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Corrosion resistant layers produced by conventional and high-speed laser cladding with recycled powder

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Abstract

Stainless steel powders, produced from machining scrap, were used as coating material for corrosion resistant layers deposited on cylindrical parts by both conventional and high-speed laser cladding. Powders of two different particle sizes were analyzed and compared with commercial AISI 316L powders by optical and scanning electron microscopy. The final coatings were also studied in terms of chemical composition, microstructure and hardness, and their corrosion behavior was evaluated by a salt spray test chamber. The results show that laser cladding with recycled material can be a potential methodology, aligned with the principles of circular economy, for producing corrosion resistant layers to work under critical conditions, such as coastal marine environments.

Keywords: Laser cladding; Corrosion; Recycled powder; Stainless steel

1. Introduction

In the steel sector, specifically in the production of special steels, the design of the chemical composition is crucial to achieve the required demanding characteristics. Elements such as Silicon, Chromium, Cobalt, and Vanadium are commonly used. The costs of these virgin raw materials significantly impact the production costs and market placement of the affected steel products. Moreover, the European Commission has considered

iron (Fe) and its alloying elements chromium (Cr), manganese (Mn), and nickel (Ni) to be of relatively high economic importance [1]. The life cycles of these metals are closely linked to the life cycle of iron. In fact, up to 85% of global chromium production and 61% of global nickel production are used in alloying for the manufacturing of stainless steel, which reinforces the importance of steel recycling for the recovery of these metals. In this frame, metallic chips formed during machining processes are a great alternative, since chips possess different valuable elements such as Cr, Nb, V, Ti, etc.

The authors of this work are actively collaborating within a frame of an M-ERA.NET project [2], where powders with different particle size have been produced from machining scrap (metallic chips) following a route described in detail under a pending patent [3]. The chemistry and microstructure of these powders is analyzed in a currently in review publication by F. Kateusz et al. [4] where the feasibility of the presented recycling method is confirmed, so that these powders could be successfully used as a batch in additive manufacturing techniques. In order to confirm this statement, the present work aims to use these powders as a coating material for producing corrosion resistant layers by both conventional (CLC) and high-speed laser cladding (HSLC).

There are several factors or characteristics of powders that affect the deposition process, such as particle size distribution, flowability, absorption/reflection coefficients, thermal conductivity, oxidation, moisture or hydrogen content, and particle morphology [5]. Regarding particle size, powders with a balanced distribution are typically used, typically ranging from 45-90 µm, although it is possible to work with sizes ranging from 10-20 µm to 150-200 µm. This type of distribution allows for improved compactability of the deposited layer, as it allows smaller particles to fill the voids left by larger particles, thus minimizing porosity [6,7]. Flowability is a critical aspect in maintaining a constant powder flow, as poor flowability can cause the powder to agglomerate in the conduits that transport it from the feeder to the deposition head, resulting in variable flow that ultimately affects the uniformity of the deposited layers [8,9]. The absorption/reflection coefficients of the powder are another aspect to consider, especially if they vary from one batch to another, as this variation has a direct effect on the absorbed energy and, therefore, on the temperatures and thermal cycles during the deposition process, resulting in layers with different properties, from cord geometry to microstructure and mechanical properties [10]. Thermal conductivity plays a similar role, although to a lesser extent, as materials with higher thermal conductivity tend to dissipate heat more quickly, often requiring an increase in laser power to compensate for this factor [11]. The oxygen content of the powder is another important aspect to consider, as oxide formation usually occurs during the solidification phase of the deposition process when the content reaches around 0.1-0.2%. This oxide formation can weaken the deposited layer [12]. If oxidation occurs on the surface of the powder particles themselves, the oxide layer can affect not only the absorption coefficient but also the melting temperature of the filler material, ultimately affecting the outcome of the deposition process [13]. Moisture and the presence of hydrogen in the powder particles, in turn, affect both the flowability of the powder and the microstructure of the deposition, potentially leading to the formation of pores due to the trapping of hydrogen gas during solidification [14,15]. Finally, the morphology of the powder particles plays a crucial role in the deposition process. Particles with irregular shapes, such as elongated particles, satellites, hollows, or porosity, can affect the flowability of the powder and the final porosity of the deposited layer [16]. In particular, spherical particles are commonly used as they enhance flowability and are free from internal porosity, which can significantly impact the mechanical properties of the deposition. The surface roughness of the powder particles can affect the absorption coefficient, thereby influencing the thermal cycles of the process.

Due to all these factors that affect the LMD deposition process, powder manufacturers usually control exhaustively all aspects related to powder production, from the selection of raw materials to all aspects related to the atomization process. As a result, there are currently no precedents for powders manufactured using recycled raw materials since even a slight change in the raw material can potentially impact the deposition

process and ultimately the properties of the deposited material. However, in recent years, the effect of reusing powder over multiple LMD cycles has started to be studied. It has been concluded that by repeatedly reusing the feedstock material, the average particle size and oxygen content increase, although these changes do not significantly affect the quality of the deposition, even after 9 cycles of powder reuse [17].

In this work, the feasibility of using recycled powders for producing corrosion resistant layers by both CLC and HSLC is studied. The features of the coatings produced by with these powders are compared with those produced by commercially available AISI 316L powders to validate the use of these powders for laser cladding.

2. Materials and experimental procedure

2.1. Materials

C45E carbon steel cylinders with dimensions of Ø69.9x250 mm were used as the substrate for both CLC and HSLC experiments. The reference material for HSLC was a commercial AISI 316L powder manufactured by LSN (LSN F-316L-HV2), with a particle size distribution of 20-53 µm. For CLC, a powder manufactured by Högänas (Amperprint 0717) with a particle size distribution of 45-90 µm was chosen instead. Both recycled powders were obtained from the same atomization batch, after sieving them into different fractions. Sieves with mesh sizes corresponding to the targeted powder size ranges of 20-50 µm and 50-100 µm were used. The powder size distribution (volume weighted) was determined using an Anton-Paar PSA 1190 particle size analyzer by dispersing the powders in water.

Chemical analysis of the powders was conducted with a Bruker S8 TIGER WDXRF spectrometer, equipped with an X-ray tube with Rh anode, using 50 kV accelerating voltage. The data were analyzed by the semi-quantitative program Quant-Express of Spectra Pluss software. For the determination of carbon and sulfur, LECO CS-200 apparatus with two separated infrared cells, was used. The results of this analysis are shown in Table 1.

Table 1. Particle size distribution and chemical composition of the commercial and recycled powders

Powder	Particle Size (µm)	Element (wt%)									
		C	S	P	Cu	Mo	Si	Mn	Ni	Cr	Fe
F-316L-HV2	20-53	0.01	0.005	0.021	-	2.46	0.69	1.26	12.1	16.26	Bal.
Fine Recycled	20-50	0.11	0.005	0.024	0.56	3.5	0.80	0.70	8.2	22.5	Bal.
Amperprint 0717	45-90	0.02	0.005	0.024	-	2.44	0.71	0.17	12.3	17.5	Bal.
Coarse Recycled	50-100	0.13	0.006	0.023	0.49	3.4	0.85	0.82	8.5	21.5	Bal.

A small sample of each powder was hot mounted in resin and polished for comparing the commercial and recycled powders in terms of particle size and shape, as well as internal porosity. Fig. 1 shows the cross sections of the powder particles, where commercial and recycled powders show no significant differences between each other, which enforces the hypothesis that the recycled powders are suitable for CLC and HSLC technologies. A more detailed analysis of the recycled powders is presented in the paper by F. Kateusz et al. [4].
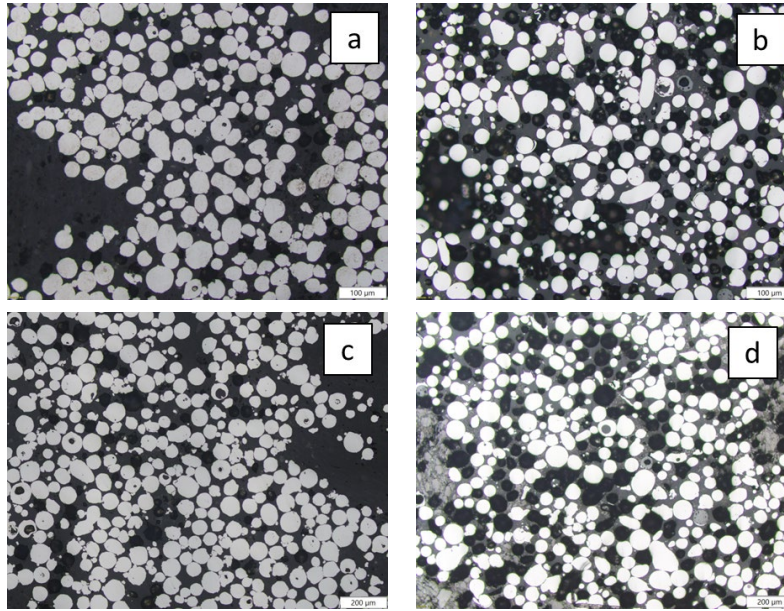
Fig. 1. Cross sections of a) F-316L-HV2, b) Fine Recycled, c) Amperprint 0717 and d) Coarse Recycled powders

2.2. Experimental procedure

A 2 kW fiber laser by IPG Photonics was used for producing both CLC and HSLC coatings. The laser beam was guided to the workpiece through an optical fiber with a diameter of 0.6 µm, a collimator with a focal length of 200 mm and focusing lens with a focal length of 200 mm. A HighNo 4.0 laser cladding nozzle, manufactured by Harald-Dickler, was used for both deposition technologies, the only difference being the spot size in the working plane, which was set to 1.2 mm for HSLC and 2.7 mm for CLC. A high-speed rotary table was used for the rotating motion of the cylinders and a 6-axis robot was used for moving the laser head along the cylinder axis. Argon was use as both carrier and shielding gas.

Table 2. Process parameters used in CLC and HSLC

	CLC	HSLC
Laser Power (kW)	0.7 – 1.4	2.0
Peripheral speed (m/min)	0.5 – 1.0	25 – 100
Powder feed-rate (g/min)	6.5 – 15.9	20.0 – 40.0
Step-over (mm)	1.4	0.2 – 0.4
Shielding gas flow rate (l/min)	6.0	10.0
Carrier gas flow rate (l/min)	8.0	8.0
Laser spot diameter (mm)	2.7	1.2

The cylinders were cleaned thoroughly to remove any contaminants or surface impurities before carrying out the cladding trials. A batch of experiment was carried out to determine the optimal parameters for each technology and powder. Table 2 shows the parameter range used in this initial experimentation, for CLC and HSLC. The same trials were carried out with commercial and recycled powders. Each set of parameters was

used to apply coatings on 10-15 mm long patches along the cylinder axis. To determine the powder catchment efficiency for each parameter set, the cylinders were weighed before and after each trial, and the difference in weight was calculated.

The cross sections of all the coatings produced in this experimental batch were prepared for metallographic investigations. The samples were hot mounted using conductive resin. The metallographic mounts were polished using 220 – 1200 grade SiC papers, followed by a mechanical polishing on diamond suspensions. The cross sections were first etched by Nital etchant with 4% nitric acid volumetric fraction to differentiate the substrate from the coating and then with oxalic acid to reveal the microstructural features of the coatings, which were analyzed by optical microscopy. Microhardness measurements were performed by a Futuretech FM700 Vickers microhardness tester with a load of 300g.

After selecting the best process parameters for each technology and powder, cylinders were almost completely coated with each technology/powder for salt spray chamber tests. All these coatings were ground until reducing the final diameter of the cylinders to 70.15 mm, so that all the coatings had the same surface-end and thickness (125 µm). The uncoated regions of the cylinders were protected before introducing the in the salt spray chamber. The salt spray test was conducted following the UNE-EN ISO 9227:2017 standard, using a saline solution consisting of 5% sodium chloride and 95% demineralized water with a conductivity of 1.9 – 3.9 µS/cm.

3. Results and discussion

3.1. Parameters optimization

In order to select the best process parameters for both CLC and HSLC experiments, several considerations were considered. The objective was to achieve high-quality coatings with minimal defects, minimal dilution, and maximum productivity. The following factors were considered in the parameter optimization process:

- Defect-free Coatings: One of the primary considerations was to ensure the absence of defects such as porosity, cracks, inter-run porosity, and lack of union in the coatings. These defects can significantly affect the integrity and performance of the coatings.
- Minimal Dilution: Dilution refers to the mixing of the base material with the deposited material during the cladding process. Excessive dilution can alter the desired composition and properties of the coating. A minimal dilution ensures that the coating retains its desired composition and properties.
- Maximum Productivity: Another important consideration was to maximize the productivity of the laser cladding process. This involved optimizing the powder feed-rate, which determines the amount of powder being fed into the system per unit time. Higher powder feed-rates can lead to increased deposition rates and improved productivity.
- Powder Catchment Efficiency: Powder catchment efficiency refers to the ability of the cladding system to capture and utilize the powder effectively. A higher catchment efficiency ensures that a larger proportion of the powder is successfully deposited onto the substrate, reducing material waste and improving process efficiency.

In both high-speed laser cladding (HSLC) and conventional laser cladding (CLC), the behavior of the recycled powders closely resembled that of the commercial powders.

The primary challenge in HSLC was to achieve coatings with a uniformly smooth surface and strong adhesion to the substrate. Higher step-over values resulted in coatings with a more irregular surface. Conversely, coatings produced with a high ratio of powder feed-rate to speed exhibited poor adhesion, leading to small gaps between the coating and the substrate.

Regarding CLC, excessive dilution was observed when using high laser power. On the other hand, increasing the powder feed-rate to speed ratio resulted in thicker coatings. However, when the coating thickness exceeded approximately 1 mm, inter-run porosity began to appear in the region between consecutive tracks.

Taking these considerations into account, the optimal process parameters, along with the corresponding coating thickness and powder catchment efficiency values, are presented in Table 3.

Table 3. Optimal process parameters for CLC and HSLC

	CLC	HSLC
Laser Power (kW)	1.3	2.0
Peripheral speed (m/min)	0.6	50
Powder feed-rate (g/min)	14.0	30.0
Step-over (mm)	1.4	0.2
Shielding gas flow rate (l/min)	6.0	10.0
Carrier gas flow rate (l/min)	8.0	8.0
Laser spot diameter (mm)	2.7	1.2
Layer thickness (mm)	0.9±0.1	0.21±0.03
Powder catchment efficiency (%)	91±3	85±2

The cross-sectional images of the selected coatings for different deposition technologies and powders are depicted in Figure 2, providing a visual assessment of the coating quality.
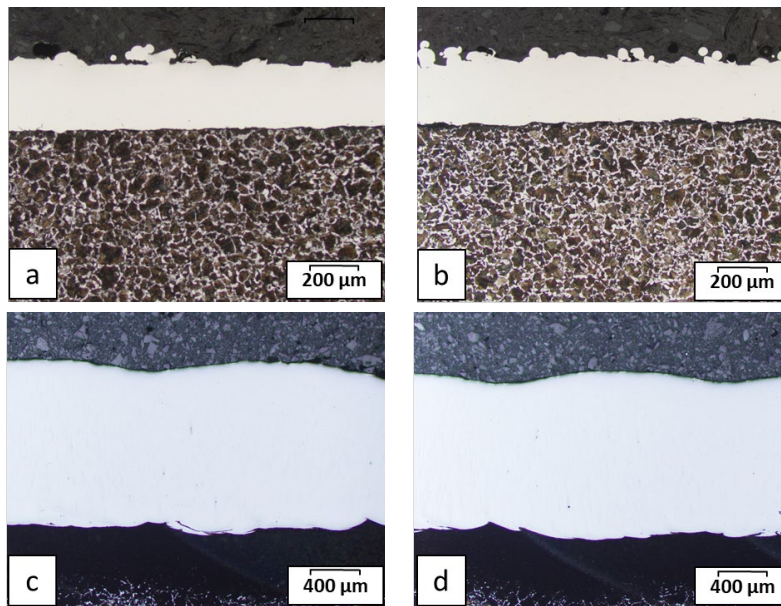

Fig. 2. Cross sections of a) F-316L-HV2 coating and b) Fine Recycled powder coatings deposited HSLC and c) Amperprint 0717 and d) Coarse Recycled powder coatings deposited by CLC

3.2. Microstructure and microhardness

The microstructure of all the coatings, shown in Fig. 3, consists of a fine dendritic structure. The dendrites are composed of austenite phase, while the interdendritic regions primarily contain a combination of austenite and ferrite phases. The coatings produced by HSLC present finer and more refined dendrites. Rapid cooling restricts the growth of dendrites, promoting the formation of numerous nucleation sites and shorter dendritic arms.
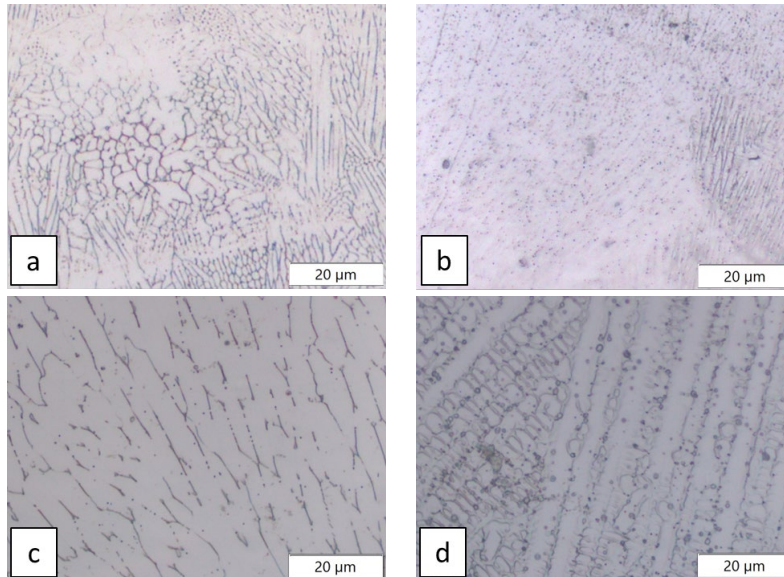

Fig. 3. Micrograph of a) F-316L-HV2 coating and b) Fine Recycled powder coatings deposited HSLC and c) Amperprint 0717 and d) Coarse Recycled powder coatings deposited by CLC

Fig. 4 shows the microhardness profiles measured across the coatings produced by HSLC and CLC with recycled and commercial powders. In both higher hardness is observed in the coatings produced with the recycled powders (~300 HV0.3) compared to the commercial ones (~200 HV0.3). This can be attributed to the higher carbon, chromium, and molybdenum content in the recycled powders.

The increased carbon, chromium and molybdenum content in the recycled powders can lead to the precipitation of carbides during solidification and cooling. Carbides are hard and wear-resistant compounds that can form within the microstructure of the coating. The precipitation of carbides can further increase the hardness of the coating by providing additional strengthening mechanisms.

The hardness in the heat-affected zone, just below the coating, significantly increases, reaching values exceeding 500 HV0.3. These measurements are obtained in the region where the substrate undergoes quenching. The heat-affected zone in HSLC is narrower compared to CLC due to the reduced energy input of the HSLC technology.
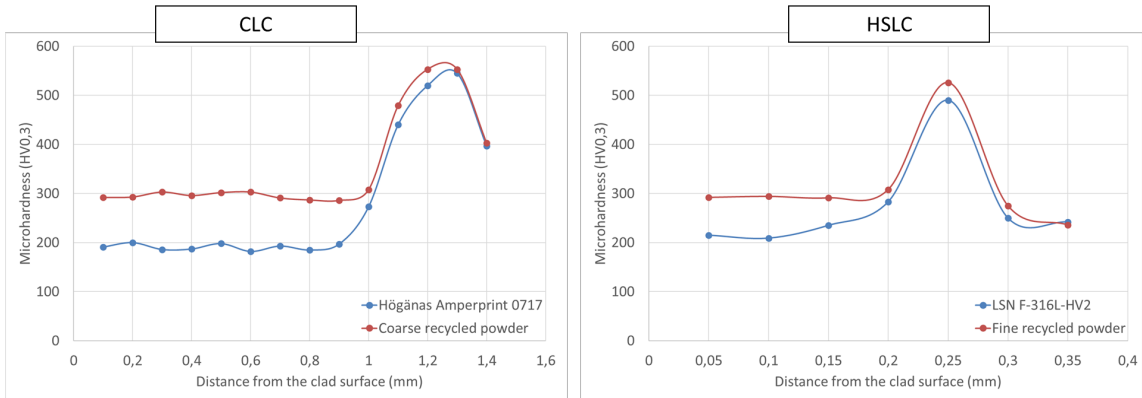
Fig. 4. Microhardness profiles measured across the coatings produced by CLC (left) and HSLC (right)

3.3. Corrosion resistance

Fig. 5 illustrates the progression of corrosion in various coating combinations and materials during the salt spray chamber test. The uncoated C45E sample exhibited complete corrosion within 24 hours of the test, emphasizing its susceptibility to corrosion. Conversely, all the coated samples demonstrated improved corrosion resistance, indicating the effectiveness of the applied coatings in mitigating corrosion.

For both commercial and recycled powders, the CLC coatings show a slower progression of corrosion over time, indicating better long-term corrosion resistance. The cylinders coated by CLC lasted about 250 hours with low corrosion values while in the case of HSLC the corrosion started to be critical after 100 hours in the case of the recycled material and after only 50 hours in the cylinder coated with the commercial material. This difference between different coating technologies may be caused by the higher effective layer thickness achieved by CLC. Despite all cylinders being ground to the same final diameter, the greater dilution produced by CLC results in a thicker corrosion-resistant layer (coating + dilution) compared to HSLC. Consequently, this effectively retards the progression of the corrosion layer on the surface.
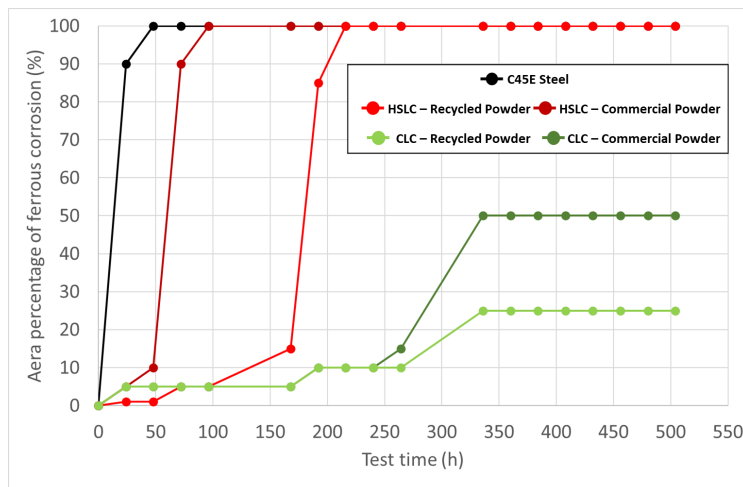

Fig. 5 Evolution of corrosion during the salt spray chamber test for different combinations of coating technologies and coating materials

The corrosion resistance of the recycled material surpasses that of the commercial material for both deposition technologies. However, it is crucial to consider that the chemical composition of the recycled material differs from that of the commercial variants. Specifically, the recycled material exhibits a higher chromium content, which is a key element in stainless steel's overall corrosion resistance. Chromium plays a vital role in the formation of a thin oxide layer, known as the "passive layer," on the stainless steel surface. By increasing the chromium content, the protective passive layer becomes more robust, leading to improved corrosion resistance.

Fig. 6 shows the appearance of all the samples after 48 hours of salt spray chamber test, where differences between different materials/coating technologies are already visible.
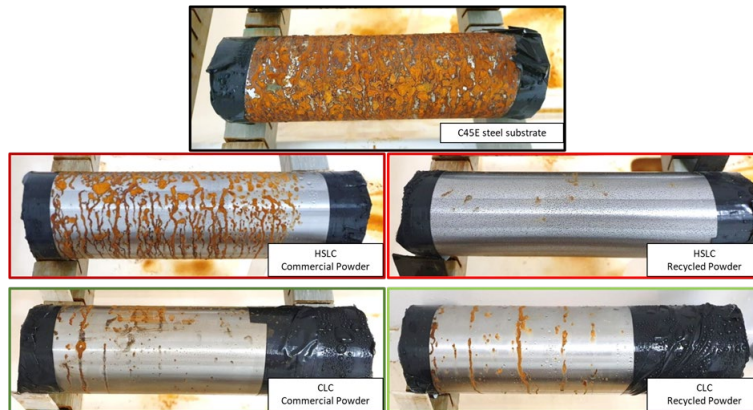

Fig. 6. Traces of ferrous corrosion on the surface of different samples after 48 hours of salt spray chamber test.

4. Conclusions

The feasibility of utilizing recycled powders for producing corrosion-resistant layers through high-speed laser cladding (HSLC) and conventional laser cladding (CLC) processes was investigated. The objective was to evaluate the performance and suitability of these recycled powders as a viable alternative to commercially available AISI 316L powders in laser cladding applications.

The results demonstrated that the coatings produced with the recycled powders exhibited favorable characteristics and comparable performance to those fabricated with commercial powders. The microstructural analysis revealed similar dendritic structures and distribution of alloying elements in both types of coatings. This suggests that the recycled powders possess the necessary metallurgical properties required for producing high-quality coatings.

Additionally, it was observed that the coatings produced with the recycled material exhibited higher hardness and improved corrosion resistance compared to the commercial AISI 316L layers. This superior performance can be attributed to the differences in chemical composition between the two materials.

In conclusion, the findings of this study validate the feasibility and effectiveness of utilizing recycled powders for laser cladding applications. Further research and development in this area are encouraged to explore the full potential of recycled powders and advance the field of laser cladding technology.

Acknowledgements

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