

## ADVANTAGE OF ADVANCED EROSION-CORROSION RESISTANT NANO-STRUCTURED COATINGS: A REVIEW

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### ABSTRACT

*Hot corrosion is recognized as serious problems in coal based power generation equipment, fluidized bed combustion, gas turbines, internal combustion engines, industrial waste incinerators and paper and pulp industries. High temperature corrosion is a severe problem which may result in premature failure of the boiler steel. One countermeasure to overcome this problem is the use of nano-structured protective coatings. To find the performance of the nano-structured coatings in actual conditions the bare as well as the coated steels were subjected to cyclic exposures, in the actual Boiler plant environment. To evaluate the performance of the coatings in actual conditions the bare as well as the coated steels were subjected to cyclic exposures, in the actual boiler power plant environment. nano-structured coatings have high abrasive resistance, very low porosity, high hardness, good wear resistance with a strong ability to resist high-temperature corrosion resistance. The effect of coatings thickness, residual stresses induced in the substrates, pre and post heat treatment of the nano-structured coatings have been reviewed with the aims of summarizing their high-temperature corrosion resistance properties.*

**Keywords:** Nano-structured coating, Hot corrosion, Corrosion resistance.

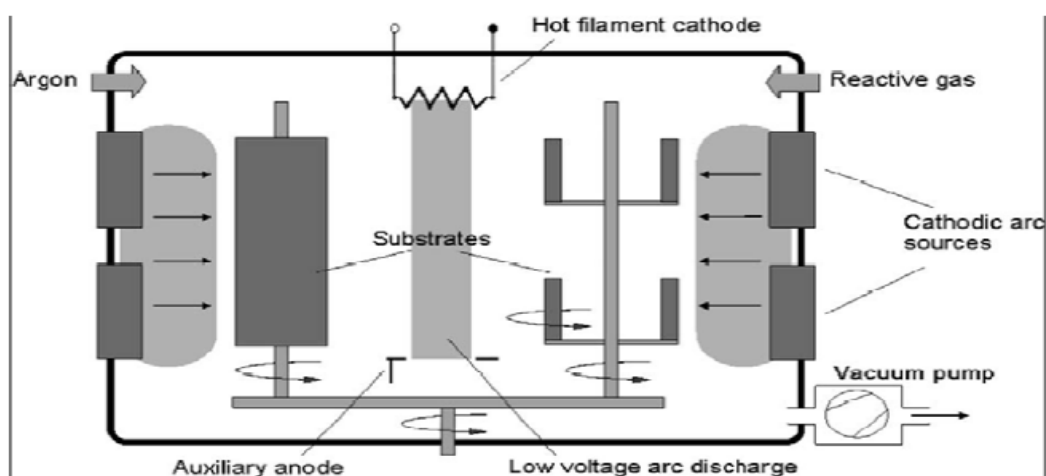
### 1. INTRODUCTION

Structural materials in many high tech industries have to operate under extreme conditions of temperature, pressure and corrosive environment [1]. So, degradation of materials at very high temperature range is become a serious problem in high tech industries. Sugar industries, Fossil fuelled power plants, Petrochemical industries and Gas turbines in aircraft are some examples where corrosion limits their use and reduces their life. So it affects their efficiency [2]. Coating protects the materials of high temperature equipments. It protects the materials from oxidation and corrosion attacks [3]. Coating enhances the limit of use of the materials at the upper end of their performance capabilities nano-structured coating is much better than conventional coating which provides a good surface characteristic such as hardness wear resistance etc [4]. A recent study investigates the effects of nano-structured Chromium based thin coatings on oxidation behaviour of T-22 steel under the cyclic heating conditions. T-22 grade of steel is used in making boiler tube materials due to its performance in stringent service conditions of pressure and temperature.

## II COATING TECHNIQUES

### A. Physical Vapour Deposition Method

In physical vapour deposition (PVD) process (Fig.1), the coating is deposited in vacuum by condensation from a flux of neutral or ionized atoms of metals. There are also other PVD techniques available for deposition of hard coatings such that magnetron sputtering (or sputter ion plating), combined magnetron and cathodic arc vapour (plasma or arc ion plating) deposition and arc processes are most widely used techniques to deposit titanium-aluminum based coatings. This process is carried out in high vacuum at temperature between 150°C and 500°C. The high purity solid coating material (metals such as titanium, chromium & aluminium) is either evaporated by heat or by bombardment with ions (sputtering). At the same time, a reactive gas (e.g. nitrogen or a gas containing carbon) is introduced; it forms a compound with the metal vapours and is deposited on the tools or components as a thin, highly adherent coating. In order to obtain a uniform coating thickness, the parts are rotated at uniform speed about several axes. The PVD techniques are widely used nowadays for improvement of the mechanical and other properties, of a broad range of engineering materials. Employing the PVD techniques for the deposition of coatings (namely multilayer coatings) ensures high corrosion and wear resistance. Besides, the ceramic nitrides, carbides present interesting colours which allow them to be used in decorative components (e.g., golden or a polished brass-like) [6]. In. S. Choi et.al. [7] have studied the corrosion behavior of TiAlN coatings prepared by PVD in a hydrofluoric gas atmosphere. TiAlN coating has one of the highest working temperature (800°C) due to the surface being covered with a stable and passive aluminum oxide layer. When TiAlN is exposed to a HF gas atmosphere in working conditions, it reacts with HF and forms aluminum fluoride (AlF<sub>3</sub>), which is chemically very stable to various corrosives such as acid, alkaline, alcohol and even HF. The process was quite successful and the coating exhibit better corrosion resistance. Sugehis Liscano et al. [8] have studied corrosion performance of duplex treatments based on plasma nitriding and PAPVD (Plasma Assisted physical vapour deposition) TiAlN coatings. The nanograined TiAlN coating has shown better results than the conventional counterpart.



**Fig. 1 Schematic illustration of the coating device used for the film deposition (Ranjeet et al. [5])**

### B. Thermal Spraying

The coating materials which are used to protect components from erosion wear, adhesive wear, abrasive wear, surface fatigue and corrosion are coated by thermal spraying. The materials which does not dissociate, vaporize, decompose or sublime on heating can be thermally sprayed. So a wide range of metals, non-metals, polymers, ceramics and alloys can be thermally sprayed. Heath et al [9] has summarized the thermal spray processes that have been considered to deposit the coatings, are enlisted below:

1. Flame spraying with a powder or wire
2. Electric arc wire spraying
3. Plasma spraying,
4. Spray and fuse
5. High Velocity Oxy-fuel (HVOF) spraying
6. Detonation Gun.

The technique of thermal spraying has developed at a fast pace due to progress in the advancement of materials and modern coating technology. Plasma-sprayed ceramic coatings are used to provide lubrication and thermal insulation, and used to protect metallic structural components from corrosion, wear and erosion [10]. In particular, coatings made of  $Al_2O_3$  containing 13 wt%  $TiO_2$  ( $Al_2O_3$ -13 wt%  $TiO_2$ ) are commonly used to improve the vapour deposition) TiAlN coatings. The nanograined TiAlN coating has shown better results then the conventional counterpart.

wear-corrosion and erosion resistance of steel. In conventional plasma-spray processing of  $Al_2O_3$ -13 wt%  $TiO_2$  coatings, powder particles are injected into plasma jet, causing them to melt into droplets that are propelled towards the substrate [10]. The processing is performed at “hot” plasma conditions which ensure complete melting of the powder particles so that chemical homogeneity can be obtained in the coating [11].

S.B. Mishra et. al.[12] has deposited coating of nickel-aluminide on Fe-based super alloys. The coatings had shown better erosion resistance as compared to the uncoated samples. H.Singh et. al. have studied high temperature oxidation behaviour of plasma sprayed  $Ni_3Al$  coatings. He studied that,  $Ni_3Al$  powder was prepared by mechanical mixing of pure nickel and aluminium powders in a ball mill. Subsequently  $Ni_3Al$  powder was deposited on three Ni-base superalloys: Superni 600, Superni 601 and Superni 718 and, one Fe-base super alloy. H.Singh et. al. [13] have studied hot corrosion performance of plasma sprayed coatings on a Fe based superalloy. Hot corrosion studies was done on both uncoated material as well as plasma sprayed coated after exposure to molten salt at 900 °C. The coated specimens have shown better performance as compared to the uncoated specimens.

### C. Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition method is a process which is used to deposit the coating on metal as well as non-metal such as carbon and silicon [2]. The first step is the production of metal vapours. Many chemical reactions can be used such as reduction, pyrolysis, oxidation, nitridation thermal decomposition etc. The main reaction is carried out in a separate reactor. The formed vapors then transferred to the coating chamber where the sample is



mounted and maintained at high temperature. This method cannot work under high substrate temperature which changes the microstructure of the substrate. This is the limitation of CVD method. S. Tsipas et. al. [14] have studied Al–Mn CVD-FBR protective coatings for hot corrosion application. He studied that new Al-Mn protective coatings were deposited by CVD-FBR on two ferritic steels (P-92 and HCM12). To obtain Mn containing aluminide coating on ferric steels, this technique is found to be powerful and effective. These coatings could be potential candidates for steam oxidation protection of ferritic steels.

The CVD-FBR technique has been shown to be a very interesting surface modification technology because aluminium diffusion coatings can be produced at lower temperatures and shorter times than by conventional pack cementation. Overall, the heat-treated aluminum coated AISI 304 specimens may find an application due to the combination of their toughness and the potential good corrosion properties.

### III NANO-STRUCTURED COATINGS

Nano-structured coatings provides a good surface protection with unique physical and chemical properties that are often not attained in the bulk materials. Nano-structured materials enhanced the materials properties as well as structural length scale between 1 and 100 nm. Pavitra Bansal et al [10] compared conventional and the nano Al<sub>2</sub>O<sub>3</sub>- 13wt% TiO<sub>2</sub> plasma sprayed ceramic coatings on steel substrate. These coatings have good abrasive properties and good bond strength which is two times greater than that of the conventional plasma sprayed coatings, measured using ASTM pull test. These new coatings are referred as “nano”, since they are derived from nanocrystalline powders. Leon L.Shaw et al [15] studied the dependency properties of nanostructure and properties of nanostructured coating on plasma spray conditions. Wear test reveals that the coating produced from nano powder feedstock could have better wear resistance than the coatings produced using commercial coarse-grained powders. The higher wear resistance of nano-structured coating improved micro hardness and attributed to their optimized micro structure. L. Leblanc [16] has evaluated micro-structural as well as abrasion and sliding wear properties of APS (Atmospheric plasma spraying) and VPS (Vacuum plasma spraying) sprayed Al<sub>2</sub>O<sub>3</sub>-13TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>-3TiO<sub>2</sub>, and TiO<sub>2</sub> coatings from micro-structured and nano-structured powders. Performance and characteristics of VPS-applied coatings are generally superior or equal to those of APS-applied coatings. VPS provide a better environment for applying nano-structured oxide ceramic materials, as compared to APS.

**Table I: Comparison study of various types of coatings and coating techniques**

S. NO.	Coating	Substrate	Thickness (µm)	Coating Technique	Ref.
1	Co-Al	Superni 718	5µm	DC/RF Magnetic Sputtering	[17]
2	Ni-Al	Superni 718	5µm	DC/RF Magnetic Sputtering	[18,19]
3	TiAlN	Cemented Carbide	3+.02µm	Blazer’s Rapid Coating System	[20-21]
4	AlCrN	Cemented Carbide	3+.02µm	Blazer’s Rapid Coating System	[20-21]
5	TiN	Steel	6µm	PVD	[22]
6	Ni-20Cr	SAE 213-T22	4.5+.15m	HVOF	[23]

7	TiAlN	T22 Boiler Steel	4±1µm	Blazer's Rapid Coating System	[24]
8	AlCrN	T22 Boiler Steel	4±1µm	Blazer's Rapid Coating System	[24]
9	Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	Austenitic Stainless steel	500µm	Plasma Spraying	[25,26]
10	WC-NiCrFeSiB	Superni 75	250-300µm	HVOF	[27]
11	NiCrBSi	Superni 75	100-300µm	HVOF	[28,29]
12	TiAlN	Superfer800H	4±1µm	Blazer's Rapid Coating System	[30]
13	AlCrN	Superfer800H	4±1µm	Blazer's Rapid Coating System	[31]

#### IV HOT CORROSION

According to Hancock [31] and Eliaz et al. [32], when metals are heated in the temperature range 700–900 °C in the presence of salts deposits formed as a result of the reaction between sodium chloride and sulphur compounds in the gas phase surrounding the metal is called as hot corrosion. Khanna and Jha [33] have reported about the formation of salt during the combustion of coal/fuel. At high temperatures, deposits of Na<sub>2</sub>SO<sub>4</sub> (m.p. 884 °C) can cause accelerated attack on the Ni and Co-base super alloys. This type of attack is commonly called hot corrosion. Accelerated corrosion can also be caused by the other salts, viz. sulphates or vandates and in the presence of solid or gaseous salts, such as chlorides [34]. These salts are common impurities in low grade petroleum fuels. Due to the condensation of combustion products of such fuels are extremely corrosive to high-temperature materials in combustion systems [35].

#### V DISCUSSION

The nano-structured chromium coated T-22 boiler steel showed better corrosion resistance in Na<sub>2</sub>SO<sub>4</sub>-60%V<sub>2</sub>O<sub>5</sub> (molten salt) environment at 900°C and weight gain was relatively higher as compared to the other coating. The parabolic behavior is due to the diffusion controlled mechanism operating at 900°C under cyclic conditions [36]. Small deviation from the parabolic rate law might be due to the cyclic scale growth. This, in turn, will make the weight gain and hence the oxidation rate steady with the further progress of exposure time [37, 38].

#### VI CONCLUSION

Nanostructured coatings have strong technological potential, Once the oxides are formed at places of porosity and splat boundaries, the coating becomes dense and the diffusion of oxidizing species to the internal portions of the coatings gets slowed down and the growth of the oxides becomes limited mainly to the surface of the specimens. The nano-structured TiAlN coatings has shown higher hot corrosion resistance as compare to other nanostructured coatings. Application of a proper combination of preventive approaches should lead, in practice, to a significant decrease in the number of failures due to hot corrosion.



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