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NEW ADDITIVE MANUFACTURING TECHNOLOGY BASED ON SELECTIVE METAL-POLYMER COMPOSITE FORMATION

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ABSTRACT: Although additive manufacturing technologies have been growing along the last years, new applications have been created in addition to new challenges to be overcome. For that reason, the main goal of this work is to present a new additive manufacturing technology which is based on selective metal-polymer composite formation. In this work, this brand new and innovative technology is introduced and the potential application and perspectives for this process is discussed. By the end, the benefits and disadvantages of this technologies are presented in addition to future researches and development that is needed to make this technology a new product in market.

INTRODUCTION
Along the last years, the additive manufacturing started playing an important role in global point of view. In general way, this is consequence of benefit that these processes provided to product development process and business competitiveness, such as the shorting of products release, errors reducing and support for new products concepts and shapes development (GIBSON, ROSEN ET AL. 2010; GRUNBAUM 2012; FORD 2014; HUANG AND LEU 2014; CUNICO 2015).

As result of such advantages, several researches and developments have been done in order to optimize materials and processes, in addition to creating new applications and developing new technologies which are based on additive methods (GIBSON, ROSEN ET AL. 2010; CUNICO 2015).

In this work, the main goal is to introduce a new and innovative additive manufacturing technology which is based on selective formation of metallic and polymeric composites. This process was patented in 2015 as result of a research which was developed in University of São Paulo in partnership with the Concep3D R&D organization (CUNICO AND CARVALHO 2015). It is also possible to highlight that the proposed technology was inspired on SCF process, which is a technology that was also developed in University of São Paulo in partnership with Concep3D in 2013 and is based on the selective formation of polymeric and cellulosic composites (CUNICO 2013; CUNICO AND CARVALHO 2016).

Along this work, we have also discussed some advantages that this process might deliver, such as the possibility of metallic objects manufacturing with low power lasers or light sources and the possible use of this technology in office environments. On the other hand, this paper also presents some challenges which this process still need to overcome in order to become a commercial product, whereas the technology is still in preliminary stages of development.
By the end, we summarized some general aspect of the proposal technology and compared with other additive manufacturing processes in the earliest days. In addition, the potential applications for this proposal were exposed in order to summarize the looming impact that this technology might provide in the market.

THE PROCESS

The proposed technology that is introduced in this work is based on selective formation of composites compounded by polymer and metallic matrix. The main working principle of this technology can be seen in Figure 1, where a schematic of the process main steps is presented. In general way, we divide the process in three stages: building, cleaning and finishing.

![Figure 1 - Schematic of the main working steps of Selective Metallic Composite Formation](image)

During the building stage, each layer is created by the follow steps: substrate feed, substrate impregnating with photopolymeric resin, laser trace exposure (layer profile building). These steps are repeated until all object layers are completed.

![Figure 2 - Specimen fabricated by selective metal-polymer composite formation after removing residual material](image)

After finishing the building stage, the object (polymerized composite material) and residual material (non polymerized material) are found in a basic block. In the cleaning stage, the residual material is removed by oxidants and solvents, resting only the polymerized material, as presented in Figure 2. By the end, the object is finished in order to remove burrs, edges and layers marks besides increasing the mechanical strength of object.
THE MATERIALS

The metallic composite is compounded by structured fiber substrates and polymeric material. The polymeric material is based on acrylate polymers in addition to being UV curable. The substrate is initially based on copper weaves, even though other metallic materials are still being evaluated.

The main formulation of polymeric material is leaded by low viscosity, low shrinkage and high polymerization rate. The low viscosity is necessary for the substrate impregnation and layer adherence, otherwise the resin would remain only on surface and no layer adherence would be achieved (Cunico 2013; Cunico and Carvalho 2013; Cunico and Carvalho 2016).

As this process concerns fibers which make the light penetration hard, high polymerization rate was target in order to a better polymerization profile besides high building speed. In spite of that, the process still promotes low building speeds and needs several developments in order to be improved (Cunico 2013; Cunico and Carvalho 2016).

The mechanical strength of polymerized material is find between 40 and 45 MPa, in addition to the resin viscosity can be find between 1 and 2 cP and the thermal strength is around 80°C. With respect to polymerization rate, the time to convert 80% of resin in polymer with 120mW LED is 30 seconds (Cunico 2013; Cunico and Carvalho 2016).

In order to ensure the adherence between layers, each substrate layer is compounded by metallic textile and cellulose fibers, as shown in Figure 3.

![Microscopy of substrate composition](image)

With respect to the metallic part of substrate, we mainly used square copper weaves with 0.08mm of wire diameter, spacing of 0.078 mm between wires (mesh 160) and 0.08mm of thickness. Additionally, the tensile strength of this textile is 125 MPa. In spite of this substrate description, this work is still in development and other textiles are still in phase of evaluation.

In addition, we used a short fibers laminated cellulose with 0.06 mm of thickness, 40 g/m of grammage and tensile strength of 2.8 MPa. In this cellulose fiber, the bleaching and was removed in order to allow resin impregnation and light penetration.

The composite is created by the polymerization of liquid resin which was previously impregnated in the substrate. As the resin is liquid, the voids between layers are filled and the surface of copper is cover and protected from redox agent, as presented in Figure 4.
In order to remove the residual material which was not polymerized, the basic block is cleaned and the residual copper is removed by redox agent, such as iron chloride. In this case, the chemical reaction is shown in Eq.(1) and Eq.(2) (CLUGSTON AND FLEMMING 2000; KHANDPUR 2005):

\[
\text{FeCl}_3 + \text{Cu} \rightarrow \text{FeCl}_2 + \text{CuCl}
\]  

(1)

\[
\text{FeCl}_3 + \text{CuCl} \rightarrow \text{FeCl}_2 + \text{CuCl}_2
\]  

(2)

After removing residual copper by redox reaction, the composite can be found in addition to residual cellulose substrate, as presented in Figure 5.

**EARLY RESULTS SUMMARY**

With respect to the profile generation, polymerization lines were shown to behave like Selective Cellulosic Composite Formation (SCF) processes (convex), differing from Stereolithography processes (concave) (CUNICO 2013; CUNICO AND CARVALHO 2016). Consequently, peripheral polymerization area is generated, creating restriction related to the distance between laser trace lines (CUNICO 2013; CUNICO AND CARVALHO 2016).
In this case, it was found that distance between lines that follow 1.5 time of laser diameter implies on intermittent behavior, while higher values results in line separation. For distances below 1.5 time of laser diameter, the lines become homogeneously united.

As result of resin impregnation, the cellulose fibers swell besides the resin fulfill voids and cover copper surface. Therefore, 100 μm was evidenced to increase the layer thickness in comparison with the raw substrate thickness. In addition, the cross section exposes the material homogeneity along the layers, as presented in Figure 7.

As preliminary result of mechanical strength analysis, we could identify that the tensile strength of composite in x-y directions was 125 MPa in addition to 40 MPa of tensile strength in z direction.

**FUTURE PERSPECTIVES**

This proposal is still in a preliminary development stage and still has several challenges to be overcome. Nevertheless, the presented results exposed the possibility of creating objects with high mechanical strength, in addition to potential increase thermal and chemical strength.

These results is not comparable with several additive manufacturing technologies that is find in the market. Nonetheless, these results are still compatible with the results of the current processes in earlier days. That emphasizes the potential of this proposal in the early future.

In order to investigate such potential, the characterization of physical and chemical properties of the final object is about to be investigated. Additionally, the cleaning stage and finishing process stages are also being studied and optimized, in order to accelerate the cleaning time, increase mechanical strength and reduce object mechanical anisotropy.
CONCLUSIONS

In this work, a new additive manufacturing technology was introduced in addition to early results related to the proposed process.

The geometrical restrictions of the layer building and increase of thickness as a function of curable resin were presented. Where the peripheral polymerization was evidenced and resulted in a transient composite area. In addition, the mechanical anisotropy of final object was presented, where the tensile strength was found to be 40 MPa in z direction and 125 MPa in x-y directions.

Moreover, although the proposed process is still being investigated, the functional process feasibility and the process future potential application were presented. Furthermore, there are still several studies to be done in order to better understand this new technology in addition to introduce this concept product in market.

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