

Título: LASER DIRECTED ENERGY DEPOSITION FOR REVALORIZATION OF TRADITIONAL METALLIC MATERIALS

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Resumen: Abstract

1. Introduction

Throughout history, the development of civilization has relied on the discovery, development and application of metals. Since the man discovered copper (around 9000 BC), starting from a very basic interest about the behavior of this new material and its applications, metallurgy has evolved from an art to a science. As our knowledge of metallurgy has advanced, metals have been essential in the development of technology.

Nowadays, we can consider traditional metallic materials and alloys those that have been widely used by industry during last decades, like steel, cast iron, aluminum, bronze, titanium, etc. These materials are

commercially available, relatively affordable and they are very common in the manufacturing of products. However, industry requires improving the performance and durability of the mechanical components; so, these traditional materials need to enhance their properties to satisfy this demand.

2. Overview of Laser Directed Energy Deposition

Laser Directed Energy Deposition (LDED) technology is gaining popularity in the industry for commercial applications, encouraged by the development of reliable and robust industrial high power lasers. Laser Directed Energy Deposition (LDED) is an Additive Manufacturing (AM) method, so it is a technology to make objects by adding material, usually layer upon layer, as opposed to subtractive manufacturing technologies. LDED includes techniques named under a wide range of terminology and acronyms: laser cladding, Direct Laser Deposition (DLD), Direct Metal Deposition (DMD), Laser Metal Deposition (LMD), Laser Powder Deposition (LPD), Directed Laser Fabrication (DLF), Laser Engineered Net Shaping (LENS), Laser Consolidation (LC), etc.

LDED utilizes a laser beam source to generate a molten pool in a substrate or workpiece. The laser beam is moved relatively to the workpiece melting its surface. Feedstock material, in the form of particles or wire, is delivered into the molten pool. The laser moves leaving backwards the molten material that immediately solidifies transmitting the heat mainly by conduction to the substrate. The relative movement between the laser head and the workpiece makes possible depositing material to generate single clad tracks with dimensions of millimeters or microns. The overlapping of single clad tracks allows creating a bidimensional layer or coating. Finally, a component can be build-up by depositing material layer-by-layer. This process is typically used with metals, but it can be used with any material that can be melted including ceramics.

The research carried during last decades demonstrated the feasibility of LDED technology to be employed not only with a wide variety of metallic materials, but even ceramics, in the following applications:

1. Generate specific coatings by means of laser cladding or laser alloying to protect the surface of mechanical components enhancing their performance and increasing their lifetime.
2. Repair and refurbish high-value mechanical components that have suffered either damage or considerable wear and corrosion in service.
3. Manufacture parts by means of AM ranging from thin-walled structures to complex bulk components.
4. Produce Functionally Graded Materials (FGM) and heterogeneous multimaterial components that allow interesting new materials design with special functionalities.

LDED technology is displaying great application potential and advantages in the aerospace, automotive, biomedical, and energy industries. Specifically, LDED is a time efficient and cost-effective way to produce low volume of high added-value components that cannot be manufactured by other more conventional methods. The extra value given by this technology is the customization and advanced material properties that can be achieved.

There are several factors to expect a future growth on the application of this technology like more affordable equipment such as lasers, continuous improvement in computational hardware, software and automation and more knowledge about metallurgy and laser processing. However, LDED is still viewed as a niche technology by

most industries. In order to gain further acceptance several scientific and technological issues have to be addressed:

1. Interrelation between LDED process, structure, properties and performance of the components still requires more study for a better understanding.
2. Numerical modelling and simulation of LDED is a challenge that still requires more development because of the complexity of the process.
3. Process equipment, monitoring and adaptive control must improve to increase the repeatability, improve the efficiency and produce affordable parts.
4. Optimal processing parameters still have to be determined based on trial and error and more research is needed to improve them.
5. Wider commercial adoption of LDED technology can only be achieved by broadening the fields where it can be applied and increasing the knowledge about the processing of all kind of materials that were not studied enough, ranging from traditional alloys to functionally graded materials.

3. Objectives

The present thesis has the aim of contributing in the application of Laser Directed Energy Deposition (LDED) technology to process traditional metals and alloys that have not been widely studied yet. LDED technology can be employed to revalorize these materials by enhancing their performance and increasing their lifetime. Moreover, LDED is an opportunity to extend the utilization of affordable traditional materials in highly demanding applications.

Increase the industrial adoption of LDED technology can only be possible if it can be employed to add extra value to their products. From a technical point of view, LDED can add value in three ways: produce parts that cannot be obtained by other more conventional methods; manufacture components with enhanced properties; and repair damaged or worn mechanical parts to reclaim them. The willingness of the industry to incorporate LDED technology may be amplified by demonstrating the feasibility of this technology to add value in the processing of the materials that are commonly employed. This requires more research on the application of LDED to revalorize traditional alloys and offer new opportunities.

This thesis focuses on the use of LDED in three cases of study. The two first cases are the generation of coatings by means of laser cladding of dissimilar materials: Ni-based alloy on cast iron substrate, and bronze on alloy steel. The third case is the manufacturing of commercially pure titanium thin-walled parts. Many other materials could be studied but time and resources available are finite and only those cases were tackled. These specific combinations of materials were carefully selected because they present a potential industrial application, which will be analyzed in depth for each case in their corresponding chapters. Moreover, a lack of research was detected on the application of LDED to enhance the surface properties of cast iron substrates, generate bronze coatings and additively manufacture commercially pure Ti components.

Moreover, the materials were selected in such a way that they present a challenge. It is known that properties of coatings obtained by LDED of dissimilar materials are highly influenced by the dilution, which is the intermixing of

the deposited material and the volume of molten substrate. The thermal properties of the powder material and the substrate have a major impact on the dilution.

In the first case, cast iron is challenging because it is a heterogeneous material with heterogeneous thermal properties. In the second case, the challenge is the melting point of bronze (800-950 °C), which is much lower than the melting point of the substrate, alloy steel (1427 °C). Finally, there is a case of study of application of LDED to additively manufacture commercially pure titanium, a homogenous material, where the dilution should not play any role. However, it is interesting to analyze its influence on the solidification and grain growth. All these challenges present a scientific interest in order to progress in the understanding of the capabilities of LDED technique.

The objectives of this thesis are to demonstrate the feasibility of LDED to process the already mentioned combinations of materials. LDED with side powder injector setup was selected to develop the experiments and the substrate is going to be moved with regard to the laser head employing a CNC table. A specific high power near-infrared laser has to be chosen for each case, being preferential those that are more energetically efficient (fiber laser or diode laser). Practical processing parameters have to be determined based on a parametrical study for each specific case. Moreover, it is required to study the influence of this technology on the geometry of the deposited material, microstructure and properties. Obtained results will be a contribution to expand the knowledge about the processing of materials by LDED and further development of this technology.

4. Laser cladding of nickel-based alloy on cast iron

In the first case of study, a comparison between different types of cast iron substrates (with different graphite morphology) has been carried out to analyze its impact on the LDED process results. A fiber laser was used to generate a NiCrBSi coating over flat substrates of gray cast iron (EN GJL 250) and ductile cast iron (EN-GJS-400-15). Gray cast iron is a ferrous alloy characterized by a carbon-rich phase in form of lamellar graphite in an iron matrix while ductile cast iron presents a carbon-rich phase in form of spheroidal graphite. Graphite presents a higher laser beam absorption than iron matrix and its morphology has also a strong influence on thermal conductivity of the material. The laser cladding process of cast iron is complicated by its heterogeneous microstructure which generates non-homogeneous thermal fields.

A hardfacing coating was generated by fiber laser cladding. Suitable processing parameters to generate the Ni-based alloy coating were determined. The coating created by laser cladding on cast iron presents high dilution, 40% in the case of ductile cast iron and 55% for gray cast iron, employing the same processing parameters. The variations detected in dilution are a consequence of the different thermal properties that have the two types of cast iron. Gray cast iron presents graphite in form of flakes while in ductile cast iron, the graphite appears in form of spheres. The shape of the graphite has a major influence on the thermal properties of the cast iron, particularly, on the thermal conductivity, which is higher for gray cast iron.

Moreover, the complete coating presents more dilution than single track because the much larger laser irradiation time produces a significant increase of the temperature of the substrate. The energy of the laser beam generates the molten pool that solidifies once the laser moves. The heat is transferred mainly by conduction from

the molten material to the rest of the substrate, which acts as a heat sink. This is crucial because it reflects the importance of the dimensions of the substrate and the extension of the area that requires to be treated. The employment of LDED technique in a large area of a small volume of substrate will produce a considerable increase of the substrate temperature. If the temperature of the substrate changes, it affects the results of the process, particularly the dilution.

The elemental composition of the coating was characterized and it presents Ni, Cr, Fe, B, Si and C. The fraction of elements reveals the dilution between the substrate and the injected particles, resulting in a coating formed by a mixture between part of the substrate and the injected particles. The main crystalline phase present in the coatings is identified as FCC austenitic matrix based on nickel and iron. The elastic modulus is similar for the coating and the substrate (230 ± 30 GPa), while the Ni based coating obtained presents a significantly superior hardness than cast iron. The hardness of the coatings generated in ductile cast iron is 205% higher, from 180 ± 20 HV (substrate) grows to 550 ± 40 HV (coating); while in gray cast iron, the hardness increases 74%, from 270 ± 40 HV (substrate) grows to 470 ± 40 HV (coating). The greater dilution detected on the gray cast iron samples is the responsible of this reduction in the hardness.

5. Laser cladding of phosphor bronze on alloy steel

In the second case of study, the generation of a phosphor bronze coating on alloy steel by means of laser cladding is analyzed. Phosphor bronze is a suitable bearing material because of its good fatigue strength and excellent wear properties under corrosive conditions, high temperatures and high loads. Bronze is usually continuously cast as bar or tube and machined into bushes, cam followers, washers or other bearing components. It is common to mount bronze bushes around shafts by means of warm shrink fitting.

The feasibility of the laser cladding to produce phosphor bronze coatings on alloy steel is demonstrated. Suitable processing parameters to generate phosphor bronze coatings were determined. Several experiments were performed changing the processing parameters and none of them presented any dilution. The melting point of the bronze particles ($800-950$ °C) is much lower than the melting point of the substrate, alloy steel (1427 °C). Bronze particles are melted and deposited without increasing their temperature above the melting point of the alloy steel substrate, and dilution is avoided.

The microstructure of the bronze coatings generated consists of α dendrites surrounded by $(\alpha+\delta)$ eutectoid. Their hardness is 172 ± 12 HV, 56% higher than the one reported for cast bronze. This greater hardness is attributed to a fine microstructure and a higher presence of the harder δ -phase. The fine microstructure is achieved because laser cladding produces high cooling rates during the solidification of the molten pool. Therefore, bronze properties can be enhanced employing LDED technique to deposit this alloy. Finally, laser cladding is proposed as a method to create a bronze surface in an area of a shaft as a substitute of warm shrink fitting of machined bronze bushes.

6. Additive manufacturing based on laser cladding of pure titanium

In the third and last case of study, LDED was employed to produce thin-walled commercially pure titanium parts and their microstructure and crystallographic texture are analyzed in depth. From the results obtained, it is possible to understand better the LDED process of pure titanium. Since the material is homogeneous, it could be thought that dilution does not have an influence on the result. However, epitaxial growth of columnar β grains is produced because of remelting previously deposited layers. This remelting is achieved employing a low mass deposition rate of titanium powder and an excess of laser power. The solidification front moves as the material is being cooled when the laser leaves the interaction zone. The material that is being solidified mimics the crystallographic orientation of the previously deposited solid material, except in the external edge of the molten pool, where the equiaxed grains can appear. Selecting the proper processing parameters, the surface that contains equiaxed grains is remelted. Therefore, the dilution is crucial to achieve an epitaxial growth of these prior β columnar grains from the parent grains.

The crystal structure of commercially pure titanium changes from BCC (β -Ti) to HCP (α Ti) when its temperature is below β -transus temperature. This transformation follows the Burgers relationship and α -Ti lamellae present twelve variants of crystallographic orientation into each prior β grain. The result is a basket-weave microstructure with a strong crystallographic texture.

In the thin-walled parts generated by LDED, it can be observed that the finest α lamellae are formed in the bottom part of the samples whereas longer α -lamellae organized into bigger colonies can be found in the top. This phenomenon is caused by a reduction in the cooling rate while the part is being built. From the beginning of the process, the heat is transferred rapidly by conduction from the molten pool to the substrate and the previously deposited material. Only part of the heat is evacuated out of the part by radiation and convection and the result is the increase of the temperature of the substrate. While the part is being generated, the distance between the molten pool and the substrate grows, so the thermal conduction resistance increases. The heat transferred from the top of the part to the substrate by conduction decreases because of a lower thermal gradient resulting in lower cooling rates.

7. Overall discussion

The properties obtained in the layers of material deposited by LDED are determined by their composition and microstructure; and both depend on the dilution and the cooling rate during the solidification of the molten pool. The processing parameters (laser power, scanning speed, powder mass flow) have an influence on the results. However, it becomes clear the importance of the thermal properties and melting point of the powder material and the substrate (including the previously deposited layers of material). Moreover, the dimensions of the substrate, its geometry and deposition strategy can lead to changes in the volume of molten material and its cooling rate. The employment of constant processing parameters can be useful when the processed area is relatively small in comparison to the total volume of the component. Nevertheless, the repeatability in the properties/microstructure/composition of deposited material requires mechanisms to stabilize or control the size of the molten pool and its cooling rate.

8. Conclusions

LDED technology has demonstrated its capabilities to revalorize traditional materials:

- Improve surface properties of cast iron are by the generation of a Ni based coating.
- Produce functional bronze coatings with enhanced properties.
- Generate commercially pure titanium thin-walled parts with unique microstructural arrangements that cannot be obtained by other conventional methods.

Moreover, in the two first cases, the same technique can be used also to refurbish components and increase their lifetime: repair damaged cast iron components and reclaim worn bronze coatings. Finally, thin-walled commercially pure titanium parts produced by LDED show a unique microstructure that cannot be generated by other methods.