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MANUFACTURING OF COPPER-NICKEL PARTS BY 3D EXTRUSION PASTES

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Abstract. *Among the metal additive manufacturing, the sinter-based technologies have growing attention due the possibility of combining the versatility of 3D printing with traditional powder metallurgical routes. 3D extrusion of viscous pastes is one of the prominent sinter-based technologies, that starts from forming a green part by 3D extrusion layer by layer of a highly viscous paste loaded with the metal particles. In our research group, we are currently developing strategies to adapt 3D extrusion-based processes for production of aerospace metal alloys. Thus, this work seeks to find an appropriate Ni-Cu Alloy composition and binder system to produce suitable materials by 3D-extrusion. The methods include the production of pastes with the metallic powders and a binder, molding/ cold press and then thermal debinding and sintering. The tests performed so far were optical and electron microscopy, Vickers microhardness, and evaluation of the apparent density and porosity applying the Archimedes principle. The preliminary results showed that it was possible to produce Ni-Cu parts by compaction of 3D extrusion pastes. Ni-Cu have an apparent porosity of 30-55 % and a high oxygen uptake, which can be decreased by using reductive atmosphere during sintering.*

Keywords: *Extrusion, Ni-Cu Alloys, Processing, Additive manufacturing.*

1. INTRODUCTION

When it comes to the manufacturing processes of metals and metal alloys, which is a field highly in demand in various market niches, research and development in the area of materials is increasingly necessary, especially considering the recurrent updates. In the context of Brazilian industry and academia, the incentive for the search of new technologies and applicability has been an urgent cause in an attempt to keep up with the global scenario. In this matter, additive manufacturing, or 3D printing as it came to be known, has been widely discussed.

As a method with great potential for application, additive manufacturing is proving in practice what it aims to be in theory: a technology that helps save time and material, facilitates the manufacture of complex designs, and overall optimizes the production of parts, from decorative to components with high performance requirements (Milewski, 2017). One difficulty with this technology, however, is the printing parameters and the use of the methods, which require a great deal of theoretical background, testing time, and proper instrumentation. For applications involving metals, the sinter-based technologies, especially paste extrusion, are simpler to obtain, and, moreover, stand out due to the possibility of production of isotropic components in a shorter time, and for being similar to the fused filament fabrication and powder metallurgy (Ramazani and Kami, 2022).

3D extrusion of viscous pastes was initially developed for production of ceramic components. This technology forms a green part by 3D extrusion layer by layer of a highly viscous paste loaded with the ceramic or metal particles. After printing, post processing consists of debinding and sintering. The material extrusion process is defined as an additive manufacturing method identified by the acronym MEX in ISO/ASTM 52900:2021, and described as "additive manufacturing process in which material is selectively dispensed through a nozzle or orifice". The method became greatly popular through the plastic-based Fused Filament Fabrication (FFF) process, becoming the most widely used prototype manufacturing method worldwide (Signor *et al.*, 2023), and has recently been adapted to produce metal parts (3DEO, 2022).

According to Ramazani and Kami (2022), the process description is given by: "[...] the initial stage in the metal FDM process is to produce a feedstock composed of binder and metallic powder. This feedstock can be manufactured as rods, flaments, or pellets. Accordingly, layer-wise deposition of the material is accomplished using plunger-based, pinch feed, or screw based mechanisms, respectively. The final metallic component is ready after posttreatment (including debinding and sintering steps)."As stated by the author, the method can be identified as FDM metal without misusing the description

of the technique. Even if there are several methods that fit into it or there are minor variations not represented, using this nomenclature to generalize can serve as a way to simplify discussions about the major stages of the process.

Regarding the materials, as claimed by Klassert and Tikana (2007), CuNi-alloys are among the most corrosion resistant materials. They resist humidity, non-oxidizing acids, caustic and salt solutions, organic acids and dry gases like oxygen, chlorine, hydrochloric and fluoridric acid, sulfur dioxide and carbon dioxide, and, because of that, quite a number of copper alloys have been used in marine applications and show a very good performance. There is no risk of stress crack corrosion. The tendency towards selective corrosion is very low and pitting corrosion is a rare exception. Besides that, nickel as an alloying element for copper improves tensile strength, proof strength and hot strength.

In this study, the fabrication of nickel-copper alloys by 3D extrusion was investigated using elemental nickel and copper powders as starting materials and water based solution with Polyvinyl Acid (PVA) as binder. The main objectives of this work are to evaluate the feasibility of producing copper-nickel alloys from pastes for 3D extrusion, more specifically, to produce copper and nickel pastes that have characteristics suitable for 3D extrusion. The effect of paste composition on the microstructure of the manufactured Cu-Ni components was investigated. In this article will be presented the results of microstructural characterization by light microscopy and scanning electron microscopy. Furthermore, the results of porosity measured by Archimedes method and its effects on the mechanical properties will be discussed.

2. EXPERIMENTAL

At this first study, green samples were produced by uniaxial die compaction of viscous pastes. A schematic of the process is shown in Figure 1. Die compaction of viscous pastes enables the use of a small amount of raw materials and has some similarity with extrusion process, therefore it was performed prior to testing larger amounts of pastes in the 3D extrusion printer.

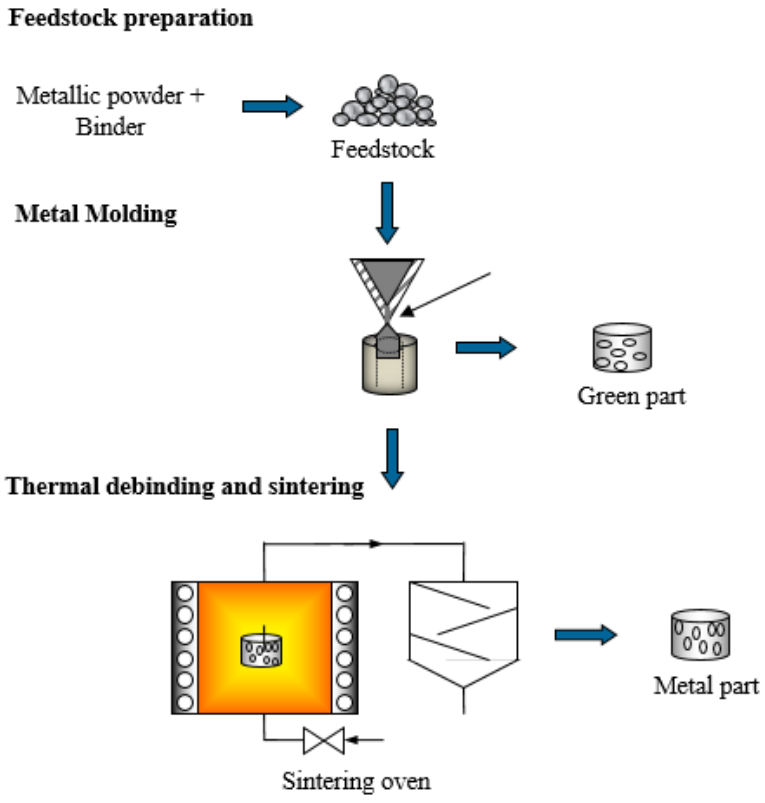

Figure 1. Schematic of the process of compactation.

The materials used for the paste preparation were metallic powders, being nickel powder (325 mesh, Brutt), electrolytic copper powder (325 mesh, Dinâmica), polyvinyl alcohol (PVA) produced by the company ACS and distilled water. Two paste compositions were prepared, wich are described in Table 1.

In this regard, the nickel and copper proportions of 50 and 70 wt% of nickel, respectively, were chosen. For both proportions, five specimens were produced by molding and compaction, for which the powders were manually mixed to the polyvinyl alcohol binder (PVA) in the proportion 88/12, after being weighed on an analytical balance. For the composition of the binder, 2 wt% of PVA was diluted in distilled water, as tested in copper samples by Signor *et al.* (2023).

Table 1. Composition and proportion of mixtures for the pastes.

Paste label	Binder	Binder/Water (wt.%)	Powder load (wt%)
Ni50Cu50	PVA	2/98	88
Ni30Cu70	PVA	2/98	88

Defining that the total mass of each specimen should be 0,005 kg, the mass of each metallic powder was calculated for this objectived weight, according with the proportions defined and together with the mass of binder added to the mixture. The force applied by the manual press for the compaction was about 50 MPa, and the result of this processes were the green parts as shown in Figure 2.

Figure 2. Samples fabricated.

2.1 Posttreatment

After compaction, the samples were submitted to posttreatment consisting of debinding and sintering procedures, and the specimens resulting are called now brown parts. Debinding is the process where the binder is eliminated of the sample, applied in this case as thermal debinding, that together with the sintering were performed in a vacuum furnace (Fortelab, Brazil). The thermal process is considered slower than other methods, but better controllable, according to Ramazani and Kami (2022). The authors also say that "To maintain the component's form and minimize thermal stress and considerable weight reduction rates, the rate of temperature decline/increase in time must be slow enough", and for this a temperature increase rate of 278 K/min was used until reaching 773 K, which was maintained for 60 minutes.

As says Ramazani and Kami (2022), "Thermal debinding and sintering are continuous operations that occur one after the other and usually in the same furnace", which is the case in this study as well. After debinding, the sintering process starts, applying quasi-vacuum pressure around 1.10^3 Pa. The temperature increase rate in this procedure is 283 K/min until reaching 1323 K, that was then maintained for 120 minutes.

This treatment is responsible for atomic difusion between metal powder particles, attaining near-total density by high temperatures, always under the metal melting point. However, the full density is not reached, due to the presence of micro-porosities. The fundamental phases and parameters for debinding and sintering treatments were defined by Ramazani and Kami (2022), respectively, as " 1- difusion of solvent, 2-dissolution of the soluble part of binder, and 3- difusion from the inside to the outside for the remaining quantity of binder" and "(1) temperature, (2) time, and (3) furnace atmosphere." The control of temperature is extremely important to define the quality of the outcome. After those processes, the brown parts were left to cool inside the furnace, until meeting ambient temperature. At last, the sintered samples went to metallography preparation.

2.2 Testing

After the preparatory processes were performed, the tests to analyze the properties in the produced material were started. The five samples were separated to perform the different analyses.

For the image testings, the sintered parts were metallography prepared by cutting it in a precision saw and polising. This group were used in microscopy and microhardness tests.

At first, using Archimedes Principle (ASTMB962 17), the variation between the measurements of total dry mass, wet mass and immersed mass, were used to calculate the porosity of the samples. For these calculations, the relationships in Equations 1 and 2 were used.

$$\frac{\mathbf{M_{dry}}}{(\mathbf{M_{wet}} - \mathbf{M_{immersed}})\mathbf{D_{water}}}, \tag{1}$$

$$\frac{(\mathbf{M_{wet}} - \mathbf{M_{dry}})100}{\mathbf{M_{dry}}}, \tag{2}$$

Where M_{wet} , M_{dry} and $M_{immersed}$ are the wet, dry and immersed masses of the specimens respectively and D_{water} is the density of distilled water at 298 K.

Only calculations from the difference in densities were considered for determining the porosity of the samples due to the error associated to the results of the method applied in specimens with high porosity.

Subsequently, the samples were evaluated for microhardness. Using a Vickers durometer, a HMV Shimadzu Microhardness tester specifically, following ASTM E92-82/2003., with a load of 980.7 mN for fifteen seconds, five hardness values for different regions were obtained for each of the three samples that were cut in the precision saw.

The microstructures of both compositions (50/50 and 30/70) were analyzed using the Scanning Electron Microscope (SEM, JSM6360, Jeol, USA) available at the university. In addition, the Energy Dispersive X-Ray Spectroscopy (EDS) technique (Bruker Nano Compact) connected to SEM were employed to map the cross section of the samples.

In order to improve the solubilization of metals, after the tests described, a new heat treatment was carried out in which the parts were subjected to 923 K for two hours. Afterwards, new tests and detailed analysis of the mechanical compression tests will be carried out and the parameters required for printing will be studied. It will be essential to assess whether the paste composition, with the binder proportion currently used, will actually ensure successful extrusion. If necessary, additional tests with more suitable compositions will be conducted to improve the printing process. The validation of these elements is crucial to ensure the quality and efficiency of the final result.

3. RESULTS AND DISCUSSION

From the acquired data, including the images shown below and the results of calculations presented in Table 2, it is observed that the samples presented a lot of porosity.

Table 2. Dry and immerse porosity and apparent density values

Sample label	Dry porosity (%)	Apparent density (kg/m^3)	Immerse porosity (%)
Ni50Cu50	59.1604	6.5187	26.8794
Ni30Cu70	47.4928	5.9731	33.0436

This results where seemingly caused by the fabrication and characteristics of the materials, and this property will be used in the determination of the application of the material if it persists in the following tests.

From the microhardness test, it is possible to notice a variation of the hardness values, which can be explained due to the nonuniformity of the sintering and non-flatness of the surfaces of the tested bodies. However, it is noticeable that the addition of copper caused an decrease in average hardness, as it shows in Table 3.

Table 3. Vickers microhardness measures.

Sample label	Microhardness (HV)
Ni50Cu50	44.7200
Ni30Cu70	42.0800

The scanning electron microscope images for the samples, presentend in Figures 3 and 4, corroborate the results of the porosity calculations.

From the images, it is perceived the presence of micropores by observing the existence of darker regions in the material. Its origin is due both to the sintering process and to a possible inhomogeneous pressure distribution during the compaction of the material.

With the EDS technique, it was possible to detect the chemical elements on the surface of the samples, illustrated in different colors according to the Figures 5, 6 and 7 and quantified in the Tables 4, 5 and 6. It is worth noting that this process is not very effective for quantifying elements with small atomic numbers, but serves as an indication for general sample analysis. Due to the heterogeneity perceived in the Ni30Cu70 parts, two distinct regions of the same sample were analyzed.

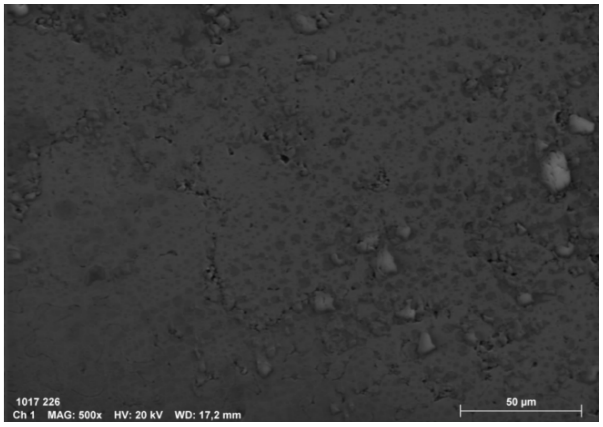

Figure 3. SEM image of Ni50Cu50 cross section

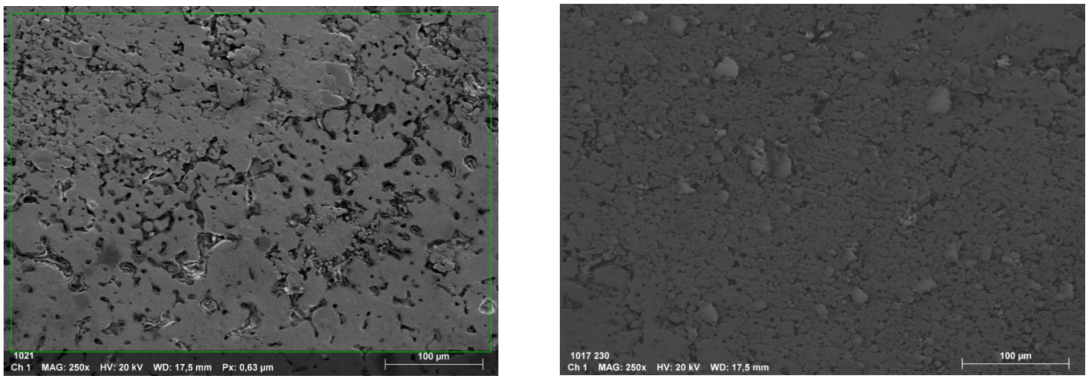

Figure 4. SEM images of Ni30Cu70 cross section

Table 4. Mass percentage of each element in the specimen Ni50Cu50.

Ni	**Cu**	**O**	**C**	**Mn**
30.15	46.54	3.69	3.47	0.16

Table 5. Mass percentage of each element in the first area analyzed of Ni30Cu70.

Ni	**Cu**	**O**	**C**	**Al**	**Mn**	**Si**
52.46	12.75	8.43	5.94	1.78	0.33	0.24

Table 6. Mass percentage of each element in the second area analyzed of Ni30Cu70.

Ni	**Cu**	**O**	**C**	**Al**	**Mn**	**Si**
17.22	48.73	6.45	7.49	1.65	0.12	0.25

The heterogeneity mentioned was caused by the incomplete mixing of nickel and copper powders in the preparation. In order to improve this effect, the use of mixers in the production of new parts is suggested. Observing the results of the EDS analysis, it is possible to notice a large presence of oxygen in the material produced, which indicates an unwanted oxidation.

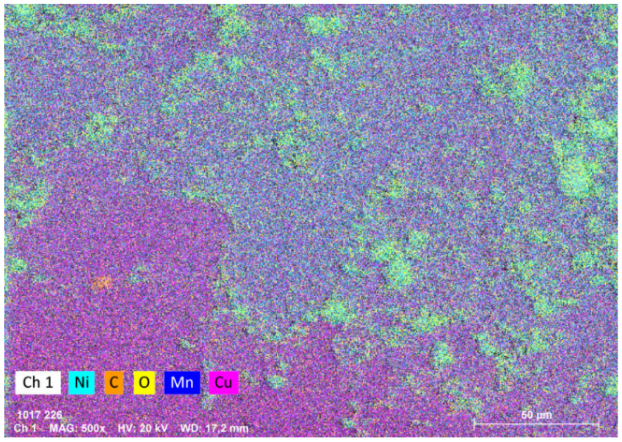

Figure 5. EDS map of Ni50Cu50 sample.

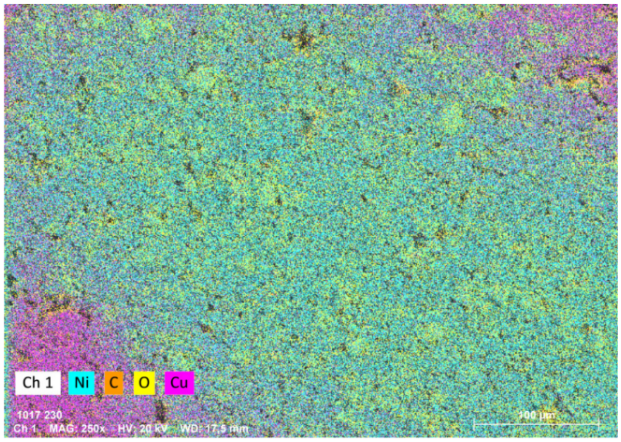

Figure 6. EDS map of first region in Ni30Cu70 sample.

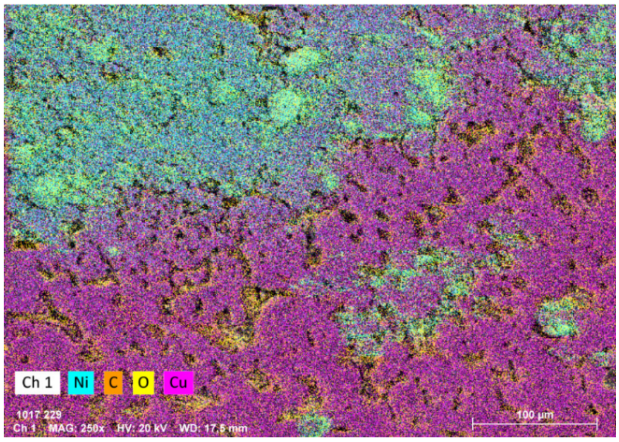

Figure 7. EDS map of first region in Ni30Cu70 sample.

4. CONCLUSIONS

Based on the aforementioned findings, it can be concluded that materials can be successfully manufactured using a binder called polyvinyl alcohol (PVA) in the ratio of 88/12 with metallic powders. This resulted in relatively porous specimens with increasing hardness, correlating with higher amounts of polyvinyl alcohol and copper content, as expected. The presence of elements like aluminum, silicon, and manganese can be attributed to impurities present in the materials used, considering the laboratory environment and handling tools, which may leave traces even after thorough cleaning.

It was observed that the nickel powder used so far had a higher oxygen concentration than expected. Nevertheless, the material produced thus far has exhibited promising properties, indicating a positive outlook for further study. The preliminary results obtained from various tests, including optical and electron microscopy, Vickers microhardness, and

evaluation of apparent density and porosity, have provided valuable insights. These findings have identified areas that require improvement, such as the excessive oxygen content in the nickel composition and unsatisfactory diffusion processes, which have negatively impacted the results. The results obtained so far will contribute to adapt and validate 3D extrusion for development and fabrication of a useful metal alloy.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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