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High-Temperature Performance of CNT-Based Nanocomposite Coatings on Boiler Tubes: A Critical and Comparative Review of Recent Advances

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Abstract*— Coal-fired thermal power plants have boiler tubes which operate in harsh conditions of high temperature including oxidation, molten salt corrosion and particle erosion which hastens the degradation of the material. Nanocomposite coating made of carbon nanotube (CNT) has recently attracted interest as a superior-protective system since it is of excellent mechanical strength, thermal stability and crack-bridging ability. This review is a critical analysis of the recent developments in CNT-based ceramic and metallic coating on boiler-grade steels. Emphasis is placed on plasma sprayed and HVOF deposited systems of the type Al_2O_3-TiO2-CNT, ZrO_2-Y_2O_3-CNT and NiCr-Cr_3C_2-CNT coatings. The effects of CNT addition on microstructural refinement, porosity, better interfacial bonding and hardness are discussed in respect of oxidation and erosion-corrosion resistance up to 900 deg C. Comparative results show that optimized CNT content is much better in terms of integrity of the coating and high temperature durability. Nevertheless, nanotube agglomeration, thermal degradation, and dispersion control are some of the main concerns that should be solved. The review synthesizes structure-property-performance association and outlines the future research to come up with dependable CNT-based protective coating in the high-temperature boiler applications.

Keywords-Carbon-nanotubes (CNTs), Nano-composite coatings, Boiler tubes, High temperature oxidation, Erosion corrosion resistance

I. INTRODUCTION

Thermal power plants have boiler tubes which are subjected to hostile conditions of high temperature (600-900 deg C), and through the combination of oxidation, hot corrosion, erosion, and thermal fatigue, facilitate materials degradation and early component failure. Long term exposure to molten salts (Na_2SO_4, V_2O_5), particles of fly ash, and cyclic changes in temperature hastens the process of oxide scales and spallation thus ultimately leading to a thinning of the wall and to a decrease in service life [1],[2]. Traditional coating or protection like NiCr, NiCrAlY, Al_2O_3- TiO_2 and ZrO_2-Y_2O_3 have been extensively used but the performance is generally restricted by porosity, micro crack formation and poor scale adherency under the impact of cyclic conditions [3], [4].

Nanostructured materials have recently made new progress in the form of carbon nanotube (CNT)-reinforced nanocomposites coating, which is promising as a high-temperature protection. CNTs are very strong in terms of their tensile strength, aspect ratio, and thermal conductivity and all of them increase their ability to bridge cracks and densify the matrix upon uniform dispersion [5],[6]. Experiments have been able to show enhanced corrosion resistance and mechanical integrity properties of CNT-based composite coatings over established systems [7], [8].

In the past five years, there has been a tremendous research on the introduction of multi-walled CNTs (MWCNTs) into ceramic and metallic matrices deposited through thermal spray and other associated methods to improve the high-temperature behavior [5],[9],[10]. The developments are critically reviewed by focusing on the degradation mechanisms, coating microstructure, oxidation resistance, erosion behavior, as well as future research direction.

II. HIGH-TEMPERATURE DEGRADATION MECHANISMS IN BOILER TUBES

Minor degradation of boiler tubes is mainly experienced as a result of high-temperature oxidation, hot corrosion, erosion-corrosion, and thermal fatigue.

Oxidation at high temperatures causes Fe_2O_3, Fe_3O_4 and Cr_2O_3 scale which continues to increase and ultimately spalls during repeated stresses [11], [12], [13]. Molten salt deposits enhance the rates of hot corrosion in coal-fired boilers, which boosts the rates of metal losses. There has been increased resistance to oxidation on the layers of the thermal spray; evidently, the porosity at microstructural levels and splat limits serve as diffusion routes of corrosive elements [13], [14], [15].

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Fig.1 Damage and perforation of the boiler tubes were caused by erosion-corrosion (TSPCL)

The Figs.(a)-(d) demonstrates the progressive erosion corrosion damages in boiler tubes that undergo service conditions of high temperatures. Localized wall thinning and pitting is also experienced because of particle impingement and corrosive attack.Splintering of oxide scales also enhances the rate of material wear.

Both extreme degradation causes through-wall perforation of the tubes.

The erosion-corrosion takes place because of high-velocity fly ash/particulate impact, which removes the protective oxides scales and the underlying substrate is exposed. The CNT reinforced NiCr-Cr_3C_2 coating has been shown to have lower erosion rates because they are better densified and offer better crack resistance [16], [17].

Repeated heating and cooling cycles cause thermal fatigue which causes stress due to thermal mismatch between coating and substrate. NT addition increases crack-bridging and prevents crack propagation, which increases coating longevity [18], [19].

III. CNT-BASED NANOCOMPOSITE COATING SYSTEMS AND DEPOSITION TECHNIQUES

A. Ceramic Matrix Systems

Hot corrosion resistance and mass gain at high temperatures have been reported to be improved by the incorporation of CNT into Al_2O_3-TiO_2, ZrO_2-Y_2O_3 matrices [20] [21], [22]. The higher hardness and toughness of fractures are credited to CNTs introducing crack deflection and crack bridging [23]. Optimized CNT content (0.5-2 wt%) decreases porosity and it enhances oxide scale adhesion [24].

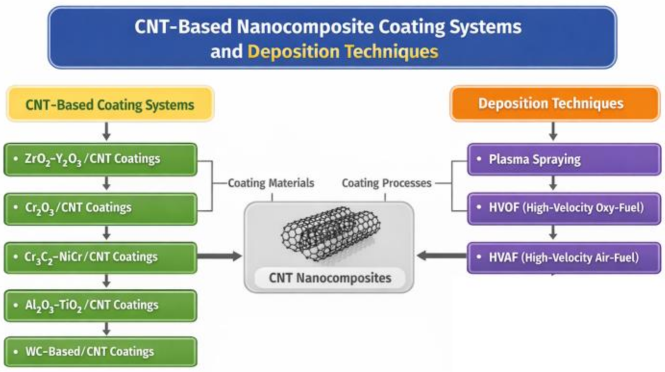

Fig. 2. Flow chart of CNT-based nanocomposites coating and deposition methods

The fig. 2 shows an overview of CNT-based nanocomposite coating systems and their classification. It highlights commonly used ceramic and cermet matrices reinforced with CNTs. Major thermal spray deposition techniques such as plasma spraying, HVOF, and HVAF are also illustrated.

B. Metallic and Cermet Systems

CNTs reinforced with metallic matrices like NiCrAlY show better resistance to oxidation and better density of the coating when deposited using HVOF methods [25]. In a similar manner, CNT-modified NiCr-Cr_3C_2 Coatings exhibit greater erosion resistance and reduced weight loss when compared to non-reinforced Coatings [2], [26]. The study on NiCo-CNT composite coatings also demonstrates the enhanced corrosion resistance because the grain is refined, and the density of the defects is low [26], [27].

C. Deposition Techniques

CNT-based coating is done by Atmospheric Plasma Spray (APS) and High Velocity Oxy-Fuel (HVOF) [28] [29]. However, the dispersion of CNTs is still a problem because of agglomeration forces [30]. CNT dispersion and matrix bonding are enhanced through surface functionalization and optimized feedstock preparation [31].

IV. COMPARATIVE HIGH-TEMPERATURE PERFORMANCE

A. Hardness and Mechanical Properties

CNT reinforcement has a large enhancement on hardness and fracture toughness. It is suspected by studies of promoting hardening of up to 15-30 percent in coating with CNT compared to conventional systems [32], [33]. The propagation rates are decreased by crack-bridging mechanisms in case of thermal stress [34].

Table 1. Comparative properties and microstructural characterization of CNT-reinforced coating

Coating System	Key Findings (H = Hardness, P = Porosity)
ZrO_2–Y_2O_3 (0%)	H: 789–796 HV; P: 4.25%; dense splats; Zr–Y–O phases [21]
ZrO_2–Y_2O_3 (1% wt% CNT)	H: ~910 HV; P: 3.62%; uniform CNT; +C peak; Zr–Y–O–C [21]
ZrO_2–Y_2O_3 (4% wt% CNT)	H: ~1050 HV; P: 3.45%; dense lamellae; stable phases +C [21]
Cr_2O_3 (2–6% wt% CNT, HVOF)	H ↑ (max 6%); P ↓; uniform CNT; Cr_2O_3 retained [12]
Cr_3C_2–25NiCr (0–7% wt% CNT, HVOF)	H ↑ (max 7%); P: 1.176% (min); dense; Cr–Ni–C [13]
Al_2O_3–13TiO_2 +1.5% wt% CNT	H ↑; P ↓; homogeneous; stable phases [45]
YSZ–Al_2O_3 +3% wt% CNT	H ↑; roughness ↓; tough morphology; YSZ confirmed [46]
WC–Co +1% wt% CNT	~30% H ↑; P ↓; better cohesion; WC retained [47]
WC–CoCr +0.3% wt% CNT	1420 vs 1357 HV; 1.81% vs 2.73%; dense; WC, Co_3W_3C [48]

As presented in Table 1 the comparative outcomes do reveal that the CNT reinforcement is greatly contributing to coating performance especially hardness and densification. Hardness in zirconia-based based on CNT addition showed a strong rise (≈ 790 HV to ≈ 1050 HV), and porosity was always reduced, showing a better compactness of the coating. The same is seen in Cr_3C_2-NiCr and WC-based coatings, in which incorporation of CNT enhanced microhardness and lowered the amount of defects. Analysis of SEM across studies reveals more homogenous and dense microstructures having superior inter-splat bonding. The analysis of XRD shows that CNTs are chemically stable and do not develop unwanted phases, whereas the EDAX/EDS method proves that carbon is incorporated successfully. All in all, CNTs are useful reinforcement agents, enhancing mechanical strength, structural integrity, and coating quality of high temperature protection systems.

B. *Oxidation and Hot Corrosion Resistance*

Hot corrosion tests has been conducted at 900 deg C and show the reduced mass gain in CNT reinforced ceramic coatings due to the denser oxide formation and the improved scale adherence [21], [35]. The performance of NiCrAlY-CNT systems is better than that of oxidation kinetics as compared to the base coating [36].

C. *Erosion-Corrosion Performance*

According to erosion researches, CNT-reinforced NiCr-Cr_3C_2 coating experiences less mass loss at high impact angles since the toughness of the matrices is increased [4]. Enhanced lamellar cohesion minimizes the crack generation and material abrasion [37].

D. *Thermal Stability*

Even though CNTs improve the performance at moderate high temperatures, the oxidation of CNTs beyond the temperature of about 800 deg C can be detrimental to the reinforcement effect of CNTs [38]. Content of CNT (>2 wt%) enhances agglomeration and poor interfacial bonding [39].

V. Limitations and Research Gaps

Despite some promising laboratory results were achieved, there are still a number of challenges:

- Oxidation CNT during very high temperatures [40]
- The problem of agglomeration and dispersion [41]
- Minimal cyclic oxidation data in the long run [42]
- Scaling up and industrial validation issues [43]
- Combined methods of CNTs with graphene or ceramic nanoparticles can be used as a method of enhancement of thermal stability [44].

VI. Conclusions

The nanocomposites developed on the basis of CNTs provide greater advances in hardness, oxidation resistance and erosion-corrosion characteristics as compared to the traditional coating applied on the boiler tubes. Ceramic-CNT systems are characterized by a better oxidation resistance and metallic CNT composites are characterized by better erosion performance. The ideal CNT content (0.5-2 wt) is essential to ensure that the maximum benefits are achieved without the agglomeration. Future work on boosting emission monitored in this area should focus on long-term cyclic oxidation studies, development of advanced dispersion techniques and industrial scale formulations to help with widespread usage in high temperature boilers.

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