Functionally Graded Materials using Plasma Spray with Nano Structured Ceramic

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Abstract. In this paper, nano structured FGM was fabricated using DC plasma spray technique. Nano structured and micro structured powder were used as the feeding powder with steel substrate. The spray parameters was optimized and characterisation of nano-ceramic FGM and micro-ceramic FGM were done using bending test and micro-hardness test. Experimental results have shown that the nano-structured FGM exhibit 20% improvement flexure strength and 10% in hardness. A comparison was made between sintered micro ceramic tile and nano ceramic FGM using simple drop test method.

1. Introduction

Functionally-graded materials (FGM) are composites comprising of different materials with a continuous transition from one material to the other, in this case from ceramic to metal. It is believed to allow the full utilisation of the best properties of ceramics and metal, whilst also giving good impact resistance from the hard ceramic frontal layer, and thermal shock resistance due to the smooth thermal coefficient transition from ceramic to metal.

Direct Current Air Plasma spray is a technology used in many industrial applications to apply ceramic and metallic coatings, such as making hard-wearing surfaces, bio-implants, thermal-barrier and chemical-resistant coatings. It is a process which uses a plasma flame to heat up and melt metallic, ceramic or composite powders and then projects the liquefied powders onto the surface to be coated using gas pressure. It is a relatively fast process, being able to produce large surface areas covered with ceramic coatings in one single process, as compared to other methods such as hot- and cold-pressing and then sintering of ceramic tiles.

In this paper, nano-$\text{Al}_2\text{O}_3$ and FeNiAl powders were used to produce FGM coatings on steel substrates using the DC air plasma spray technique.
2. The Approach
The approach was to investigate the physical properties required of nano-Al$_2$O$_3$ / FeNiAl FGM coated on steel substrate using the DC plasma spray technique, by comparing the difference in properties between functionally-graded coatings using micron-sized Al$_2$O$_3$ powder, and nano-sized Al$_2$O$_3$ powder, together with FeNiAl metal-composite powder. Requirements such as hardness, fracture strength, toughness, and density were characterised.

3. Specimen Preparation of Nano Structured FGM

3.1. Raw material
The nano-alumina powder used is a commercial product. It is a granulated agglomerated alumina powder, with an average particle spherical diameter $d_{50}$ of 70nm. It contains 99.5% alpha-phase Al$_2$O$_3$, and 0.5% MgO.

![Figure 3.1. SEM image of nano-alumina powder.](image1)
![Figure 3.2. SEM image of alumina powder.](image2)

The micron-alumina powder used is a commercial product from Praxair, with the average particle size of 45 micrometers. It is also alpha-phase Al$_2$O$_3$, but is made from 100% pure Al$_2$O$_3$, as compared to the nano-alumina powder used in this project.

The commercial micron metal composite powder was used as a FeNiAl powder. The average particle size is around 106 micrometers, with the 3 types of metal components clad together. This powder will undergo an exothermic reaction during spraying, and thus would be able to form a strong metallic bond with the base metal and other materials used in the thermal coating.

3.2. Process
In the specimen preparation, mild steel substrate of 0.3% carbon was used. The substrate was degreased, grit blasted and cleaned by an air gun before spraying. Iron composite powder and alumina powder (Al$_2$O$_3$) were used to fabricate the graded layers using DC plasma spray technique. These powders were weighted and premixed according to percentage by weight, followed by mechanical milling for 1.5 hours. The premixed powder was then fed into the powder feeder for plasma spraying. The coating was sprayed prior to preheating of the substrate. All steel plates were weighed and measured before being coated. The machine being used in this report is Taiwan Plasma Corp’s PCS-40 Air Plasma Spray system, with a maximum power of 40kW.

3.3. Characterization of the Specimen
The graded material was characterized in terms of microhardness, porosity and micrograph examination using SEM. The Vickers microhardness of the coatings was determined by using the Matsuzawa MXT70 Microhardness Tester, with a load of 1 kgf and dwell time of 15 seconds. The microstructures and cross-sectional porosity of the coatings were examined using the Scanning Electron Microscope (Jeol 5310 and 6360). The Mirage MD-200S electronic densimeter was used to measure the bulk density of the FGM samples. The 3 points bending test was performed to measure the flexural stress, strain, flex modulus, fracture load and strain of the FGM coatings using Instron 5567. The drop impact test was performed to test the impact resistance of the nano-alumina FGM system as compared to a commercially-bought pressed and sintered alumina tile.

4. Results

4.1. Functionally Graded Material Configuration

Both the micron and nano alumina FGM specimens were of the same configuration in terms of mixture ratio with iron composite powder as shown in Figure 4.1. The spraying parameters were different due to the difference in densities of the three types of raw materials used. The powder feed rate of the powder feeding system has to be matched to the relative densities of the different powder mixtures used in the FGM coating. The heavier powder has to be fed at a slower rate to reduce clogging at the feed nozzle, while lighter powder mix can to be fed at a higher rate to ensure a more homogeneous coating.

| Composition                  |
|------------------------------|
| 100% Al₂O₃                  |
| 25% Fe₃NiAl / 75% Al₂O₃     |
| 50% Fe₃NiAl / 50% Al₂O₃     |
| 75% Fe₃NiAl / 25% Al₂O₃     |
| Substrate                   |

Figure 4.1. FGM specimen configuration

4.2. Micrograph of FGM Specimens

Both the morphology of the micron and nano alumina FGM specimens were observed using SEM as shown in figure 4.2, 4.3, 4.4, and 4.5. The physical properties of the both specimens are shown in table 4.1

Figure 4.2 SEM images of the cross-section of Micro-powder alumina FGM coatings

Figure 4.3 SEM images of the interface between substrate and coating
Figure 4.4. SEM images of the cross-section of nano-alumina FGM coatings

Figure 4.5 Micrograph of nano-alumina FGM, showing nano-zones containing nano-particles within.

| Physical Properties       | Micro powder FGM specimen | Nano powder FGM specimen |
|---------------------------|----------------------------|--------------------------|
| Coating thickness (mm)    | 2.42                       | 2.19                     |
| Coating bulk density (g/cm³) | 3.595                     | 3.977                    |
| Approximated Porosity (%) | 5                          | 5                        |
| Vickers hardness (Hv)     | 1026                       | 1531                     |

Table 4.1. Physical properties of micro powder FGM and nano powder FGM material system.

Based on the micrograph in figure 4.2 and 4.3, micron-sized ceramic FGM had exhibited a low porosity and high hardness value. However, between the substrate and first coating interface, micro-cracks were observed. These micro cracks would combine with the tensile stresses generated by the thermal expansion, and lead to coating delamination.

In nano-sized ceramics FGM (refer to figure 4.4 & 4.5), the micrograph had shown second-phase nano-size particles dispersed within the matrix grains and the presence of the nano-zones. The Vickers micro hardness increased by 49.2% with a corresponding increased in the bulk density of 10.6% while maintaining the same percentage of porosity.

4.3. Vickers Hardness test

Vickers microhardness tests were conducted to find the FGM coating hardness of the nano alumina FGM and micron alumina FGM at different graded layers as shown in figure 4.6 and 4.7. The microhardness values of both nano and micron FGMs appear to be similar, although the hardness of the top layer of nano FGM had achieved a higher value of 1531HV. This is coherent with findings by other researchers, who found that the hardness of nano-structured ceramic thermal coatings were similar, or slightly higher, than conventional micron-structured ceramic thermal coatings. [1]
Figure 4.6 SEM images and corresponding Vickers microhardness that make up the layers of micron-alumina FGM.

- Pt.1 Substrate: 222.4 Hv
- Pt.2 75% Fe composite / 25% micron sized Al₂O₃: 208.5 Hv
- Pt.3 50% Fe composite / micron sized Al₂O₃: 479.5 Hv
- Pt.4 25% Fe composite / 75% micron sized Al₂O₃: 621.8 Hv
- Pt.5 100% micron sized Al₂O₃: 1028.2 Hv

Figure 4.7 SEM images and corresponding Vickers microhardness of the layers that make up the nano-alumina FGM.

- Pt.1 Substrate: 189.5 Hv
- Pt.2 75% Fe composite / 25% nanosized Al₂O₃: 228.4 Hv
- Pt.3 50% Fe composite / nanosized Al₂O₃: 370.4 Hv
- Pt.4 25% Fe composite / 75% nanosized Al₂O₃: 541.3 Hv
- Pt.5 100% nanosized Al₂O₃: 1531.2 Hv

Vickers micro-indentations were also made on the polished ceramic top layers of both micron-alumina and nano-alumina FGMs. Cracks can be seen extending out from the corners of the indentation on the micron-FGM (Figure. 4.8a), whereas little cracking was observed around the indentation on the nano-alumina FGM, as shown in Figure 4.8b.

Figure 4.8 Vickers indentations on: (a) micron-alumina FGM; (b) nano-alumina FGM.
4.4. Three points bending test

From the Instron three-point bending tests conducted on the FGM samples, it was observed that the nano-alumina powder FGM, exhibited maximum flexural fracture stress before coating failure by cross-sectional shear. The flexure strength was improved by about 20%, from an average of 450MPa in micron-alumina FGM to about 600MPa in nano-alumina FGM. The maximum flexural fracture strain that the nano-FGMs can take before failure is also around 25% higher, from 0.8% in micron-alumina FGM to about 1% in nano-alumina.

![Three points bending test on: (a) micron-alumina FGM; (b) nano-alumina FGM.](image)

From the profile of the stress-strain graphs as shown in figure 4.9, it can be observed that the nano-alumina FGMs fail less abruptly at the point of coating fracture as compared to the micron-alumina FGM, which exhibited a sharp peak at the point of brittle fracture. This abrupt initial point of failure was due to the brittle 100% micron-alumina top layer shattering under the applied load. After this layer has failed, the remaining layers underneath it then recover to take up the applied load, although not to the same stress levels as initially.

The nano-alumina FGMs on the other hand, do not exhibit this initial brittle behaviour under loading from the three-point bending test. This is due to the presence of semi-molten nano-zones that is able to arrest any interfacial and inter-splat micro-cracks [1] thereby increases the inter-splat bonding strengths of the coating. This could imply that nano-alumina FGMs are less brittle as compared to micron-alumina FGMs, thus explaining the higher fracture strains shown in the three-point bending test.

4.5. Morphology of the FGM fracture surface after bending test

After the Instron three-point bending tests was conducted, SEM images were taken on the fracture surface to study the material respond to fracture. The fracture surface of the micro-alumina FGM was found to contain a large percentage of planar cleavage planes, with the columnar sub-micron grains clearly visible within the ceramic splats. Whereas the fracture surface of the nano-alumina FGM was found to contain more step-like features, which are due to the nano-cracks within the dispersed nanoparticles and the molten alumina matrix of the shells of agglomerated nano-alumina particles [2, 3]. Semi-molten agglomerates containing nano-particles within the nano-zones can also be seen in figure 4.10b. [1]
4.6. Drop test

This test was performed to test the impact resistance of the nano-alumina FGM system as compared to a commercially-bought pressed and sintered alumina tile.

The test involves dropping a cylinder weighing a total of 3kg, with a sharp stainless steel tip at the bottom end, with tip hardness of 458 Hv / 4.5 GPa, through a PVC pipe, onto the impact surface from a height of 3m. The set-up is shown in Figure 4.11. The indenter was modelled with a sharp profile.

Figure 4.10 SEM image of: (a) the cross-sectional fracture surface of nano-alumina FGM specimen; (b) transgranular fracture of nano-alumina splats, also showing the large intergranular surfaces between molten alumina and semi-molten nano-alumina particles.

Figure 4.11 Equipment set-up of drop impact test
With an impact energy of 88.3J, little visible marking was observed on the nano-alumina FGM surface after the first two impacts. The coating only broke through on the third impact, with the nano-alumina top layer chipped off, exposing the gradient layers underneath but the steel substrate. Only the point of impact was defeated by the repeated impacts, while the rest of the coating was intact. This is shown in figure 4.12a.

Similarly, the alumina tile showed little visible marking on the impact surface during the first three impacts, nor was any visible cracks observed. However, on the fourth impact, the alumina tile was found to have been shattered into many pieces as shown in figure 4.12b.

5. Discussion
From the micrograph of the nano FGM, the presence of dispersed nano-particles (nano zone) within the molten alumina matrix makes up the morphology of the splats. Together with the residual stresses around the nano particles, it act to increase the process zone area around the crack tip by initiating nano-cracks. The larger process zone requires higher fracture energy, thus increasing fracture toughness of the nano-ceramic material. Changes in the fracture mode was observed, from intergranular of micron-particle alumina to transgranular fracture of nano-alumina ceramics. Nano-zones work as crack arrestors, increasing fracture toughness as it makes it much more difficult for a crack to propagate, expanding energy by spreading the energy out over a large interface between nano-particles and splats. [1] Thus, no cracking was observed around the indentation on the nano-FGM, apart from the large holes and cracks which appeared to be due to inherent porosity and defects, also observed on the micron-FGM indentation.

The higher hardness of nano-ceramics is due to the dense packing of semi- and un-melted nano-particles, held together by molten ceramic which had infiltrated into the nano-zones packed with unmelted nano-particles. The higher inter-splat bond strength in the nano-alumina FGM also results in a higher hardness.

The presence of these nano-zones was also found to improve the adhesive bond strength of The differences in reactions to the drop impact test between the nano-alumina FGM and the alumina tile also shows the nano-structured FGM is able to better withstand tensile stress waves due to impact loading as compared to conventional pressed and sintered micron-structured alumina tiles.

6. Conclusion
Nano-alumina FGM had shown increased in fracture strength and micro-hardness with improved interface bond strength between the substrate and the first coating. The drop impact test has shown that the nano- FGM system is able to withstand multiple impact hits by a sharp point, and is able to localise impact damage and resist shattering.
7. References

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