27th ABCM International Congress of Mechanical Engineering
December 04-08, 2023, Florianópolis-SC, Brazil

COB-2023-1267
FABRICATION OF NICKEL PARTS USING HYDROGEL PASTES

Luana Dalla Vecchia de Lima
Allana Anniele Barros da Silva
Maicon Barcellos Chaves
Ana Luisa Cavalheiro de Oliveira
Luana Crozatti Rocha
Marcelle Melo de Oliveira
Natália de Freitas Daudt
Universidade Federal de Santa Maria, Grupo de Tecnologia e Mecânica dos Materiais, Avenida Roraima, 1000, RS - Brazil.
luana.vecchia@acad.ufsm.br , allana.silva@acad.ufsm.br, maiconbchaves@gmail.com, ana.cavalheiro@acad.ufsm.br, luh.crozatti@gmail.com, marcelle.oliveira@acad.ufsm.br, natalia.daudt@ufsm.br

Abstract. *Additive manufacturing is an economical route for the production of high-value materials, such as nickel alloys used in the aerospace industry. In recent decades, new technologies have emerged enabling 3D printing of metallic powders. Among these technologies, 3D extrusion techniques frequently reported for the production of ceramic components, is an alternative for processing metal powders. This technology is suitable for testing new materials and producing small batches, as it enables the use of reduced amounts of raw materials and has a post-processing similar to those commonly used in powder metallurgy. In this study, we investigated the sinterability of nickel parts produced from Ni paste developed for 3D extrusion. For this purpose, we prepared a nickel paste by mixing nickel powder and a hydrogel. At this initial study samples were produced by deposition and compaction of nickel paste. Sintering behavior and microstructure were investigated using light and scanning electron microscopy, X-ray diffraction, and Vickers microhardness. The fabrication of nickel parts through 3D extrusion of the developed pastes are currently under investigation. 3D printing based on extrusion of metallic pastes can be an attractive route for the cost-effective production of small batches of complex shaped parts.*

Keywords: *Additive manufacturing, nickel alloys, aerospace materials, 3D extrusion.*

1. INTRODUCTION

Nickel is a widely used metal in the aerospace sector for aeronautical structures and propulsion systems. In this regard, nickel alloys exhibit excellent performance against high-temperature creep and high corrosion resistance, enabling them to withstand extreme environments where most metallic alloys would fail. Consequently, numerous nickel-based superalloys have been developed in recent decades. The aerospace industry has been the main driving force behind the development of nickel-based superalloys, as Ni-based alloys allow for increased combustion temperature and pressure, thereby enhancing the performance of aircraft jet engines (Smith et al., 2001). Inconel alloy is an example of a nickel-based superalloy widely used in combustion chambers and disc brakes due to its high mechanical strength and resistance to thermal deformation. To meet the demands of the aerospace industry, various alloying elements such as chromium, iron, molybdenum, and copper are added. The high content of alloying elements forms a complex microstructure, making the processing of these alloys challenging through traditional casting and hot forming methods due to segregation and cracking issues (Reed, 2006). To overcome these processing challenges, powder metallurgy routes and, more recently, additive manufacturing (AM) have been applied in the processing of nickel-based superalloys (Sreenu et al., 2020; Babu et al., 2018). Through additive manufacturing, it is possible to produce turbines with innovative designs and customized properties. Given the importance of nickel in the aerospace sector, it is necessary to optimize new additive manufacturing routes to ensure the highest quality of the final component.

Additive manufacturing (AM) has been receiving increasing attention due to its significant advantages over conventional production methods. This technology enables the production of complex-shaped parts using less raw material. It is particularly attractive for the production of high-value materials such as nickel alloys used in aerospace engines. In recent decades, new technologies have emerged, enabling 3D printing, including the printing of metallic components. These technologies are generally classified into two main categories: fusion-based technologies and sintering-based technologies. Fusion-based technologies, such as selective electron beam melting (SEBM) and selective laser melting (SLM), have been the focus of many studies aiming to process nickel alloys and superalloys (Babu et al., 2018; Qiu et al., 2019; Strössner et al., 2015). However, the solidification process during SLM and SEBM results in directional microstructure formation, crack formation, and segregation, which hinder the application of their mechanical properties. On the other hand, sintering-based AM technologies have the ability to produce isotropic parts, including nickel alloys and superalloys, with mechanical properties similar to those produced by powder metallurgy. Sintering-based AM technologies, such as binder jetting and material extrusion, allow for the production of parts with complex geometries, isotropic properties, and potentially higher printing speeds as no metal melting is required during the process. Mostafei et al. (2018), Martin et al. (2021), and Dahmin (2021) demonstrated the production of nickel superalloys using binder jetting, obtaining a homogeneous microstructure, and applying hot isostatic pressing after sintering, resulting in nearly dense parts with excellent mechanical properties. However, binder jetting equipment is not widely available in most research centers, and the high equipment costs make it challenging to apply in most laboratories and industries in Brazil.

Another sintering-based additive manufacturing technology is 3D printing by paste extrusion, also known as direct ink writing. This technology allows for the construction of a 3D part through the deposition of layers of paste. Initially, a paste is prepared by dissolving/dispersing ceramic or metallic powder in a suspension. Then, the paste is deposited layer by layer using a screw or pneumatic extruder. Finally, post-processing steps such as binder removal and sintering can be applied. Extrusion-based technologies have been frequently applied for the production of ceramic components (Faes, 2015), but there is a lack of investigation in metal fabrication. Recently, this technology has started to be adapted for the production of metallic components, such as titanium alloys (Elsayed, 2019). The extrusion technology is suitable for testing new materials and producing small batches, as it allows for the use of reduced amounts of raw materials and has a post-processing process similar to those commonly used in powder metallurgy. Nocheseda et al. (2021) fabricated copper and SS316L parts by 3D extrusion of biodegradable cellulose hydrogels. The advantage of using hydrogels is their lower environmental impact compared to solvent-based or toluene-based pastes.

In summary, recognizing that AM processes are particularly attractive for the processing of higher-cost materials, such as nickel alloys used in the aerospace sector, in this preliminary study, we investigated the sinterability of nickel pastes used for 3D extrusion of metallic pastes. Nickel pastes based on hydrogel were developed, and the parts were produced by depositing the nickel paste into a mold followed by cold compaction. The effect of binder composition on sintering behavior and microstructure was then investigated.

2. MATERIALS AND METHODS

In this section, the experimental procedures, starting materials, paste composition and characterization techniques conducted are presented. Deionized water and polyvinyl alcohol (PVA, ACS) were used for preparing the polymer water solution. The starting powder was characterized by Scanning Electron Microscopy (SEM) as shown in Figure 1 and Energy-Dispersive X-Ray Spectroscopy (EDS) as can be seen in Table 1, in spite of EDS not being the most suitable technique for measuring oxygen, it gives an indication that the start powder has a higher oxygen content.

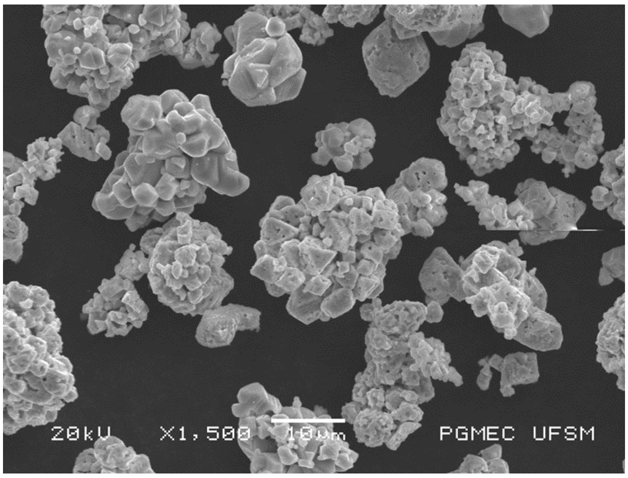


Figure 1. SEM image of starting Nickel powder.

Table 1. EDS composition.

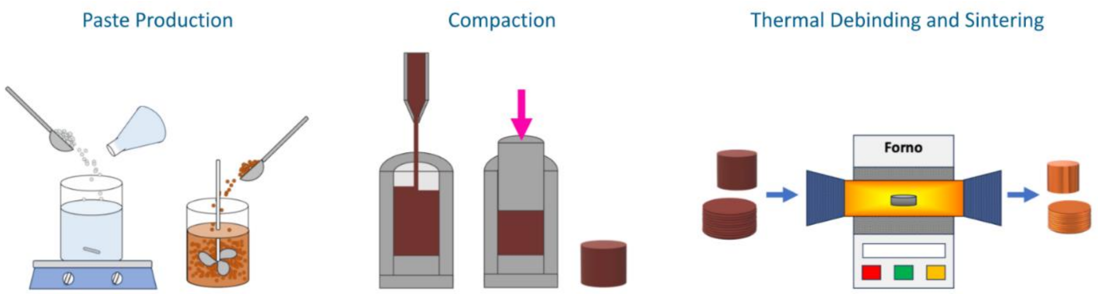
Element	Mass (%)
Ni	91.06
C	6.25
O	2.69

The polymer water solution was prepared by dissolving the binder (PVA) in deionized water; two compositions containing 2% and 7% of PVA were tested. Afterwards the paste was prepared by adding the nickel powder to the polymer solution in a ratio varying from 75% to 80 wt.% The composition of the pastes are shown in Table 2.

Table 2. Composition and proportion of mixtures for nickel paste.

Paste Label	Binder	Binder/Water (wt.%)	Powder load (wt.%)
Ni 88_2PVA	PVA	2/98	88
Ni 75_2PVA	PVA	2/98	75
Ni 75_7PVA	PVA	7/93	75

In order to investigate the effects of hydrogel composition on the sinterability of nickel parts, preliminary samples were prepared by deposition of nickel hydrogel pastes in a die of 10 mm diameter followed by compaction at 50 MPa. Thermal debinding and sintering were performed in a vacuum furnace (Fortelab, Brazil). Compacted samples were heated up to 500°C at 2 K min^{-1}, where the temperature was held for 60 min to remove the binder. Afterwards, samples were heated under vacuum (< 10^{-1} Pa) up to 1200°C at 10 K min^{-1} followed by a dwell time of 120 min at sintering temperature. Then, the samples were cooled in the furnace until they reached room temperature as depicted in Figure 2.



(a)

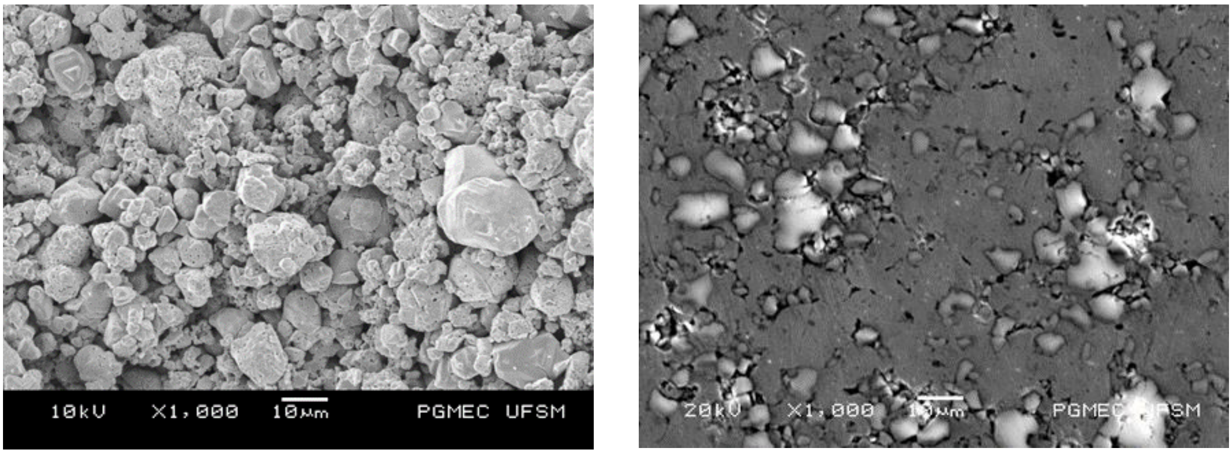
(b) (c)

Figure 2. Schematic of the manufacturing process (a), samples after heat treatment and cross section cutting (b) and after grinding and polishing (c).

Sample microstructure was evaluated by light microscopy (Olympus B220, Japan) and Scanning Electron Microscopy (SEM, JSM6360, Jeol, USA), for that sample were cross-cut and polished. The elemental composition of the samples was determined by Energy Dispersive X-Ray Spectroscopy using the EDS system (Bruker Nano Compact) connected to SEM. Porosity was estimated by image analysis using ImageJ software. Vickers Microhardness was measured in the cross section of the polished samples using a HMV Shimadzu Microhardness tester applying a load of 1.916 N for 15 s following to ASTM E92-82/2003. Compression tests were performed in the compacted samples using a universal electromechanics tester (DL-10000, EMIC, Brazil).

3. RESULTS AND DISCUSSION

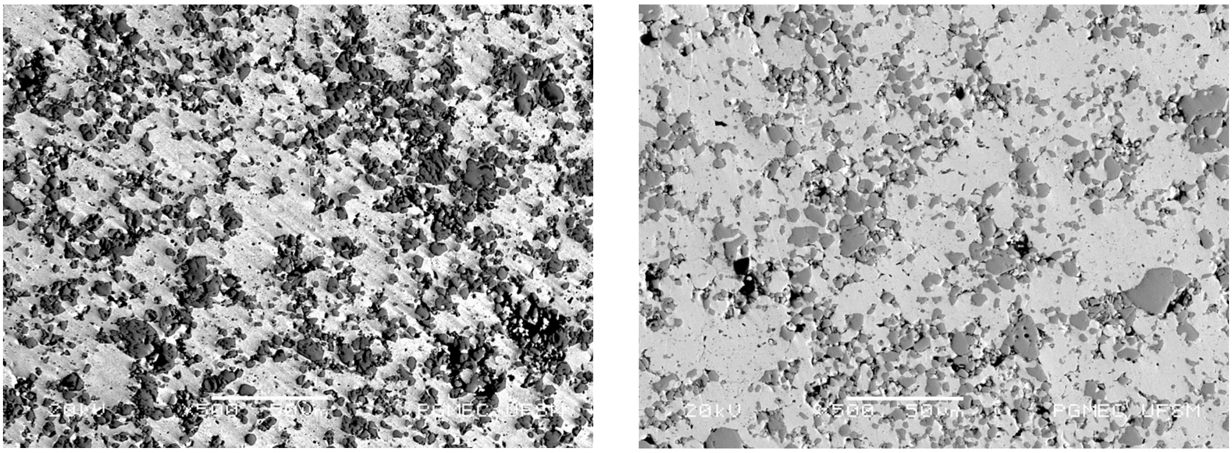
In Figure 3 is shown the SEM image of the Ni 88 part before and after sintering. It is possible to notice there was diffusion among the nickel particles leading to densification.



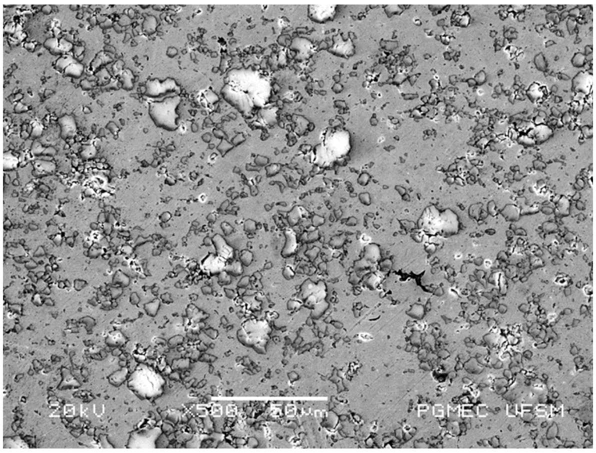
(a) (b)

Figure 3. Cross section of Ni 88_2PVA part: green part before sintering (a) and after sintering (b).

In Figure 4 is shown the SEM image of the cross section of Ni 75_2PVA, Ni 75_7PVA and Ni 88_2PVA parts after sintering. It is possible to notice the presence of small pores and a second phase in all parts, which may be a Nickel oxide phase due to high oxygen concentration in starting powders.



(a) (b)



(c)

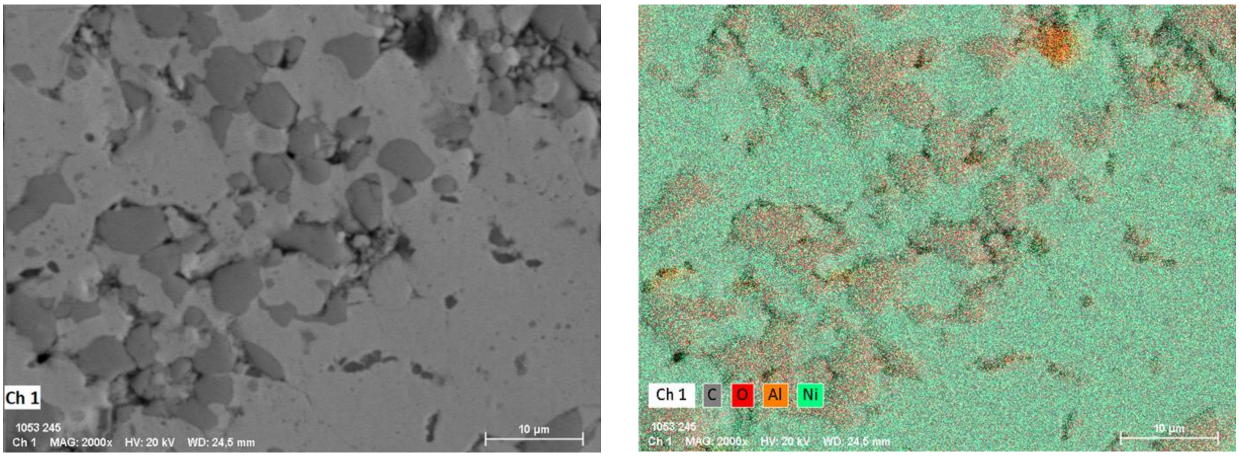
Figure 4. Cross section of as sintered 88Ni_2PVA (a), Ni 75_2PVA (b) Ni 75_7PVA (c).

In Table 3 are presented the results of shrinkage, porosity and microhardness. As expected, the high amount of powder load resulted in a lower porosity. On the other hand, the samples, with lower powder load have a higher hardness, these results may be related with possible carbide precipitation and high oxygen content due high binder amount. These results will be further analyzed in our ongoing study.

Table 3. Porosity, Shrinkage and Microhardness values.

Sample Label	Shrinkage in height (m)	Shrinkage in diameter (m)	Porosity (%)	Microhardness (HV)
Ni 88_2PVA	-	-	2.31	33.02
Ni 75_7PVA	0.000825	0.0008	3.43	44.58

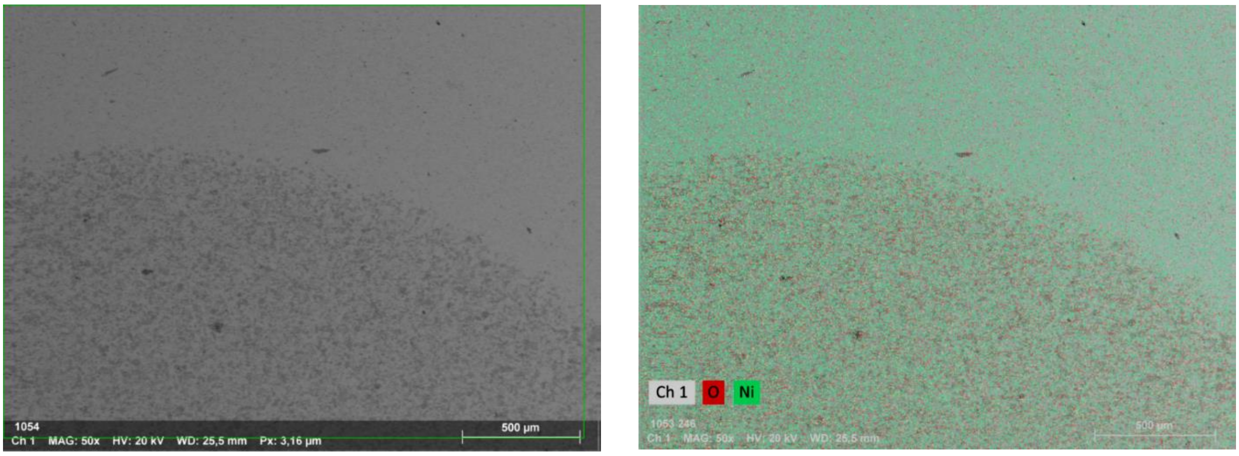
In Figure 5, is shown the SEM image of the cross section and EDS map of Ni75_2PVA sintered part. In the EDS map, the red dots are related to oxygen and the green dots to nickel. It is possible to notice in Figure 5(a) that there is a concentration of oxygen in the darker grains, which suggests the formation of nickel oxide.



(a) (b)

Figure 5. SEM of the cross section (a) and EDS map (b) of as sintered Ni75_2PVA.

In Figure 6, is shown the SEM image of the cross section and EDS map of the sintered Ni75_7PVA part. It is possible to notice in Figure 4(a) that there is a concentration of darker grains in the central area of the sample, which suggests the nickel oxide formation was higher in the middle of the sample. For sintering an oxygen getter material was used to decrease sample oxidation, this getter material could be the reason for higher oxygen removal from the sample surface than the inner.



(a) (b)

Figure 6. SEM of the cross section (a) and EDS map (b) of as sintered Ni75_7PVA.

In all Ni parts the EDS analysis verified that the darker regions present higher oxygen concentration, indicating the formation of nickel oxides in the samples. To reverse this situation, the use of a hydrogen atmosphere during the sintering processes is proposed, since the hydrogen can reduce the Ni.

In Figure 7 the results of the compression test are shown, in spite of the presence of oxide in the samples, they showed a ductile behavior, compression strength of ca. 330 MPa was achieved in 40 % of deformation.

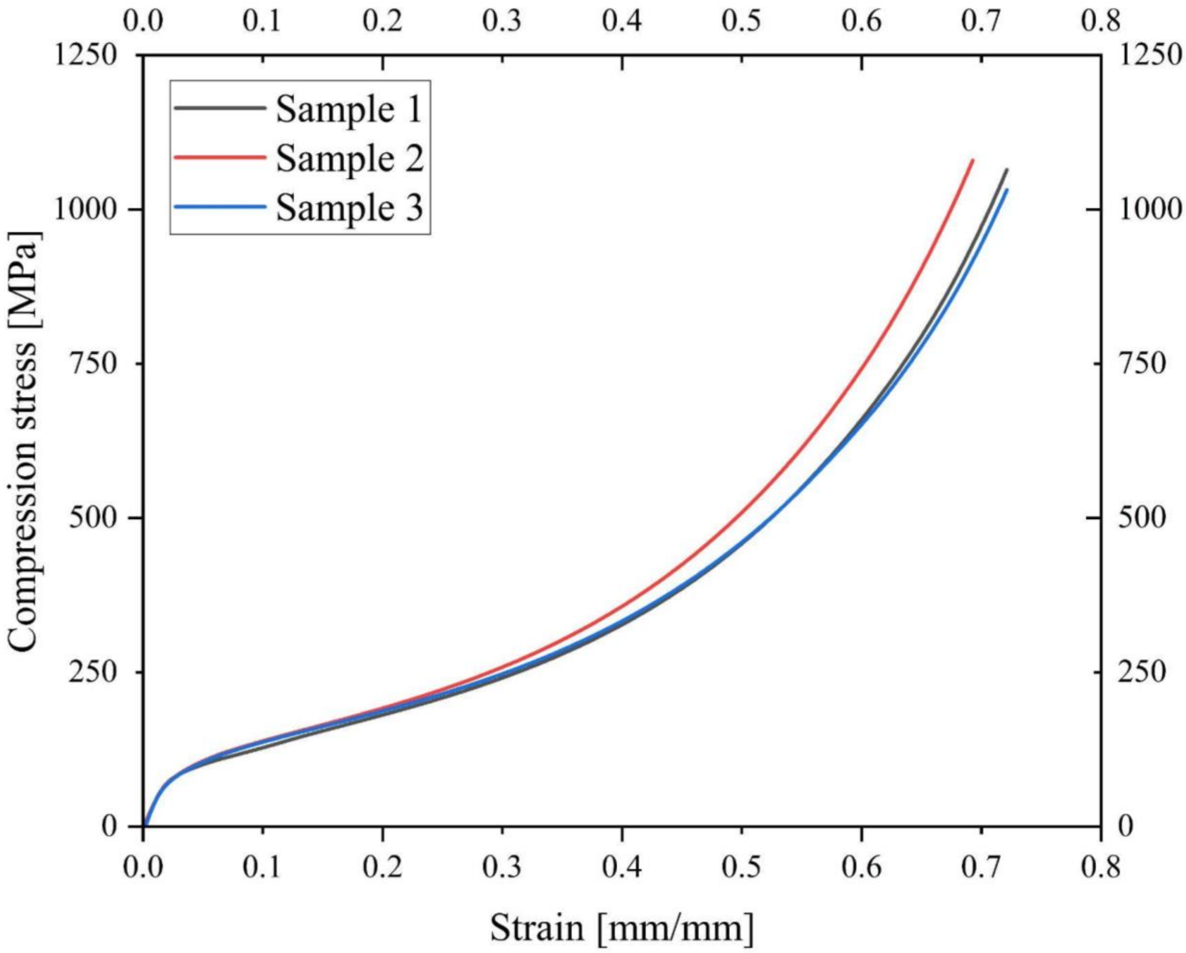


Figure 7. Compression test of Ni75_7PVA.

4. CONCLUSION

Based on the aforementioned results, it is concluded that nickel parts with ductile behavior can be manufactured using a hydrogel nickel pastes. Sample density and hardness can be improved by increasing the powder load in the paste, however higher powder loading increases paste viscosity, which is expected to reduce printability. Therefore, in our ongoing study we will optimize the powder loading to achieve suitable printability and density.

Microstructural analysis by SEM revealed the presence of nickel oxide and microporosities in the samples, suggesting the need for adjustments in the sintering processes to improve the uniformity and quality of the parts. In spite of the oxide, the nickel parts showed a ductile behavior. In summary, the studies carried out provided promising information on the composition, hardness and microstructure of the nickel samples after compaction, sintering and subsequent treatment. The observations and analyses performed allow an initial assessment of the properties and characteristics of the parts produced, highlighting areas that can be improved in the manufacturing processes. In addition, they contribute to the advancement of knowledge in the area of nickel materials and may provide insights for the development of more efficient additive manufacturing processes.

5. ACKNOWLEDGEMENTS

We thank Professor Dr. Inacio Limberger for their experimental support and CNPq for financial funding and the university for the opportunity.

6. REFERENCES

Babu, S.S., Raghavan, N., Raplee, J., Foster, S.J., Frederick, C., Haines, M., Dinwiddie, R., Kirka, M.K., Plotkowski, A., Lee, Y., Dehoff, R.R., 2018. Additive Manufacturing of Nickel Superalloys: Opportunities for Innovation and Challenges Related to Qualification, Metallurgical and Materials Transactions A, Vol. 49, pp. 3764–3780.

Dahmen, T., Henriksen, N.G., Dahl, K.V., Lapina, A., Pedersen, D.B., Hattel, J.H., Christiansen, T.L., Somers, M.A.J., 2021. "Densification, microstructure, and mechanical properties of heat-treated MAR-M247 fabricated by Binder Jetting". Additive Manufacturing, Vol. 39, pp. 101912.

Elsayed, H. Rebesan, P., Giacomello, G., Pasetto, M., Gardin, C., Ferroni, L., Zavan, B., Biasetto, L., 2019. "Direct ink writing of porous titanium (Ti6Al4V) lattice structures". Materials Science and Engineering: C, Vol. 103, pp. 109794.

Faes, M., Valkenaers, H., Vogeler, F., Vleugels, J., Ferraris, E., 2015. "Extrusion-based 3D Printing of Ceramic Components". Procedia CIRP, Vol. 28, pp. 76-81.

Kumar, L.J., Pandey, P.M., Wimpenney, D.I., 2019. *3D Printing and Additive Manufacturing Technologies*. Springer Nature, Singapore.

Martin, E., Natarajan, A., Kottilingam, S., Batmaz, R., 2021. "Binder jetting of 'Hard-to-Weld' high gamma prime nickel-based superalloy RENÉ108". Additive Manufacturing, Vol. 39, pp. 101894.

Miura, S., Yamagishi, R., Miyazaki, R., Yasuda, K., Kawano, Y., Yokoyama, Y., Sugino, N., Kameda, T., Takei, S., 2022. "Fabrication of High-Resolution Fine Microneedles Derived from Hydrolyzed Hyaluronic Acid Gels in Vacuum Environment Imprinting Using Water Permeable Mold". Gels, 8(12), 785.

Mostafaei, A., Neelapu, S.H.V.R., Kisailus, C., Nath, L.M., Jacobs, T.D.B., Chmielus, M., 2018. "Characterizing surface finish and fatigue behavior in binder-jet 3D-printed nickel-based superalloy 625". Additive Manufacturing, Vol. 24, p.p. 200-209.

Reed, R.C., 2006. *The Superalloys Fundamentals and Applications*. Cambridge University Press, Cambridge.

Signor, F., Carvalho, M., Pozzebon, A., Bevilaqua, W., Limberger, I.F., Daudt, N.F., 2023. "Fabrication of Copper Parts by 3-D Extrusion of Highly Viscous Paste". *Euro PM2023 Congress & Exhibition*.

Smith, R.J., Lewi, G.J., Yates, D.H., 2001. "Development and application of nickel alloys in aerospace engineering". Aircraft Engineering and Aerospace Technology. Vol. 73, pp. 138-147.

Sreenu, B., Sarkar, R., Kumar, S.S.S., Chatterjee, S., Rao, G.A., 2020. "Microstructure and mechanical behavior of an advanced powder metallurgy nickel base superalloy processed through hot isostatic pressing route for aerospace applications". Materials Science & Engineering A, Vol. 797, pp. 140254.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.