Utilization of Stainless Steel 316L and Red Mud Composite on Binder Jetting for Innovative Direct Carbon Fuel Cell Anode production

Naiqi Shang¹, Davide Mombelli¹, Marco Mariani¹, Gianluca Dall'Osto¹, Nora Lecis¹, Marco Zago², Ilaria Cristofolini², Vigilio Fontanari²

¹Dipartimento di Meccanica, Politecnico di Milano, Via La Masa 1, 20156 Milano, Italy
²Dipartirtimento di Ingegneria Industriale, Università di Trento, Via Sommarive 9, 38123 Povo (TN), Italy Keywords: red mud, binder jetting, direct carbon fuel cell Presenting author email: naiqi.shang@polimi.it

Red mud, a solid biohazard waste from the Bayer process, is a concerning byproduct of the aluminium industry. The production of one tonne of alumina is accompanied by nearly 0.8 to 1.5 tonnes of red mud (Yulikasari et al., 2024). It potentially damages the environment and affects living organisms since it is highly alkaline (Pei et al., 2023), has high salinity (Jia et al., 2024) and contains heavy metallic elements. The contribution of metal oxides (Fe₂O₃, SiO₂, Al₂O₃, Na₂O, CaO, ...) to red mud exceeds 80% (Bai et al., 2024). However, recovering valuable metals from red mud residues is not financially viable. The utilization of metal-oxides composite containing red mud, therefore, has become a promising approach to waste treatment.

The ongoing research, referred to as the JetCell project, aims to apply red mud to the anode of direct carbon fuel cells (DCFC) with the help of additive manufacturing. DCFC is a solid carbon-fueled power generator in which the electrochemical reaction takes place in the anode (Cao et al., 2007). Researches indicate some metallic oxides (e.g., CaO, MgO, and Fe₂O₃), which are enriched in red mud, provide catalytic effects on the oxidation of carbon fuels (Li et al., 2010). In some works, catalytic materials have been added to the anode of DCFC to enhance the electrochemical reaction (Ahsan et al., 2023; Li et al., 2024). Binder jetting, as one of the metal additive manufacturing techniques, has been employed to fabricate the anodes with high accuracy and functionality. Its non-fusion-based production feature naturally provides the possibility of couple unmixable materials. Stainless steel AISI 316L (SS316L) is selected as the main anode material due to its excellent electrical conductivity and corrosive resistivity, whereas red mud is added to improve the catalytic effects. To address the anisotropic dimensional shrinkage of sintered samples, the mixture samples are analyzed using metrological methods by the coordinate measuring machine.

This study focuses on fabricating SS316L and red mud mixtures on binder jetting, which is the first time in the binder jetting field. The print- and sinter- ability of SS316L and red mud mixtures are tested. Powder characterizations (particle size distribution, flowability, powder morphology) have been performed on red mud and SS316L, and mixtures with a ratio of 1, 2, and 5 wt.% red mud have been printed. The samples are debinded in argon at 470 °C and sintered at 1260 °C and 1360 °C under vacuum, followed by material characterizations that prove the feasibility of fabricating the mixtures on binder jetting, which includes a light optical microscope (LOM), a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), and density.

The density of the mixtures was measured by Archimedes' Principle, as shown in Table 1. The density of samples sintered at 1360 °C is around 92%, a little bit lower if compared with pure 316L samples. Thus, the red mud particles hinder the densification at high temperature. At the low sintering temperature (1260 °C) the density of mixtures is relatively equivalent to pure 316L samples, near 83.5%, and the red mud concentration has little effect on it.

	1 wt.%	2 wt.%	5 wt.%	SS316L (Jamalkhani et al., 2022)
1360 °C	92.96%	91.81%	91.77%	95.2% (1355 °C)
1260 °C	83.48%	83.33%	87.23%	83.5% (1250 °C)

Table 1. Density of SS316L and RM mixtures sintered at 1360 °C and 1260 °C

Error! Reference source not found. illustrates the microstructure images of the sintered SS316L and RM mixtures with different concentration of red mud. Red mud particles are usually larger than the pores and also are irregular. It can be observed the red mud particles are well distributed. It is easier to see the red mud particles at 1360 °C since the particles are irregular while the pores are relatively small and round. For samples sintered at 1260 °C, the grain sizes are smaller compared with 1360 °C. The excessive sintering temperature inevitably leads to grain growth. The insufficient sintering temperature, nevertheless, degrades the densification. Both cases affect the final strength of the workpieces. The matrix is mostly stainless steel 316L, while red mud particles are well bonded to the matrix because no voids at the interface between the matrix and particles are observed. However, iron oxides, originally in the red mud, were not found in EDS results. It is presumed that the iron oxides are reduced during the vacuum sintering. Since the debinding gas atmosphere is argon, it is difficult to remove the carbon from the binder during debinding. The residual carbon reacts with iron oxides in the sintering step. Thus, the catalytic effects of the mixtures and the way of preserving iron oxides need to be investigated further.

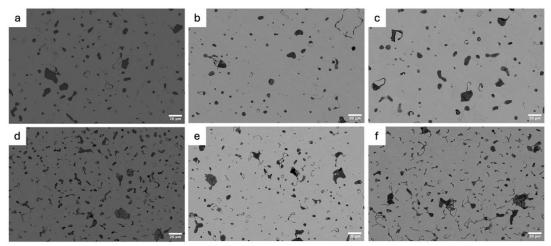


Figure 1. SEM images of the mixtures of stainless steel 316L and red mud: a) 1 wt.% RM, b) 2 wt.% RM, c) 5 wt.% RM at 1360 °C, d) 1 wt.% RM, e) 2 wt.% RM, f) 5 wt.% RM at 1260 °C

In conclusion, this article investigates an innovative combination of SS316L and RM as raw materials in the powder-based additive manufacturing technique, which is the first time that these two materials have been studied in combination in this context. The incorporation of industrial waste red mud not only provides a sustainable solution for the recycling of red mud but also has the potential to improve the properties of the final component. The results of the study provide important insights into the fabrication of composite materials, which can particularly help to improve the structural and functional properties of DCFC anodes.

References

- Ahsan, M., Fu, P., Bie, K., Irshad, M., Liu, Y., & Xu, T. (2023). Investigation of ceria-molten carbonate electrolyte, composite anode and its catalytical effect on various carbon fuels in molten carbonate direct coal/carbon fuel cell. *Fuel*, *335*, 126937. https://doi.org/https://doi.org/https://doi.org/10.1016/j.fuel.2022.126937
- Bai, B., Chen, J., Bai, F., Nie, Q., & Jia, X. (2024). Corrosion effect of acid/alkali on cementitious red mud-fly ash materials containing heavy metal residues. *Environmental Technology & Innovation*, *33*, 103485. https://doi.org/https://doi.org/10.1016/j.eti.2023.103485
- Cao, D., Sun, Y., & Wang, G. (2007). Direct carbon fuel cell: Fundamentals and recent developments. *Journal of Power Sources*, 167(2), 250-257. https://doi.org/https://doi.org/https://doi.org/10.1016/j.jpowsour.2007.02.034
- Jamalkhani, M., Asherloo, M., Gurlekce, O., Ho, I.-T., Heim, M., Nelson, D., & Mostafaei, A. (2022). Deciphering microstructure-defect-property relationships of vacuum-sintered binder jetted fine 316 L austenitic stainless steel powder. *Additive Manufacturing*.
- Jia, K., Zhou, Z., Singh, S. V., & Wang, C. (2024). A review of the engineered treatment of red mud: Construction materials, metal recovery, and soilization revegetation. *Results in Engineering*, 24, 102927. https://doi.org/https://doi.org/10.1016/j.rineng.2024.102927
- Li, L., Xie, Y., Han, T., Zhang, J., Yu, F., Li, G., Sunarso, J., Yang, N., & Li, Y. (2024). BaO-modified finger-like nickel-based anode for enhanced performance and durability of direct carbon solid oxide fuel cells. *Fuel*, 368, 131656. https://doi.org/https://doi.org/10.1016/j.fuel.2024.131656
- Li, X., Zhu, Z., De Marco, R., Bradley, J., & Dicks, A. (2010). Evaluation of raw coals as fuels for direct carbon fuel cells [Article]. *Journal of Power Sources*, 195(13), 4051-4058. https://doi.org/10.1016/j.jpowsour.2010.01.048
- Pei, J., Pan, X., Wang, Y., Lv, Z., Yu, H., & Tu, G. (2023). Effects of alkali and alkaline-earth oxides on preparation of red mud based ultra-lightweight ceramsite. *Ceramics International*, 49(11, Part B), 18379-18387. https://doi.org/https://doi.org/10.1016/j.ceramint.2023.02.210
- Yulikasari, A., Tangahu, B. V., Nurhayati, E., Arliyani, I., Mashudi, Titah, H. S., Lam, Y. M., & Wang, Y. (2024). A comprehensive review of integrated phytoremediation and nanoparticle methods for heavy metal in red mud. *Ecotoxicology and Environmental Safety*, 288, 117381. https://doi.org/https://doi.org/10.1016/j.ecoenv.2024.117381

Acknowledgments

Funded by the European Union - NextGenerationEU, under the National Recovery and Resilience Plan (PNRR), Mission 4, Component 2, Investment 1.1, PRIN PNRR 2022 project - JETCELL, CUP D53D23018060001, Prot. P20225LHPX