

PAPER • OPEN ACCESS

Plasma sprayed nano refractory coatings

To cite this article: S Gowtham Sanjai *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **577** 012100

View the [article online](#) for updates and enhancements.

You may also like

- [Characterization of a chiastolite-type andalusite: structure and physicochemical properties related to mullite transformation](#)
Mossaab Mouiya, Abdelhak Arib, Yassine Taha et al.
- [Fluorescence and thermal stress properties of Yb³⁺-doped aluminosilicate glasses for ultra high peak power laser applications](#)
Mirko Tiegel, Andreas Herrmann, Stefan Kuhn et al.
- [Enhanced performance of an S-band fiber laser using a thulium-doped photonic crystal fiber](#)
A R Muhammad, S D Emami, J K Hmood et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Plasma sprayed nano refractory coatings

Gowtham Sanjai S¹, Ratan Pinto², Parvati Ramaswamy³

¹Research Scholar, CHRIST (Deemed to be University), Bangalore, India.

²Graduate Student, CHRIST (Deemed to be University), Bangalore, India

³Professor, CHRIST (Deemed to be University), Bangalore, India

Department of Mechanical and Automobile Engineering, Faculty of Engineering

E-mail: gowthamsanjai.s@christuniversity.in

Abstract. Nano powders may be reconstituted into micron sized plasma sprayable powders either by using a spray drier or a manual process by employing organic binders to agglomerate them. This paper deals with the synthesis of nano sized alumino-silicate plasma sprayable powders and plasma sprayed coatings prepared from them. Nano sized raw materials involving kyanite and andalusite refractory powders were converted into plasma sprayable powders by using polyvinyl alcohol (PVA) binders. The preparation methodology involved obtaining free flowing, micron sized agglomerated nano –alumino-silicates particles which could be plasma spray coated by using an Atmospheric Spray Coating Facility. About 220 microns thick nano-alumino silicate coatings were deposited on 75 microns thick commercial NiCrAlY bond coat on stainless steel substrates. The challenges involved in plasma spray coating the nano material with low density was in obtaining good deposition efficiency, retaining the nano micro structures and the structural phase composition of the coating. The coatings were evaluated for materials characteristics such as crystal structural phase via XRD, microstructure via SEM and chemical composition via EDS. The microstructure depicted fine grained nano-sized surface morphologies, kyanite and andalusite phase structure, with high potential for application as refractory coatings.

Keywords: Nanostructured coatings; Plasma sprayable powder, kyanite

1. Introduction

Refractory technology is fairly mature and has a long R& D history. If further refinement is needed, then revolutionary concepts have to be introduced. In a foundry, the moulds and cores of the coatings symbolize an integral part for the production of castings. The vital role of earthenware coatings is to structure a competent refractory barrier between the sand substrate and liquid metal flow during the period of casting, solidification and forming of the castings. Though it can give a flat and spotless surface of castings, it should also provide with the advantages of no adhered sand or defects due to metal saturation into the pattern (lumps, dents, rough surface and alike). Dimension accuracy and surface exterior of castings depend both on metal and mould. Function of higher quality ceramic coatings drastically influence either drop or removal of steep cast house tidiness and machining operations for the castings, thus directly sinking the creation costs of a foundry [1].

¹ To whom any correspondence should be addressed.



Materials with fine-scale structures have long been recognized to exhibit remarkable and technologically attractive properties. Of the new technologies, nanotechnology is considered especially promising. Generally refractories are made up of small particles which are fine and in the range of micron sizes. Nanostructured materials and coatings propose the prospective of the most important developments in engineering properties based on improvements in mechanical properties ensuing from dropping micro structural features by factors of 100 to 1000 times compared to recent engineering materials. The concern for the nano structured ceramic materials which are synthesized in dimensions smaller than 100 nm has been increasing in the last decades which has been stimulated by the huge range of applications in industries such as production of dense ceramics, sensors, batteries, capacitors, corrosion-defiant coatings, thermal barrier coatings, concrete electrolytes for fuel cells, catalysts, cosmetics, health, automotive, bio-engineering, opto-electronics, computers, and electronics etc [2].

1.1. Ceramics, nano-ceramics and refractories

Ceramics are non-metallic inorganic solids, which can serve low / high temperatures, wear, harsh environment etc. While ceramics are strong, hard, brittle, possess high melting point, compressive strength, oxidation & corrosion resistant properties; refractories are another manifestation of ceramics involving retention of strength at high temperatures. Nano-ceramics are also composed of ceramics, but very important difference is that the grains comprising the ceramics are nano sized and therefore the huge improvement in the ceramic properties may be anticipated due to the modified microstructure. Nano-ceramics are finding wide application for coating technologies due to their unusually favourable microstructures leading to improved properties: toughness, better thermal shock, wear resistance etc. One useful industrial refractory is with chemical formula Al_2SiO_5 , but different mineral names (Kyanite and andalusite) due to their different crystal structures and physical properties [3]. They are used primarily in refractory and the earthenware products, as well as in electronics, electrical insulators and abrasives.

1.2. Thermal Spraying and Nano Coatings

Thermal spraying [4] is a well-established coating technology used worldwide and offers new possibilities to prepare nano-sized or nano-structured coatings. Nano ceramic coatings [5] may be prepared via thermal spray technology and specifically by employing atmospheric plasma spray (APS) technique [6]. In thermal spray coatings process spray powder/particles are accelerated and then melted before impacting onto the prepared substrate where they flatten and form packed down lamellae, called splats, from the layering of which results the coating. Particles melting occur in rather short times and their solidification in even shorter times with strong temperature gradients and cooling rate sensing sometimes in meta stable or amorphous phases. The coating microstructure is multifaceted with many features such as voids, cracks delamination and interfaces of different length scales. Nano coatings are almost molecular scale and may be the smallest unit to show refractory properties. They may exhibit unique activation, and likely enlarge appealing fact in terms of stuffing, pore formation, binding etc.

1.3. Nano Plasma Spray Powders

Nanopowders are powdered materials with individual particles having their sizes less than 100 nanometres in any one direction. Nano plasma sprayable powders are solid powders of nano particles containing micron - sized nano particle agglomerates, and thus rendering them suitable for the process of plasma spray processing. R & D needs are directed and focussed towards creating characteristics microstructures by controlling the plasma spray process and the reaction process of organic binders with the plasma. Emphasis of this development is on building a nano structural matrix and nano microstructure by this process which retains the crystal crystallographic structures of the intended refractory. Typical examples of functional nano coatings that are applied to protect the substrates involve protection from corrosion, wear or effects of temperature etc. Spray drying [7] is one method of producing a dry powder

from a liquid or slurry by hastily drying with a hot gas. Spray dried process may be used to prepare plasma sprayable powders by varying the spray parameters. All spray dryers employ some category of vaporizer or spray nozzle to dissolve the liquid or slurry into a required drop size spray. It is also possible to develop a work procedure to prepare plasma sprayable powders via manual methods involving the same result of spray drier technology. Manual process of making plasma sprayable powders can employ organic binders to agglomerate the raw material powder composition followed by fractionating the particles by sizes via sieving. Polyvinyl Alcohol (PVA), a water-soluble white, colourless and odourless synthetic polymer is an example of organic binders.

1.4. Challenges

Some of the biggest challenges in thermal spraying nano-materials are to make the nano sized feed powder through the atmospheric plasma flame and to preserve the nanostructure of the feedstock (agglomerated to microns) to set down [8]. If the feed fine particle does not flow easily through the plasma flame, isolated patches of non-uniform deposition are found on the substrate. If the nanostructured fine particles are entirely melted through spraying, the conventional performance of thermal spray particles, such as solidification, nucleation and grain growth will take place. Such processes will wipe out the original nanostructured quality of the feedstock. During plasma spraying of nanostructured ceramics [9] it is essential to partly melt the powder particles to accomplish the crucial physical conditions for cohesion and adhesion.

Results of an attempt to prepare nano sized plasma spray coating from plasma spray powders comprised of nano sized ceramic powders involving kyanite and andalusite refractory [10] is presented in this paper. Our prime importance is the development of the capability to (1) convert nano powders into plasma sprayable powders, (2) develop fine grained/nano-sized surface coating morphologies and (3) retention of kyanite/andalusite phase structure. Hardness measurements were carried out as part of mechanical property analysis, which is important to understand the material resistance to plastic deformation [11– 12].

2. Experimental Procedure

2.1. Processing of plasma sprayable powders

Commercially available nano alumina powders, further synthesized (un-published) to form nano sized alumino-silicate (refractory) composition (kyanite) were used as a starting material for the process. The refractory based starting nano powders were mixed with organic binder(PVA), subjected to manual sieve processing, involving ASTM meshes of (1) 25 mesh: 710 microns, (2) 140 mesh: 106 microns and (3)270 mesh: 53 microns and oven heated at various stages of synthesis. Figure 1 shows the flow chart of the powder synthesis process.

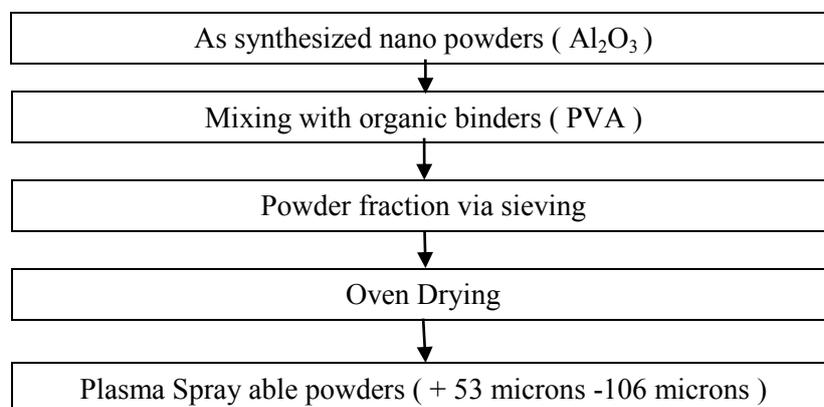


Figure 1: Plasma Sprayable Powders Synthesis (Flow chart)

The pictorial representation of the various steps involved in the plasma sprayable powder preparation that is shown in the form of flow chart (Figure. 1) is now shown in Figure. 2.



Figure 2. various stages during synthesis of Plasma Sprayable Powders

The powders were characterized for crystallographic structural phase by using X-ray Diffractometer (XRD), particle size and morphology by using Scanning Electron Microscope (SEM) and chemical composition via Energy Dispersive Spectroscopy (EDS) associated with the SEM. The final powder composition, devoid of moisture was used as plasma sprayable powders followed by plasma spray coating and characterization (XRD, SEM-EDS)

2.2. Processing of plasma spray coated specimen

A 100 KW Sulzer Metco Atmospheric Plasma Spray (APS) system was used to spray coat the laboratory prepared plasma sprayable powders. The flowability of the plasma sprayable powders was evaluated by allowing the powder to flow through the spray gun with only the primary and secondary flow gases, followed by measuring the amount of powder flowing through the system per minute. The flowability was determined to be about 30 grams/minute. This also allowed the estimation of the deposition efficiency which was found to be good.

The alumino-silicate plasma sprayable powders were spray coated on stainless steel (SS) substrates. The substrates measuring 80mm x 80mm x 3 mm (thick) were grit blasted with alumina, degreased prior to being bond coated with ~80 microns NiCrAlY (AMDRY 962) bond coat. The top coat was ~200 micron thick alumino silicate. The spray parameters used in the preparation of the bond coat and the top coat are shown in Table 1.

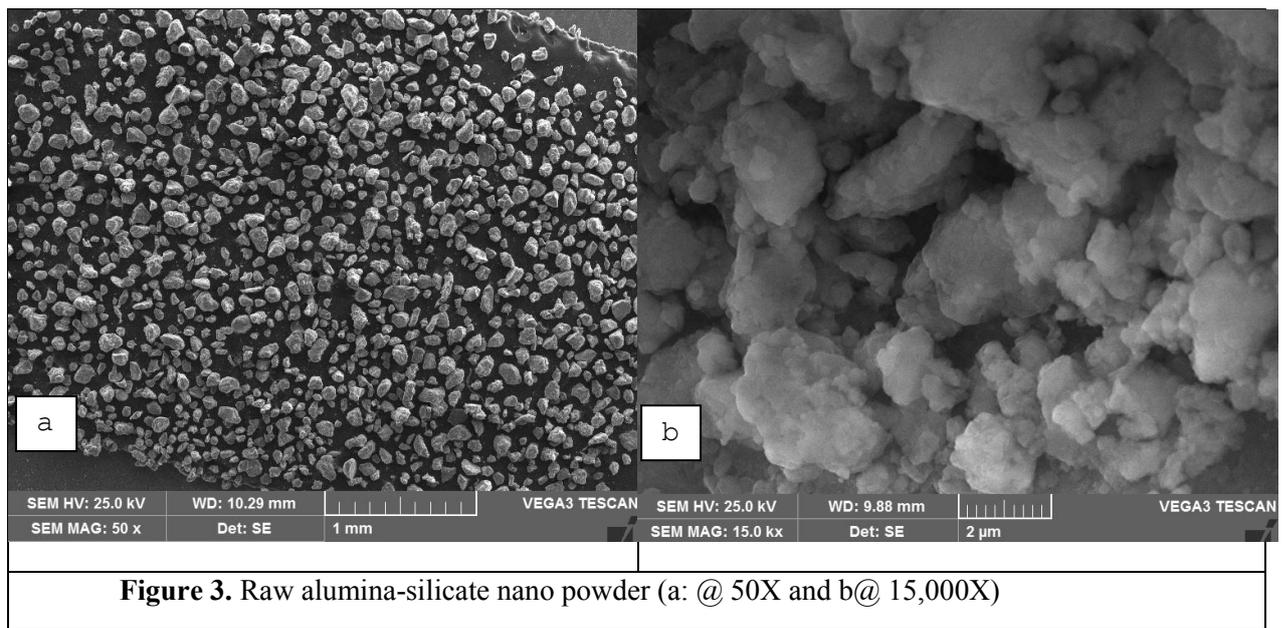
Parameters	Bond Coat (NiCrAlY)	Ceramic Top Coat (Alumino-silicate)
Argon (l/min)	36	44
Hydrogen (l/min)	14	13
Current (A)	600	630
Voltage (V)	71	70
Nozzle /Electrode (mm)	6	6
Injector Diameter (mm)	1.5	1.8
Injector angle (Degrees)	90	90
Injector Distance (mm)	6	6
Powder gas (l/min)	3.4	3.4
Powder Feed Rate (g/min)	34	40
Spray Distance (mm)	120	120
Substrate Air cooled	Yes	Yes

It has reported that the hardness and wear resistance of plasma sprayed nano coatings can be increased by (a) increasing the critical Plasma Spray Parameter (CPSP) which is a function of current, voltage, and primary gas feed rate or (b) decreasing the spray distance [13]. The improvement in hardness and therefore wear resistance characteristics may be explained on the basis of partially melted regions that might compensate a deleterious effect of the hardness decrease, attributed to varying CPSP. In this work, the parameter suited for plasma spray coating micron sized plasma spray powders of Al₂O₃ was used.

3. Results and Discussion

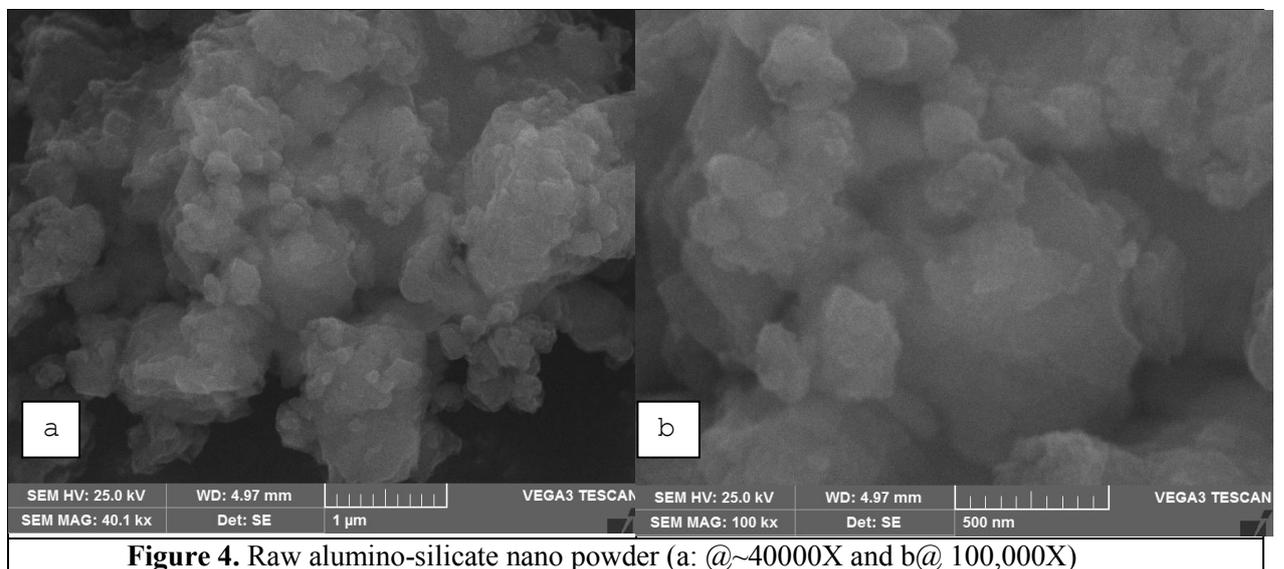
3.1. Plasma spray powder characteristics:

The raw material powder morphology, of the plasma sprayable powder, studied under SEM is shown in Figure 3 and 4 (a and b).



The study of powder morphology via SEM provided a realistic image of the size and the shape of the plasma spray powders. The SEM images of the raw Alumina – Silicate nano powders, studied at fairly low magnifications (50 X and 15,000X) identified the basic morphology of the powder particles, which were found to be rounded and agglomerated.

It was not possible to determine the individual particle sizes of the expectedly nano sized grains. The individual sizes of the nano particles became visible and clearer at higher magnification images. The images at higher magnification are shown in Figure 4 (a and b): at 40,100 X and 100,000 X respectively.



On an average the nano grains measured about 100 nanometers with a minimum of 50 nanometers and a maximum grain size of 150 nanometers.

3.2. Plasma spray coated specimen

Plasma spray coating of a material on a specimen plays a vital role to allow the understanding of the capability of the material to perform in an application and environment in spite of being thin. The main purpose of nano coatings is to compare the properties with nano sized morphology with some another

The glassy matrix regions in the microstructure were expected to enhance the hardness and wear characteristics [13]. Preliminary hardness measurements indicated the spray coated specimen, studied in mounted metallographic cross section to be $610 \pm 90 \text{ Hv}_{0.2}$. the somewhat large variation in microhardness numbers is most likely attributable to the twin morphologies, namely nano grains in glassy matrix. A detailed hardness measurement was beyond the scope of this paper.

The chemical analysis of the plasma spray coated alumino-silicate, determined via EDS associated with SEM, is shown in Fig 7. The selected area (shown within red block in the SEM micrograph) comprised of both the nano grains and the glassy matrix.

The qualitative analysis of the region revealed the presence of Al and Si peaks in addition to the expected peak of oxygen. The quantitative analysis gave the percentages of Al, Si and O contents: the oxygen content (not an accurate analysis) was as high as~ 45% (wt. %). This established that the phase/s was (or were) most likely comprised of an oxide of aluminum and Silicon. EDS is not the tool to determine if the oxides pertained to Al and Si (Al_2O_3 and SiO_2) as individual entities or in combined form (AlSi_2O_5). This aspect was verified by subjecting the coated surface to XRD analysis.

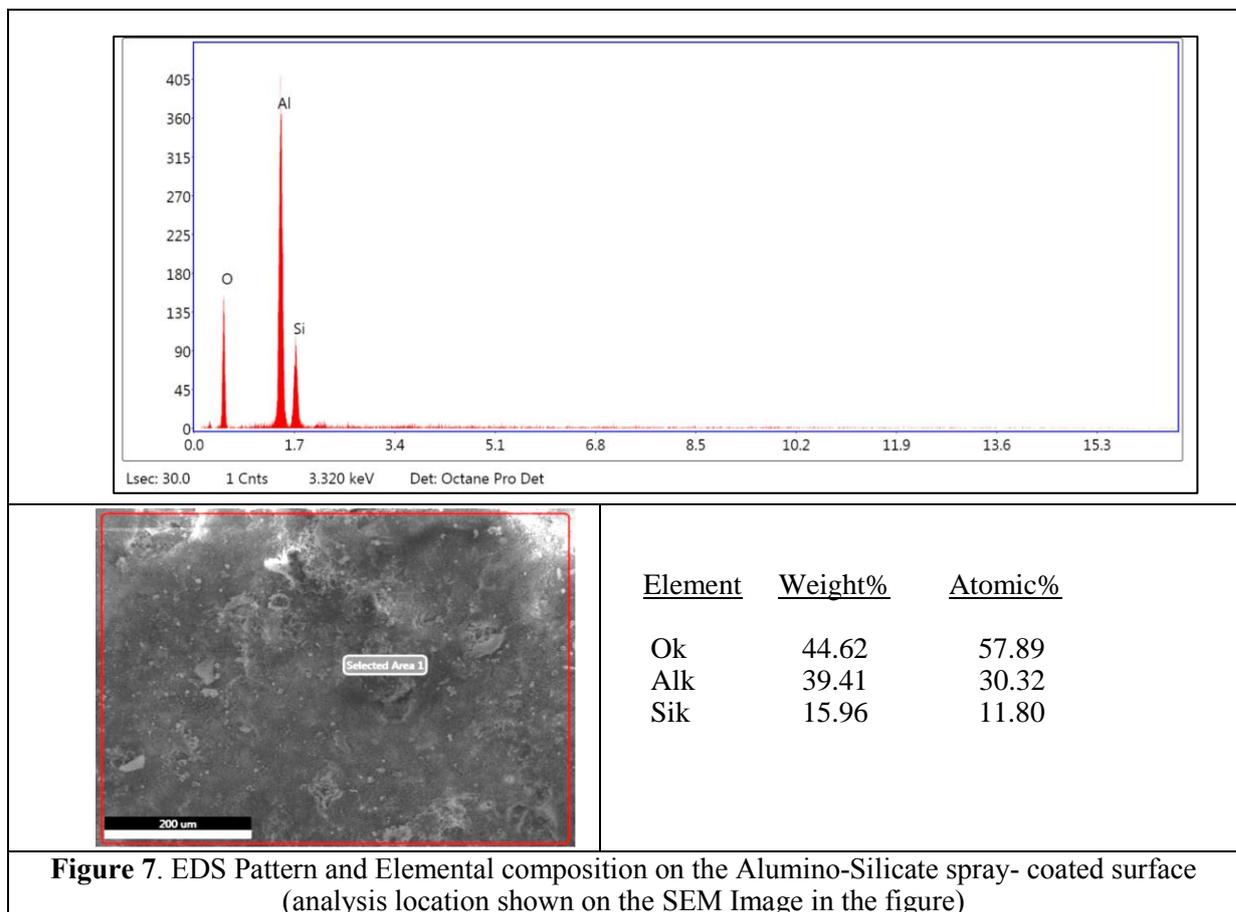


Figure 7. EDS Pattern and Elemental composition on the Alumino-Silicate spray-coated surface (analysis location shown on the SEM Image in the figure)

3.4 Crystallographic structural phase analysis

Based on the EDS results, as shown in Fig 7, It was expected that the XRD pattern of the as-coated surface will comprise of a single phase with aluminium, silicon and oxygen or two phase with oxides of Al and Si separately. This was confirmed by analyzing the XRD pattern which is shown in Figure 8.

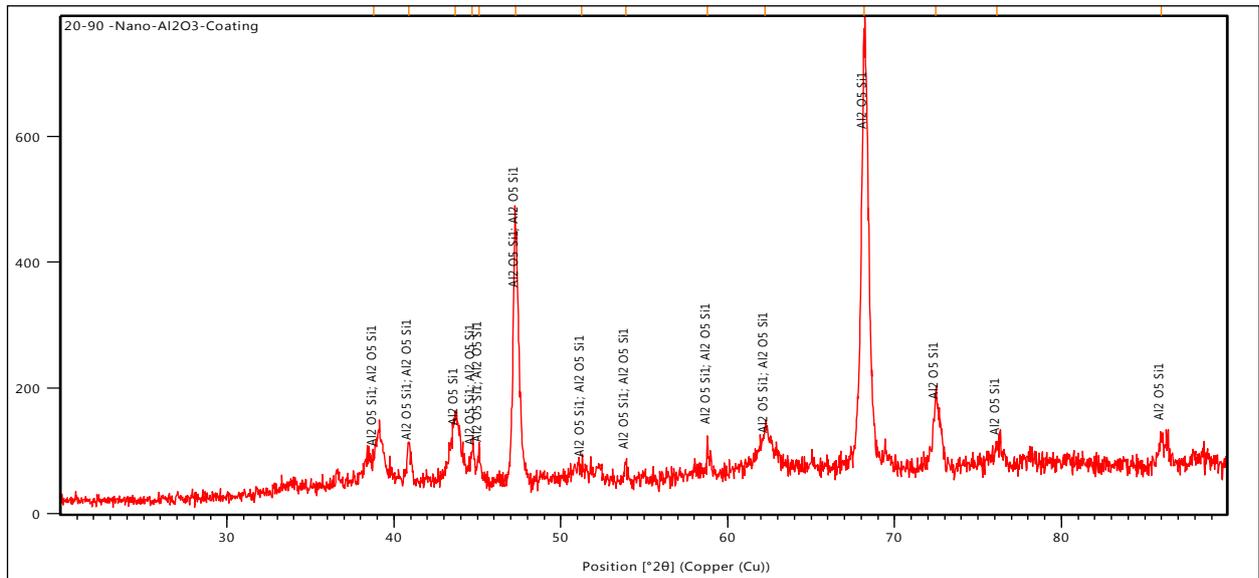


Figure 8. XRD Pattern of plasma spray coated surface

The crystalline nature of the coating was revealed via the sharp nature of the patterns: however the base was not even and suggestive of some amount of glassy phase. The glassy nature of the coating has occurred due to the plasma spray coating process which was also reflected in the SEM micrographs shown in previous pages.

The indexing of the patterns was carried out and the coatings comprised of two major phases: namely (1) kyanite and (2) andalusite. The chemical formula of the two phases is the same namely: Al_2SiO_5 . Kyanite, and andalusite are naturally occurring anhydrous aluminum silicate minerals with the same chemical formula, Al_2SiO_5 , but differing crystal structures, making them mineral polymorphs.

Kyanite and its related minerals are used to make a variety of refractory materials which are resistant to very high temperatures. As a result, more than half of the kyanite consumed is used in refractories for the production of steel and is also used to produce refractories for nonferrous (non-iron-bearing) metals. It is also consumed to make refractories for glass and heat-resistant ceramics, make spark plugs etc.

4.0 Concluding Remarks

Nano sized plasma sprayable powders were synthesized from alumina-silica based nano-sized raw material composition. The synthesis comprised of blending the alumino-silicate nano powders (~100nm) with organic binders (PVA), followed by manual processing steps involving uniform distribution of binder in ceramic matrix, oven drying, grinding, and sieving (ASTM sieves 53 – 106 μm) to suitable sizes as was desired for good flow characteristics in the atmospheric plasma spray system. The plasma sprayable powders were plasma spray coated on bond coated (NiCrAlY) stainless steel substrates up to a thickness of 200 microns.

The spray parameters were made to suit the retention of the nano sized individual grains within the micron sized spray powder particles. Microstructure and chemical composition analysis followed by crystallographic structural phase analysis confirmed the presence of pure nano-sized kyanite and andalusite phases in a melted ceramic matrix.

The refractory coatings developed in this work were found to consist of nano sized grains in a glassy matrix. Both Kyanite and andalusite, with same chemical formula Al_2SiO_5 , are materials with slight variances in crystal structure and are expected to give unique physical properties with great potential for

application in modern industries. The potential benefits of nano ceramics or coatings include improved materials characteristics such as higher hardness, strength and toughness resulting from reduced grain size and slip distance, reduced defect size and enhanced grain boundary stress relaxation, even at ambient temperature. Diffusivity is greatly increased, associated with a larger volume of grain boundaries. Thermal conductivity in ceramics or refractories may be reduced because of enhanced phonon scattering from grain boundaries and other nanoscale features. Thus Nano sized refractory coatings based on kyanite and andalusite have great potential for engineering industrial applications. One typical application may be in-situ repairs of blast furnace by providing coatings of nanoparticles that can satisfy requirements of protection from high temperature corrosion.

5. Acknowledgements

The authors gratefully acknowledge the CHRIST (Deemed to be University) Management headed by Vice Chancellor, Dr. (Fr.) Thomas C Mathew, Engineering Director Dr. Fr. Benny Thomas, Associate Director (Research) Dr. D.N.S. Kumar, Associate Dean, Faculty of Engineering Dr. Iven Jose, and Mechanical Department HOD and Associate Professor, Dr. Gurumoorthy S Hebbar for encouraging this R&D work and permission to present and publish.

6. References

- [1] Zagorka Aćimović-Pavlović et. al. 2012 Ceramic coating for cast house application *ceramic coatings – application in Engineering* 261-286
- [2] Anna Leinonen & Sirkku Kivisaari 2012 Nanotechnology perceptions *J. pub med* **8** (1) 7-16
- [3] Michael J. Potter, 2003 Kyanite and Related Materials *U.S. geological survey minerals year book* 42.1 – 42.3
- [4] P.Changon, P.Fauchais 1984 Thermal spraying of ceramics *Ceramics International* **10** 119-131
- [5] C.Richard, C.Kowandy, J.Landoulsi, M.Geetha, M.Ramaswamy 2010 Corrosion and wear behaviour of thermally sprayed nano ceramic coatings on commercially pure titanium and Ti-13 NB-13Zr substrates *J. Refractory Metals and Hard Materials* **28** 115-123
- [6] Yi Zeng, S W Lee, L Gao, C.X.Ding 2002 Atmospheric Plasma Sprayed Coatings of Nanostructured Zirconia *J. European Ceramic Society* **22** 347-352
- [7] Baohe Hang, Wenbo zhang, Wei Zhang, Arun S Mujumdar & Lixin Huang 2005 Progress in drying Technology for nanomaterials *J. Drying Technology* **23** 7-32
- [8] Jo Ann Gan and Christopher C. Berndt 2015 Nano composite coatings: thermal spray processing, microstructure and performance *J. Materials Reviews* **60** 195-244
- [9] Jianxin Zhang, Jining He, Yanchan Dong, Xiangzhi, Dianran Yan 2008 Microstructure characteristics of Al₂O₃ – 13 wt. % TiO₂ coating plasma spray deposited with nano crystalline powders *J. Materials Processing Technology* **197** 31-35
- [10] Chaouki Sadika a, Iz-Eddine El Amrani b, Abderrahman Albizanea c 2014 Recent advances in silica-alumina refractory: A review *J. Asian Ceramic Societies* **2** (2) 83-96
- [11] E. H. Jordan, M. Gell, Y. H Sohn, D. Goberman, L. Shaw, S. Jiang, M. Wang, T. D Xiao, Y.Wang, P.Strutt 2000 Fabrication and evaluation of plasma sprayed nano structured alumina – titania coatings with superior properties *Material science and engineering* **301** 80-89
- [12] Vinay pratap singh, Anjali sil, R Jayaganthan 2011 A study of sliding and erosive behaviour of atmospheric plasma sprayed conventional and nano structured alumina coatings *Materials and design* **32** 584-591
- [13] Eun Pil Song, Jeehoon Ahn, Sunghak Lee, Nack J. Kim 2008 Effects of critical plasma spray parameter and spray distance on wear resistance of Al₂O₃–8 wt.%TiO₂ coatings plasma-sprayed with nanopowders *Surface & Coatings Technology* **202** 3625–3632.