Reviewer 1

Comment 1: Lines 39-41. Authors suggest that conventional powder based thermal spray is limited by poor flowability and clogging and that SPS (suspension plasma spray) is a preferred technology to overcome such limitation. This is highly inaccurate and misleading. In fact, the challenges involved in the handling and flowing of suspensions are orders of magnitude greater than traditional powder-based spray technology. Only at very fine particle sizes (<15 -10microns) does gas-based transport of particles pose significant challenges, hence suspending them in a liquid medium becomes necessary. However, to suggest that SPS is more reliable from a flowability and clogging prevention over tradition thermal spray is incorrect. Please remove the statement.

Response: We have included the suggested modifications to the text, which are as follows:

“*Conventional powder-based thermal spray is widely accepted and employed in various industries but when it comes to depositing very small particles (<10 microns), poor injection due to low inertia of particles restricts the use of gas as a carrier. Therefore, liquid carrying submicron particles (suspension) or a solution of chemical precursors of the coating material, forming solid particles during flight are preferred so that coatings with nano- and micro-scale features can be obtained*.”

The modification can be found on page #1, lines 53-58.

Comment 2: It is unclear why authors chose TiO2 as a chemistry for corrosion protection when there are several known material classes in thermal spray which superior corrosion performance. What are the specific components and environment within a geothermal heat exchanger that necessitate the use of TiO2 as opposed to other material classes. This needs to be very established early in the manuscript. Please elaborate on the material considerations and the rationale behind arriving at this material chemistry.

Response: This research work is part of an EU project focused on improving the efficiency and lifetime of geothermal heat exchangers using advanced coatings, and suspension plasma spray TiO2 coatings are one of them. The titania coatings were chosen not only to protect the geothermal heat exchangers’ components against corrosion but also for erosion protection, as geothermal fluids contain abrasive particles, high-temperature stability as geothermal heat exchangers are exposed to extreme heat conditions, chemical stability of coating in the presence of geothermal fluid, and improved thermal conductivity of the heat exchanger. There are many reports available mentioning the use of TiO2 coatings in heat exchangers [1]–[4]. Besides, TiO2 coatings possess ease of application and can be applied using various methods.

We have included this in the manuscript as following:

“*TiO2 coatings were chosen to protect the geothermal heat exchangers’ components against corrosion and erosion as geothermal fluids contain abrasive particles, and to provide high-temperature stability and chemical stability to geothermal heat exchanger components protecting them against extreme heat conditions. Besides there are many reports available mentioning that the use of TiO2 coatings in heat exchangers improving their thermal conductivity* [1]–[4]*.”*

The modification can be found on page #2, lines 88-93.

[1] X. Zhang, Y. Wang, D. Zhao, and J. Guo, “Improved thermal performance of heat exchanger with TiO2 nanoparticles coated on the surfaces,” *Applied Thermal Engineering*, vol. 112, pp. 1153–1162, Feb. 2017, doi: 10.1016/j.applthermaleng.2016.10.148.

[2] W. Yan, W. Lin-lin, and L. Ming-yan, “Antifouling and enhancing pool boiling by TiO2 coating surface in nanometer scale thickness,” *AIChE Journal*, vol. 53, no. 12, pp. 3062–3076, 2007, doi: 10.1002/aic.11345.

[3] L. L. Wang and M. Y. Liu, “Pool boiling fouling and corrosion properties on liquid-phase-deposition TiO2 coatings with copper substrate,” *AIChE Journal*, vol. 57, no. 7, pp. 1710–1718, 2011, doi: 10.1002/aic.12405.

[4] K. Yim, J. Lee, B. Naccarato, and K. J. Kim, “Surface wettability effect on nucleate pool boiling heat transfer with titanium oxide (TiO2) coated heating surface,” *International Journal of Heat and Mass Transfer*, vol. 133, pp. 352–358, Apr. 2019, doi: 10.1016/j.ijheatmasstransfer.2018.12.075.

Comment 3: Authors allude in passing that the coatings are being developed for geothermal heat exchanger applications, but there is no mention of the coating system requirements.  Since this research is focused on the processing of SPS coatings, more discussion is warranted on the microstructural requirements for this application (dense, porous, vertically cracked, columnar variants). In thermal spray and more so in SPS the plasma parameters have a profound effect on the resulting coating microstructures. Currently it appears as though the authors fixed a constant plasma parameter and made simple variations to generate some coatings. There is no discussion on how the spray parameters were tailored for the specific application.

Response: There is no specific microstructure that is suitable for each geothermal heat exchanger as the choice of microstructure is influenced by different factors including geothermal plant location (as the geothermal fluid chemistry and constituents vary with the location of the geothermal plant) and types of heat transfer (boilers, condensers, and evaporators). Geothermal heat exchangers’ components are exposed to high temperature and pressure, harsh chemicals and mechanical stresses. Therefore, microstructure of thermal spray coating needs to be engineered to resolve these issues, accordingly. For example, coatings with columnar microstructures are suitable for facilitating thermal cycling resistance but simultaneously, they might not be suitable for providing proper protection against corrosive environment due to the ingress of corrosive agents into the substrate. Similarly, coatings with vertically cracked microstructures could allow stress relief, decreasing the risk of coating delamination. But simultaneously, excessive cracking might compromise the structural integrity of the coating. Generally, dense coatings with controlled cracking or columnar structures are preferred in geothermal environment, providing better protection against corrosive agents along with the tolerance for thermal cycling. Also, as it was mentioned earlier that this study is a part of an EU project ‘GeoHEX’, where various advanced coatings for improved heat transfer efficiency and lifetime of heat exchangers are developed. We already performed various pretrials varying different parameters including injection angle, plasma gas, number of passes, ways of injections etc. The better results (in terms of coating quality) were obtained using the parameters mentioned in this manuscript.

We have included this information in the manuscript that can be found on page #2, lines 65-80.

Comment 4: Why did the author choose an aqueous suspension as opposed to an ethanol-based suspension. Both are quite readily available in the market. Given that the plasma device used in this research is not a high enthalpy plasma source it would have made more sense to choose an ethanol suspension. Please elaborate on the rationale for this.

Response: It is true that considering the used plasma device, ethanol-based suspension could be better option. However, we chose an aqueous solution because of the cost-effectiveness (used aqueous suspension did cost ~ 5K GBP/5liters; ethanol-based suspension medium would have increased the overall cost further), environmental considerations (no harmful emissions or volatile organic compounds (VOCs)), safety concerns (especially, in industrial environment; this work was done at TWI Ltd., Cambridge, UK) and waste disposal.

We have included this information into the manuscripts as:

“*These coatings are formed using an aqueous suspension of TiO2 nanoparticles as the feedstock material. The aqueous suspension was chosen due to cost-effectiveness, environmental considerations, safety concerns and avoiding waste disposal issues.*”

The modifications can be found on page #2; lines 95-97.

Comment 5: For a manuscript claiming to be focused on spray processing parameters and the ensuing microstructure, there is minimal details on several critical elements. Some of them are as follows :

o   In SPS process, the surface characteristics of the substrate (or underlying layer) is one of the most critical aspects that governs both coating integrity as well as the resulting microstructure. At the bare minimum the authors should include the surface roughness of the grit blasted substrates.

Response: We have included the roughness data for bare substrate (after grit blasting) in the manuscript, and can be found on page #3, lines 119-120.

o   What is the particle size distribution of the TiO2 material in suspension? What is the morphology of the TiO2 particles? What is the suspensions’ viscosity? What is the relative settling rate/ settling velocity of the particles in suspension for the chosen solids concentration?

Response: As it was mentioned earlier, the feedstock used was an aqueous suspension of TiO2 nanoparticles was purchased from Promethean Particles Ltd., UK. Some of the information was proprietary to the supplier. They specified the solid content to 5% to have a stable suspension. However, the particles used for the suspension are spherical with particle size between 5-10nm as characterised by the supplier using TEM. The crystal structure of the TiO2 used in the suspension was Anatase.

o   Why did the authors choose an abnormally low solids content of 5 wt% suspension? From a practical application perspective such a suspension would not be feasible for use particularly to coat large components (geothermal heat exchangers).

Response: As it was mentioned earlier that the feedstock used was an aqueous suspension of TiO2 nanoparticles that we purchased from Promethean Particles Ltd., UK, which did cost us around 5K GBP for 5liters. The company mentioned that it was difficult to formulate a stable and uniform suspension using higher weight percentage of TiO2. Therefore, 5 wt.% of solid content was chosen for the study.

o   There are several build types possible for the SG100 plasma device, please provide the exact build configuration used for these spray trials.

Response: Praxair/TAFA SG100 APS was used for the deposition. .The plasma console was 3710 with HF 2210 starter kit. This information has been added to the manuscript.

o   The 46V mentioned by the authors for plasma voltage – was it measured at the plasma torch or the power supply?

Response: It was the power supply.

Comment 6: The plasma parameters that the authors have currently used for the study is only producing approximately 32-33kW of power. Why was such a low power level used? To effectively produce SPS columnar microstructures one would typically expect to require upwards of 60kW (depending on plasma torch and technology). Although cascaded plasma devices can accomplish this at lower power levels, that is not the case here. The hardware that has been used (SG100 plasma torch) can operate at up to 80kW in its subsonic configuration. Why was the full operation window of plasma’s spray parameters not explored? The inferior quality of coating microstructures as presented in Figure 4 clearly indicate that the required due diligence to understand spray parameters – microstructure relationship is missing in this work.

Response: Yes, we agree that plasma power level plays a critical role influencing the coating microstructures, and we chose power level of 32-33kW after considering several factors. Firstly, this power level for our SG100 plasma gun was chosen after conducting extensive preliminary experiments considering our specific experimental setup. After exploring different power levels, we obtained stable and reproducible plasma conditions, providing uniform coating deposition. Also, 32-33kW power level was selected considering the low thickness of the prototype plate heat exchanger (0.6mm). Higher power levels might generate excessive heat input, causing thermal stress or distortion into the substrate. Besides, selecting 32-33kW power level allowed us to achieve our research goals efficiently while optimizing energy consumption and cost-efficiency.

Comment 7: There are several kinds of plasma devices, and each have their own design in terms of introducing feedstock material. Most plasma torches being used today were originally designed for powder based thermal spray, which are currently being modified to accommodate the requirements of SPS technology. The SG100 is a bit unique in its design in that, it is neither an external radial feed nor an axial internal feed design. It is designed to receive feedstock (originally powder) INSIDE its anode radially, with various configurations possible. The reason for this is that, when powder is fed EXTERNALLY (outside the anode) in an SG100 device it does not produce enough enthalpy to effectively melt the powder. There is a configuration available to externally – radially feed powder to SG100, however it requires build modifications and the torch to operate at high power levels (60-80kW) to melt the powder. The authors claim in Line 86 that the suspension was fed radially into the plasma, but there are no further details. It is most likely that the authors did not feed the suspension INSIDE the anode (per the standard SG100 design) since this would result in suspension containing water to enter inside the nozzle which is detrimental to the device. Hence one can only assume that the authors introduced the suspension externally-radially. This would have hardly been able to produce enough enthalpy to melt the suspension feedstock. Considering that the already low power plasma further gets depleted of its thermal energy by the introduction of an aqueous suspension, it is no surprise that the microstructures generated in this work are sub-standard.

Response: It was mentioned that the suspensions were fed radially into the plasma through a syringe pump (ISCO® 260D) connected to the EXTERNAL nebulizer (constructed from a modified RS air brush AB931), which means it was fed externally-radially into the plasma. While injecting suspension into the plasma flame, several measures were used to mitigate the risk of water entering into the device and damaging it. To prevent the excessive atomization, the nebulizer parameters such as pressure and feedstock flow rate were controlled and calibrated. The syringe pump was also calibrated to maintain a uniform and controlled flow rate, diminishing the chances of suspension entering the system. Besides, a routine inspection and maintenance of the entire system was done to check leaks, blockages or malfunctions for the sake of the integrity of the process.

Comment 8: In line 90, the authors mention that Argon of 3L/min was used as a carrier gas. What was the purpose of introducing this gas since there was no powder to be carried in the current experiment? Please elaborate.

Response: Even though no powder feedstock was carried, using a consistent carrier gas (Argon) helped in achieving stable, controlled and inert plasma environment, essential for repeatable and comparable coating conditions.

Comment 9: By keeping the number of coating passes constant, the authors have chosen an oversimplified approach in their experimental design. Coating thickness plays a significant role in governing the elastic strain energy within the coating. By having varying thicknesses, discussions such as those attempted by the authors from lines 183-191 fall apart. The presence or absence of microstructural features (crack for e.g.) could easily be due to thickness differences. Fabricating coatings of equivalent thicknesses is not at all difficult particularly since the authors are only doing so on flat coupons and not on any actual component with complex geometry.

Response: We agree that the coating thickness plays a crucial role in controlling the elastic strain energy within the coating. However, we maintained a constant number of coating passes while varying other parameters for clarity and specificity in our findings because the down-selected coatings were supposed to be deposited on plate- and tube-type heat exchanger prototypes. The elimination of variability in the number of coating passes reduced the complexity. Also, the selection of number of passes was done after performing preliminary tests, where number of passes were varied within the range of 10-50.

Comment 10: Since this research is focused on the processing of SPS coatings, it is reasonable to provide more details on the intricacies involved in the feeding of suspensions . A lot of this is acquired knowledge which the thermal spray industry has learnt over several years of applying SPS to different components. Following are some of the comments related to the feeding of suspensions as it pertains to the authors’ experimental design:

o   What was the orifice/ injector size used for the experiment?

Response: It was 0.5mm in diameter.

We have included this information into the manuscript on page #3, line 130.

o   For the different flow rate experiment, how was the suspension flow controlled and monitored (Coriolis / Mass flow controllers)?

Response: As it is mentioned in the manuscript that a syringe pump (ISCO® 260D) was used to inject (radially-externally) the suspension into the plasma jet. In ISCO® 260D syringe pump, the flow rate is controlled through a combination of motor drive mechanisms, microprocessor control, user input, feedback sensor and advanced flow rate algorithms, allowing the pump to attain precise and stable flow rates.

o   At an extremely low solids content (5%) such as that used by the authors, how was the settling of particles monitored and avoided. Without a feedback control on the feeder the particles would continue to fall out of suspension during the coating run.

Response: To avoid the agglomeration and precipitation of solid content (nanoparticles), a surfactant (0.1-1 wt.%) stabilised aqueous suspension was used, purchased from Promethean Particles Ltd. Further information about the chemistry of the surfactant was not shared by the company.

Comment 11: One of the fundamental aspects in feeding suspensions is ensuring that they are injected optimally into the plasma plume. With powder thermal spray there is an advantage of tweaking the carrier gas, which is absent in the SPS process.  In this study the authors have used the same setup to feed suspensions at different flow rates . How did they ensure that that in each case the suspension was optimally injected into the plume? Was any spray process diagnostics used, if so, please share the data. If the suspension is not properly entrained into the plume, particularly in the radial feed setup which the authors utilized, it can have detrimental effects and would fail to produce SPS coatings of good quality.

Response: We appreciate your insightful comment, however, we acknowledge that in our study, we did not employ real-time spray diagnostics to monitor the suspension injection into the plasma plume. We used a consistent setup to inject suspensions at different flow rates. We agree that it highlights the requirement for a more comprehensive analysis of suspension injection dynamics in future research.

Comment 12: In line 144-145. The authors state that a “larger substrate can help resolve overspray to some extent”. It is not quite clear what the authors mean by this. Regardless of substrate size, spraying beyond the edges of the part / component is a standard practice in thermal spray. This is to avoid non uniform coating thickness & microstructure near the edges. Kindly correct this.

Response: Here, we meant that a larger substrate provides larger target area for the sprayed material to be deposited on. For smaller substrate, due to being carried away with the air flow, sprayed particles tend to overshoot the edges and lost to the surrounding environment. While in the case of larger substrate, a greatest distance is travelled by sprayed particles before reaching the edges, retaining more material on the substrate. Hence, “*a larger substrate can help resolve overspray to some extent*.”

We have included this information into the manuscript on page #4&5, lines 187-190.

Comment 13: Lines 189-191. Authors attribute the mud crack formation in coatings to the interaction between solvent in the suspension and the plasma plume. The mechanism that the authors are postulating is unclear. Crack formation in coatings is a complex interplay between the coating’s elastic strain – energy release rate and the strain mismatch generated from the deposition process. If the evaporation of solvent deprives some of the plasma’s enthalpy it would result in reduced melting of the particles. This would result in partially molten / unmolten particles being deposited. The resulting splats from these would be at much lower temperature compared to a well molten particle. As a result, these would be at lower magnitude of tensile strain on the substrate (again relative to a fully molten particle). How would these generate more mud cracking?  It is the same phenomenon because of which porous coatings (partially molten particles) have lower elastic strain and thereby lower cracking tendency than a denser coating. The authors need to elaborate more and provide a sound scientific reasoning to their hypothesis.

Response: Yes, we agree that crack formation in coatings takes place due to the complex interplay between the coating’s elastic strain, energy release rate, and the strain mismatch generated during the deposition process. At higher feedstock flow rates, when suspension (water) evaporates, it cools down the plasma, leading to the reduced melting (partial melting or no melting) of coating nanoparticles. According to our hypothesis, when these partially molten or unmolten particles deposit on the substrate, there is a difference in their temperature, microstructures, mechanical properties and bonding characteristics, and the non-uniform distribution of these particles, could result in localised stress concentrations, potentially generating mud-crack formation in certain parts of the coating.

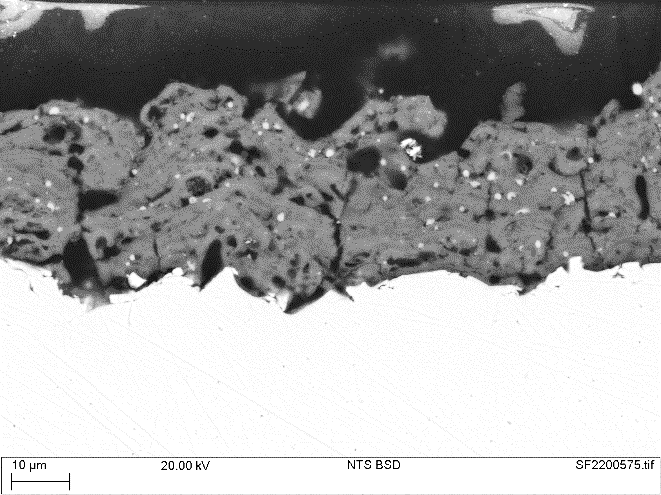
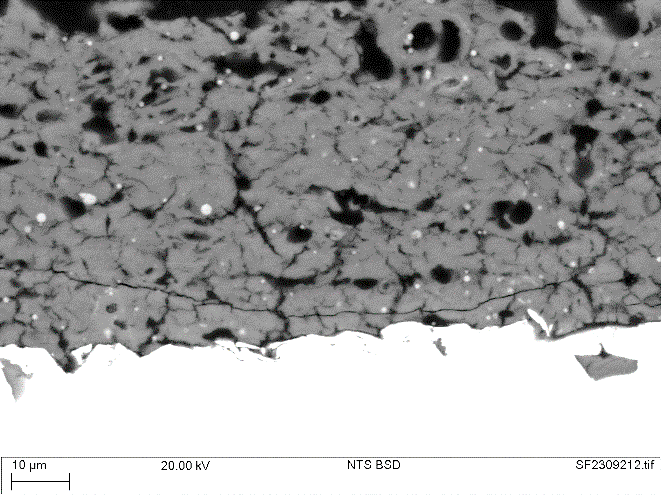
This information is been included in the manuscript on page #7, lines 238-242

Comment 14: Figure 4. The coating microstructures presented in this work does not depict any significant variations whatsoever within them. The SPS process is extremely capable of producing several microstructure types (thin dense films, porous, vertically cracked, several variations of columnar architectures). Unfortunately, this was a missed opportunity for the authors for reasons already mentioned previously related to the oversight in processing of coatings.

Response: We understand the huge potential of suspension plasma spray in developing various microstructure features however, the objective of our study was specifically focused on investigating the effect of feedstock flow rate and standoff distance on coating microstructures in our experimental setup, establishing a foundational understanding before exploring the wider range of microstructural features (which we will cover in our subsequent research work).

Comment 15: Figure 4. It appears that there was a variability in the surface roughness of the substrates that were used in this work. Since all the images are at same magnification a direct comparison suggests that *4a* had a highly corrugated surface, while several others (*4f* for e.g.) had a much lower Ra and some such as *4i* had regions on the substrate that were completely flat. Such variability in substrate roughness can inadvertently alter the SPS microstructures and no correlations to plasma processing parameters are then feasible.

Response: In this study, all substrates were pre-treated in a consistent and controlled way using the same grit blasting conditions (80 psi set pressure, 70 psi run pressure, at 80 mm SOD, #100 alumina mesh). We believe that this standardized approach for surface preparation produced almost uniform surface roughness profile (there might be an insignificant variability). Also, the flat region in the Figure 4(i) looks flat due to the text box mentioning the sample name. We have already corrected it. The SEM images were taken at three different random spots, and therefore surface finishing might look different in some images in Figure 4. We have presented alternative images for 4(f) and 4(i) that show different surface finish than presented in Figure 4.

4(i)

4(f)

Comment 16: Figure 5 . It is unclear as to what value the surface roughness measurement of the SPS coatings provide in this experimental design. It is likely that many of these are an artifact of variations in coating thicknesses and substrate finish. This graph could be removed. SPS coating roughness is quite critical in several applications wherein very smooth surface finish is unattainable from a powder feedstock. However, such surfaces mandate the coating microstructure to be extremely dense and free of defects.

Response: The surface roughness data was incorporated to provide insights about the quality of coatings produced in our experimental setup. We acknowledge that variations in coating thickness and substrate finish affect the surface roughness profile of developed coatings. However, for comparative analysis, we would like to present the surface roughness data alongside other parameters. This would allow us to recognise trends, correlations and providing a comprehensive view of the coating characteristics.