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Dissolvable HIP Space-Holders Enabling more Cost Effective and Sustainable Manufacture of Hydrogen Electrolyzers

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Abstract. Polymer Electrolyte Membrane (PEM) electrolyzers are a key to the future of global hydrogen production. However, current systems rely on titanium components manufactured through energy and resource intensive processes which make up a large proportion of the overall capital cost of an electrolyzer stack. In this work circular economy principles have been applied to investigate net shape powder manufacturing routes for these titanium plate and porous film components. Approaches include (1) direct HIP of waste stream materials such as un-melted titanium sponge fines or subtractive machining swarf (2) net shape manufacturing of complex geometries using innovative dissolvable salt space holding inserts (3) in-situ nitriding methods (4) streamlining a large number of processing stages within the existing supply chain. In order to assess the environmental impact of the proposed manufacturing routes an embodied carbon analysis was conducted comparing the emissions potentially generated via this powder process versus the traditional supply chain.

Introduction

Electrolysis is a leading hydrogen production pathway to achieve the US Department of Energy 2021 Hydrogen Energy Earthshot goal of reducing the cost of clean hydrogen by 80% to $1 per 1 kilogram in 1 decade ("1 1 1") [1]. Hydrogen produced via electrolysis can result in net-zero greenhouse gas emissions, depending on the source of the electricity used. Polymer Electrolyte Membrane (PEM) electrolyzer systems extract high purity hydrogen gas directly from water, and are widely seen as one of the most commercially viable technologies to ramp up the production of "green" hydrogen derived from renewable electricity [2].

An extensive technical assessment of suitable materials capable of enabling more economical hydrogen generation has concluded that titanium is the only commercially viable base material capable of meeting the expected service life of PEM electrolysis bipolar plate and porous transport layer components, particularly at the anode which experiences high electrochemical potentials and acidity under dynamic loading conditions [3]. As a result, titanium is currently a major contributor to the overall cost of PEM electrolyzer equipment [4]. Net shape powder metallurgy is therefore an interesting area of research with the potential to reduce overall material consumption by minimizing waste. Utilization of recycled or minimally processed titanium powder sources within a circular economy framework would also help ensure the electrolyzer stack has the lowest possible embodied carbon emissions. To that end, this paper presents a set of Hot Isostatic Pressing (HIP) feasibility trials aiming to showcase an innovative consolidation route, using dissolvable space holding inserts and unconventional powder feedstocks. This method could feasibly be used to fabricate highly intricate PEM bipolar plates with greater design freedom, allowing drastic changes such as integrating porous transport layers directly into the bipolar plate. Such a design may also improve operational efficiency and make inroads into reducing the Levelized Cost of Hydrogen (LCOH) production.

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Notably, the unconventional HIPing concepts developed here are likely to appeal for many other possible end-uses beyond the hydrogen value chain. Any application requiring complex powder metallurgy parts to be made at low cost and with minimal embodied carbon emissions could benefit, particularly where internal cavities or tailored porosity are required.

Dissolvable Space Holding Inserts

Powder Hot Isostatic Pressing (Powder-HIP) involves the application of sufficient heat and isostatic fluid pressure to deform an evacuated canister holding loose powder. This enables solid state inter-diffusion of the powder particles over a sufficient period of time to densify them into a solid object. This can lead to very low levels of porosity defects and an excellent balance of microstructural and mechanical properties, often comparable or better than that of cast and wrought engineering alloys.

One well documented drawback for Powder-HIP of intricate metallic components is the need to fabricate a complex canister via a welding/joining or forming process, then remove it through a hazardous and slow chemical leaching process. These processes often make costs and production timescales prohibitive for high throughput components.

In an attempt to address this fact, the authors have created an innovative approach that uses pre-formed dissolvable salt space-holding inserts, strategically positioned to guide the consolidation of powder into a relatively tightly tolerance geometry after full densification. These allow the use of relatively low cost cylindrical or cuboidal steel HIP canisters. The post-consolidation steps are also simplified by using this method as such simple canisters can be mechanically cut and peeled away rather than requiring chemical leaching in an acid bath. This process is aided by the use of a simple diffusion barrier (such as graphite sheet or a boron nitride coating) between the canister and the contents. The salt space-holding sections within the densified part can be removed by gradual dissolution in water (as long as an access route for flowing water is maintained). This only leaves a non-hazardous brine to dispose of or re-use. If the salt insert has suitable thermo-mechanical properties it is envisaged that a true net shape component could be fabricated with no subsequent subtractive machining needed.

High purity NaCl "table salt" crystals have a melting point of 801°C. Their tensile proof strength has been shown to reduce considerably above 300°C [5], but compressive strength is likely to be maintained at much higher temperatures, approaching the melting point under near isostatic loading. NaCl is therefore likely to be compatible with the consolidation of powder materials that are readily HIP consolidated below around 750°C.

Other soluble ionic compounds do exist with far higher melting points, most notably Sodium Aluminate ($NaAl_2O_3$) which has a melting point of 1650°C, meaning it is likely to be compatible with the high temperature and pressure Powder-HIP consolidation required for most engineering alloys.

Insert Preparation

The manufacturing concepts explored in this work include the formation of both solid salt inserts, designed to hold a geometric space during Powder-HIP and be dissolved completely post-HIP, as well as the formation of porous structures. The use of NaCl salt as a space-holding insert for manufacture of titanium porous structures and foams has been widely investigated in the biomedical field, primarily through press and sinter [6] or hot pressing technologies [7]. The authors therefore have high confidence than similar structures can be created using the HIP method outlined in this work. The key requirement for fully dissolving the salt portion is that a fully interconnected network of both titanium and salt is formed during HIP. The best way to achieve this is the carefully control the particle size (normally the titanium powder is much finer than the salt particles) and use a near 50:50 blending ratio by volume [7].

There are a multitude of methods that could be used to form pure NaCl into a pre-shaped insert with relatively high density. The methods trialled were:

1. Single crystal NaCl cast by the Kyropoulos method at a commercial vendor, and purchased in the form of polished transparent discs, termed "optical windows". These were utilized in the as-received form (Fig. 1a), but internal work has proven that they can be subtractively machined into a more complex geometry.
2. Cold Isostatic Pressing (CIP) within an additively manufactured flexible polymer mold (Fig. 1b) was used to fabricate a green compact insert from mechanically ground NaCl salt granules at 400-600MPa with the required geometry (Fig. 1c). The cold pressing method described above opened up additional opportunities to create bi material titanium/NaCl inserts, by either building up different layers of each material, or fully blending materials at a predetermined ratio within a CIP mold (Fig. 1d).
3. An additional method was employed for $NaAl_2O_3$, which was not pre-formed into a solid insert prior to HIP. Instead $NaAl_2O_3$ and Ti-6Al-4V were simply weighed out into the appropriate ratio, then vibratory blended before being layered manually directly within the HIP canister. $NaAl_2O_3$ salt is significantly more hazardous than NaCl table salt, and as a precaution all powder handling was undertaken in a dry enclosed glovebox environment in order to avoid any moisture reacting with the finely divided salt particles which are easily airborne.

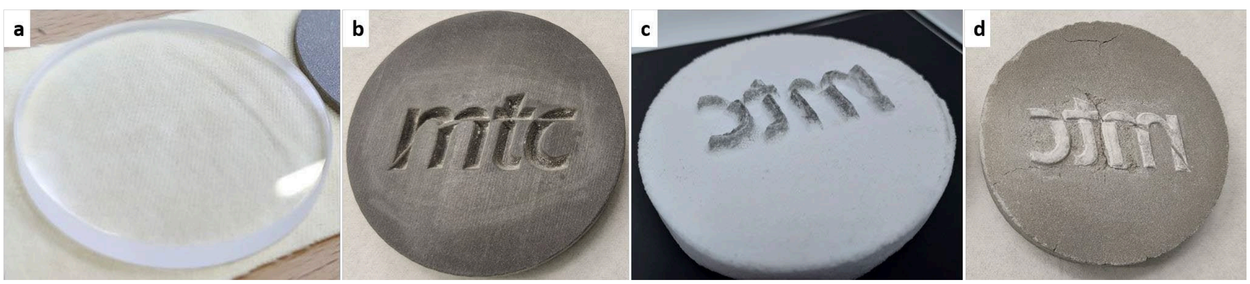

Figure 1: a) Commercially available single crystal NaCl "optical window", b) flexible polymer CIP mold with lettering, c) NaCl disc CIP compacted from granules at 400MPa (lettering filled with Ti-64 + NaCl blend), d) Ti-64 + NaCl blend disc CIP compacted from granules at 400MPa (lettering filled with pure NaCl).

Low Embodied Carbon Powder Materials

In order to enhance the circular economy credentials of HIP components, this work has also evaluated powder forms of titanium with potentially lower embodied carbon in their production than conventional gas or plasma atomization processes. These included those listed below and shown in Fig. 2:

1. Commercial purity titanium (CP-Ti) and Ti-6Al-4V obtained through the solid-state hydride-de-hydride (HDH) pulverization process at an external vendor were used.
2. CP-Ti in the form of Kroll extracted titanium "sponge dropout waste" was obtained from a commercial titanium supplier, sieved to a sub-75µm fraction, and directly HIPed.
3. CP-Ti ingot and billet machining chip was also obtained from a commercial titanium supplier and attempts were made to mechanically ball-mill it down to a usable powder fraction, but the resulting material was not suitable due to excessive contamination.

It is recognized that all of these re-processed/waste materials will have significantly higher interstitial element content, most notably oxygen and carbon, however, prior work in the literature

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has proven titanium's ability to vacuum sinter and diffusion bond with good mechanical bond strength despite the presence of such impurities. For example, angular 144 177μm HDH CP-Ti powder containing 1500ppm oxygen had been successfully HIP consolidated to 98.1% density after a 90 minute dwell at 700°C and 34MPa, with notably high rates of densification in the early stages relative to more spherical powders due to higher stresses at angular interfaces [8].

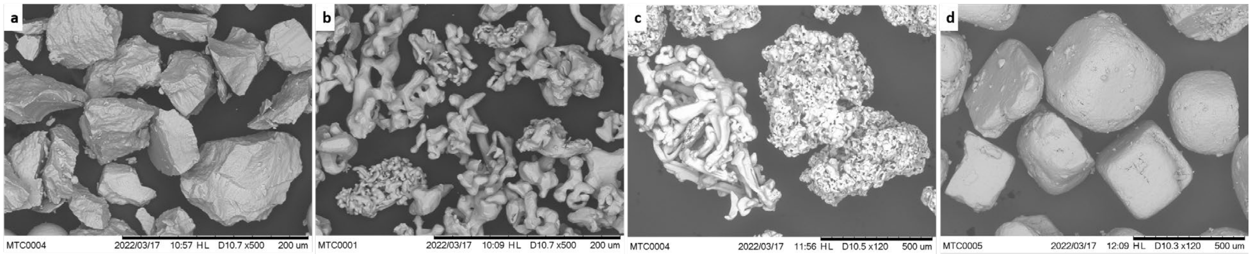

Figure 2: SEM powder analysis images of a) -75μm sieved Ti-6Al-4V HDH (x500), b) -75μm sieved CP-Ti sponge (x500), c) +75μm sieved CP-Ti sponge as received (x120), d) NaCl granules as received (x120).

HIP Conditions

All titanium powder and NaCl salt layers were manually spread within 65mm outer diameter cylindrical mild steel canisters under an air environment. $NaAl_2O_3$ blended powders were spread under an enclosed argon glovebox environment as fine salt particles easily became airborne. TIG welding was employed under argon back purge and leak checking confirmed a suitable seal had been achieved. Canisters were evacuated and crimped shortly before HIP. All HIP cycles included a 15°C/min ramp up in temperature and after the hold period natural cooling to 200°C was employed before forced cooling to room temperature and pressure.

The relatively soft commercial purity titanium grade 2 (CP-Ti) has been chosen as a material capable of full Powder-HIP consolidation under the low temperatures and pressures compatible with NaCl shape-holding inserts. Conditions of 750°C and 35MPa for 4 hours were targeted based on the work of Lograsso et al [8].

Conventionally, higher strength titanium alloys such as grade 5 (Ti-6Al-4V) are often HIP consolidated at temperatures of around 900-950°C and pressures of ~100MPa for ~2 hours [9]. However, due to the requirements of the NaCl space-holding inserts, in these feasibility trials Ti-6Al-4V powder material was HIPed using the same low temperature and pressure conditions as for CP-Ti.

A subsequent set of HIP trials investigated the potential use of sodium aluminate salt ($NaAl_2O_3$) for more conventional high temperature Powder-HIP of Ti-6Al-4V at 920°C and 103MPa for 2 hours. To the authors knowledge no assessment of $NaAl_2O_3$ as a space holding insert during Powder-HIP of titanium or any similar powder alloys has been reported in the open literature.

Post-HIP Characterization

Once HIP cycles were completed the canisters were cross-sectioned without the use of cutting fluid in order to avoid dissolving the salt inserts. Dry grinding and polishing attempted to produce a clean surface for imaging, but the result was less uniform than typical fluid-based grinding and polishing material preparation techniques.

Figure 3 summarizes the space-holding and porous features achieved within canister 1, which included the various NaCl salt and blended salt + titanium layers labelled. As can be seen, the canister 1 trial has successfully proven a number of concepts:

1. Both CP-Ti and Ti-6Al-4V HDH can be Powder-HIP consolidated to high density and bonded within the same canister under 750°C / 35MPa / 4 hour processing conditions.

Notably, other canister trials have also proven CP-Ti sponge will successfully consolidate at these conditions.

2. Both single crystal NaCl and CIP pre-formed NaCl inserts have successfully held a free space within the HIP part. In regions of inconsistent strain (most notably the domed base of the canister where the steel was not as thick) show that the NaCl inserts do deform preferentially compared to the consolidating Ti-6Al-4V powder, which is perhaps unsurprising given their differing compressive strength at the processing temperature.
3. A porous structure has been formed using blended NaCl salt granules and Ti-6Al-4V powder, and this has successfully bonded to a consolidating CP-Ti plate as would be required in the fabrication of a PEM hydrogen electrolyzer bipolar plate. More work is needed to control the blending process and produce a homogeneous and interconnected porous network, but this sample clearly indicates that the method would be viable with refinement.

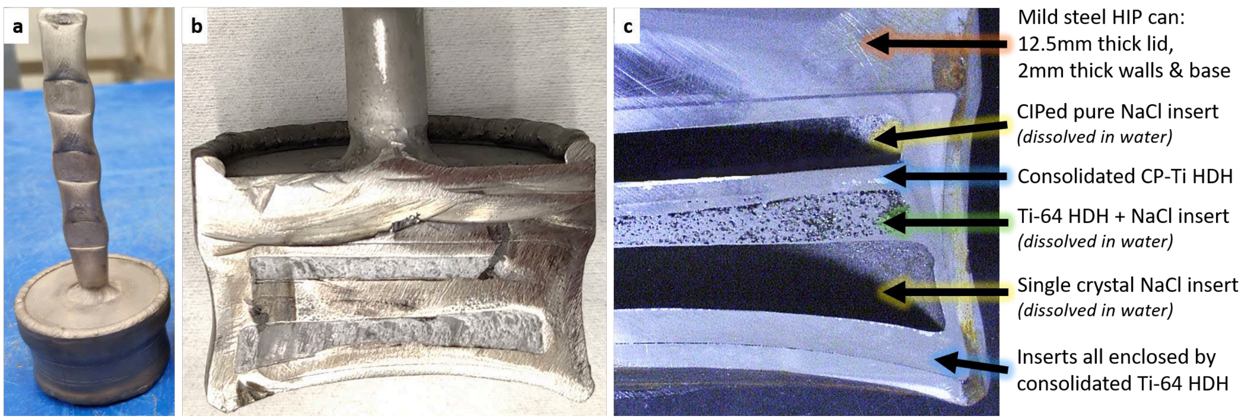

Figure 3: a) as-HIPed canister 1, b) dry cross-sectioned canister 1, c) labelled detail within canister 1 cross section after water dissolution of the NaCl salt space-holding portions.

Canister 2 (shown cross-sectioned in Fig. 4) contained a gradual transition in blended $NaAl_2O_3$ particles and Ti-6Al-4V HDH. This has successfully proven the space-holding capabilities of this ionic compound under a conventional Ti-6Al-4V HIP cycle, with both the pure salt section being easily removed to form an open cavity, and the porous structure being well defined. It was noted that post-sectioning, on exposure to air on a humid day, the $NaAl_2O_3$ salt did begin to spontaneously dissolve in air, highlighting some potential material handling challenges were this process ever to be up-scaled to a production environment.

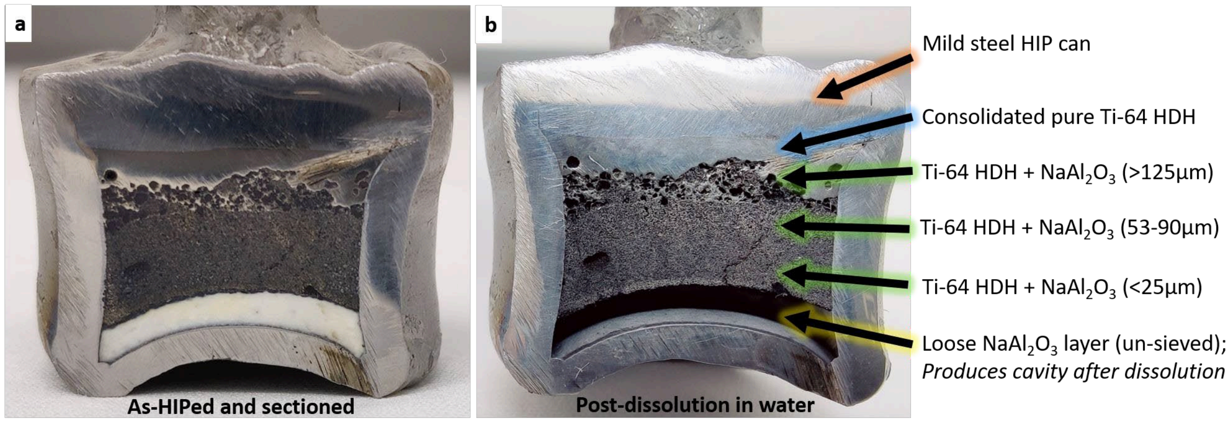

Figure 4: Cross-section of Canister 2 showing a) as-HIPed cross section with $NaAl_2O_3$ space-holders visible, and b) graded porous structure revealed post-dissolution in water.

Embodied Carbon Analysis of HIP Concept

A detailed embodied carbon analysis has been undertaken to compare against conventional titanium manufacturing routes [10]. A baseline emissions value has been estimated for a PEM electrolyzer stack containing forty individual cells, each consisting of one bipolar plate and two porous layers, manufactured using traditional commercial methods.

Estimates were then made for the total embodied carbon of various alternative titanium processing and bipolar plate forming concepts. The output from this study is shown graphically in Fig. 5. This indicates that significant reductions to the manufacturing carbon footprint can be achieved through use of HIP consolidation of recycled end-of-life titanium parts HDH crushed into usable powder (noting calculation does not take account of any carbon emissions prior to recycling).

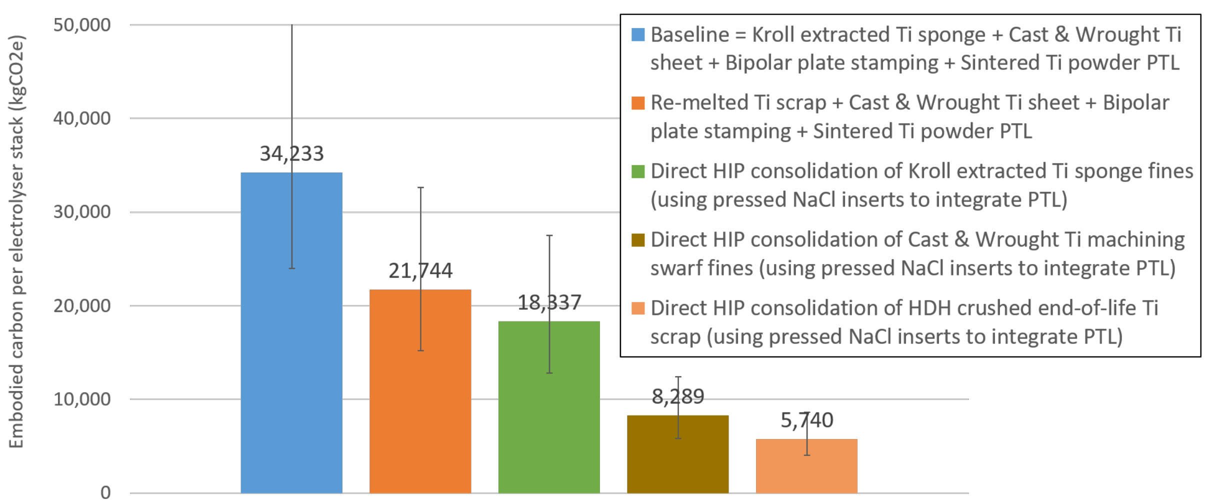

Figure 5: Estimated total embodied carbon for all titanium within an electrolyzer stack (based upon a 40-cell stack containing 260Kg of commercial purity titanium)

Conclusions

1. The feasibility studies presented highlight a new opportunity to utilize HIP to consolidate powder with intricate internal or surface features, as well as tailored through porosity, using dissolvable space holders. Space holders fabricated from NaCl table salt have been shown to be suitable for HIP consolidation at 750°C and 35MPa, whilst NaAl2O3 salt has been shown to be compatible with more conventional titanium HIP consolidation at 920°C and 103MPa.

2. A possible new route to net-shape manufacture intricate titanium PEM electrolyzer bipolar plates via HIP has been demonstrated. The potential design and performance benefits of this method have been highlighted, particularly regarding the ability to integrate porous transport layers into the plate. Notably this concept could be applied to reimagine manufacture of many other complex components beyond those used in the hydrogen energy sector.
3. An embodied carbon analysis exercise has indicated that significant circular economy benefit may be realized versus established manufacturing methods.

Acknowledgments
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References

[1] B. Pivovar, Low Temperature Electrolyzer Technology, Electrolysis Panel Session Presentation at the U.S. Department of Energy (DOE) Hydrogen Shot Summit, August 31-September 1, 2021.

[2] E. Taibi et al, International Renewable Energy Agency, Green Hydrogen Cost Reduction - Scaling up Electrolysers to Meet the 1.5ºC Climate Goal (2020): Published online at www.irena.org/publications.

[3] Ole Edvard Kongstein et al, Alternative Energies and Atomic Energy Commission (CEA), NEXPEL Project WP5 "Porous current collectors and materials for bipolar plate" bibliographic review, 2010.

[4] Luca Bertuccioli et al, E4tech Sàrl and Element Energy, Study on development of water electrolysis in the EU, Approved for publication by the Fuel Cells and Hydrogen Joint Undertaking, 2014.

[5] P.L. Pratt and R.P. Harrison, Dislocation Mobility in Ionic Crystals, Discussions of The Faraday Society No. 38, Aberdeen University Press, page 211-217, 1964. https://doi.org/10.1039/df9643800211

[6] S. Lascano et al, Porous Titanium for Biomedical Applications: Evaluation of the Conventional Powder Metallurgy Frontier and Space-Holder Technique, Journal of Applied Sciences, 9, 982, 2019. https://doi.org/10.3390/app9050982

[7] B Ye and D. C. Dunand, Titanium foams produced by solid-state replication of NaCl powders, Materials Science and Engineering A, issue 528, page 691-697, 2010. https://doi.org/10.1016/j.msea.2010.09.054

[8] B.K Lograsso et al, Densification of titanium powder during hot isostatic pressing, Metallurgical Transactions A, Volume 19A, 1767-1773, 1988. https://doi.org/10.1007/BF02645145

[9] U.M. Attia, HIPing of Pd-doped titanium components: A study of mechanical and corrosion properties, Proceedings of the 11th International Conference of Hot Isostatic Pressing, 2014.

[10] Full source references for the reported embodied carbon analysis are available upon request.