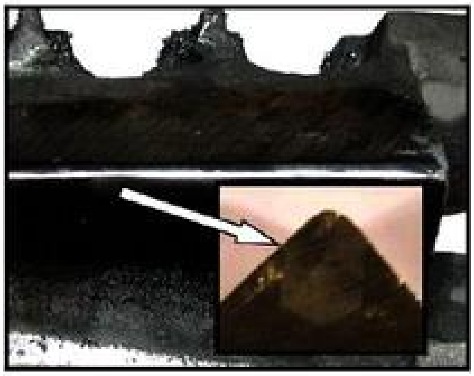

Fig. 8. Repaired casting defect by using LPCS Zn+Ni+Al_2O_3 coating. Digital camera image.

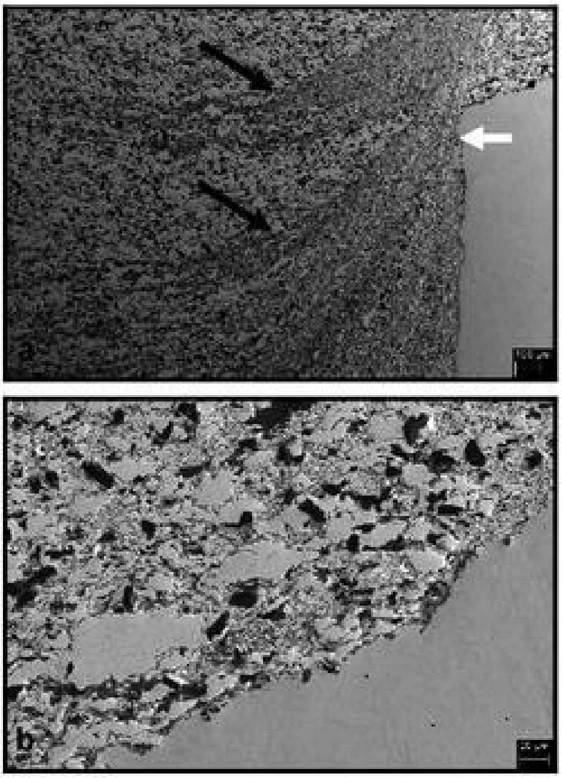

Fig. 9. LPCS Zn+Ni+Al_2O_3 coating. Cross-section of repaired part a) general (black arrows shows layered structure and white arrow coating-substrate interface) and b) detailed view. FESEM images.

All these Zn-based composite coatings with added Al, Cu or Ni particles (and Al_2O_3 particles) showed their potential to use as repairing and restoration applications using LPCS process. Typical for these repaired casting defect structures were layered structures consisted of visual layers between Zn and other metallic material. Zn particles had finer particle size than others and as material, it has the lowest melting point, which might help Zn particles to deform and stick easier than others. Obviously, the spraying angle can also have an effect on the impact behavior of the particles inside the small holes. However, all repaired holes by using LPCS composite coatings have high coating quality (dense and tight coating structure), indicating their possibility for use in technical applications.

4 Summary

This study summarizes the coating properties of LPCS Zn+Al+Al_2O_3, Zn+Cu+Al_2O_3 and Zn+Ni+Al_2O_3 coatings on Fe52 steel substrate and additionally, in the filled casting defects as repairing materials.

- LPCS Zn+Al+Al_2O_3, Zn+Cu+Al_2O_3 and Zn+Ni+Al_2O_3 coatings have dense composite coating structures according to SEM and FESEM characterization.

- Metallic (Zn, Cu and Ni) and ceramic (Al_2O_3) particles are fairly evenly distributed inside the coating structures on the flat substrates.
- The corrosion protection of the LPCS $Zn+Al+Al_2O_3$, $Zn+Cu+Al_2O_3$ and $Zn+Ni+Al_2O_3$ coatings was proven with their open-cell potential behavior. In all cases, it is based on sacrifial behavior of Zn, indicating clearly a cathodic protection mechanism.
- Particles were tightly bonded and highly deformed during impacts, which results in relatively high hardness values and good bond strength values.
- In addition to these coating properties, repaired casting defects by using these composite materials have shown high quality reparation as tight and dense layered coating structures inside the repaired defects/holes.

Summing up, LPCS $Zn+Al+Al_2O_3$, $Zn+Cu+Al_2O_3$ and $Zn+Ni+Al_2O_3$ coatings have shown their potential to use in the applications where reparation and restoration of macroscopic defects are needed, e.g., repairing casting defects. Further work will focus on deeper structural characterization and mechanical testing. Additionally, testing of different combinations of coating and substrate materials will continue in order to increase the industrial application fields.

5 Acknowledgements

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6 References

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