Thermal And Chemical Resistance Of Plasma Sprayed Al₂O₃, Al₂O₃-TiO₂ Coatings

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Abstract

In this article, the results of thermal and chemical resistance, of plasma sprayed Al_2O_3 and Al_2O_3 -13wt.% TiO_2 coatings on a steel (P265GH) sample are presented. Coatings were formed using air-hydrogen plasma direct current plasma torch at atmospheric pressure. The resistance of coatings was measured by analyzing surface structure, elemental and phase composition of as sprayed coatings and after several heating cycles, imitating application conditions. To make this technology more appealing, by decreasing exploitation cost of standard cast iron grate used in straw pellet broilers, we used cheaper stainless steel with a protective Al_2O_3 and Al_2O_3 -13wt.% TiO_2 coatings. Most of the research done in this field is by using Ar as primary gas, but to decrease the manufacturing cost even further we used Air as primary gas. It was determined that after heat treatment the minor changes in the elemental composition were observed. Meanwhile an additional crystalline phases of metal oxides were detected.

Introduction:

The need for functional materials is ever increasing, many systems and their individual parts or sections must be durable, resistant to chemical or thermal effects and corrosion. The higher longevity can be reached – the better. One of the most effective and cost-efficient way to prolong the lifespan of certain parts or systems is to apply a protective layer of material on top. Ceramic coatings are quickly becoming a viable alternative to organic and polymer-based coatings for surface protection applications. Most commonly used oxide ceramics today are alumina, zirconia, titania, yttria or their composites coatings. Ceramic coating is a protective film for all kinds of parts and can dramatically increase their useful life and productivity, by achieving longer run times before the repairs or replacement of part is needed. Thermal spray coating is one of the most common ways to apply a protective coating on the material and plasma spray is one of the most widely used techniques for this purpose [1].

Plasma sprayed ceramic coatings possesses lots of excellent properties, such as wear and corrosion resistance, high temperature resistance, therefore is widely used in various industrial equipment [2], and particularly are useful when corrosion and wear resistance is required simultaneously [3]. Alumina coatings are one of the most popular high-performance ceramic coatings being used in the industry today. Such wide applications are related to the high hardness, chemical inertness and low cost of material. To improve coating qualities, such as brittleness and friction coefficient reduction, increase of fracture toughness and corrosion resistance, addition of titanium oxide to alumina powder is widely used [4–8]. It was found that addition of TiO_2 reduces the microhardness of alumina coatings [9–12], also titanium oxide increases corrosion resistance, wear rate, elastic modulus and decreases porosity [13]. It was demonstrated that Al_2O_3 -YSZ composite coatings improves the oxidation resistance at high (1050 °C) temperatures [15]. V.C. Misra et al. [14] demonstrated that the tribological properties of Al_2O_3 coatings prepared using argon-hydrogen plasma strongly depend on process parameters and could be used in dry air and dry nitrogen environment. M. Wang et al. [16] obtained that Al_2O_3 -13wt.% TiO_2 sprayed using argon-helium plasma remained stable after thermal shock tests under temperatures below 800 °C.

Alumina and alumina-based composite coatings are a promising selection to improve the grate of a straw pellet boiler, since manufacturing high quality steel would be extremely expensive. The intention was to lower the price of the grate by using stainless P265GH steel instead of cast iron, that is typically being used in straw pellet boilers. According to manufacturing sites (alibaba.com and iron-foundry.com) the cost of cast iron is 1300–1400 \$/ton while stainless steel is only 600–800\$/ton. This change of the grate material would greatly decrease the cost of manufacturing, not to mention the increased longevity of the grate. The temperature inside the boiler is about 500–600 °C and as other scientist have confirmed, there are almost no phase changes of Al_2O_3 coatings in the range of 500–700 °C [7,14]. To decrease the manufacturing cost even further, unlike in the work of other authors [4–10], where coatings were formed mostly using Ar as primary and H_2 as secondary gas, in this research air was used as primary and H_2 as secondary gas. Because of this change it was necessary to verify if the coatings properties would stay the same. Another reason is for using alumina-based coatings, when burning straw potassium, sodium and chlorine compounds formed during combustion react with a furnace surface and destroy it via corrosion reactions. The supreme process of destruction is an etching of the metal due to the chromium reaction with chlorine produced during burning of straws. So, the deposition of the ceramic coatings on the metal surfaces could reduce the production cost and greatly improves the lifetime of the furnace, without the need to replace the grate. Because of the reasons mentioned above, alongside pure alumina, titania was selected as a suitable additive for coatings in our work.

In this paper, Al_2O_3 and Al_2O_3 -13wt.% TiO_2 coatings were deposited on steel (P265GH) samples. The aim of this research is to investigate the chemical and thermal resistance of alumina coatings with addition of TiO_2 .

Methodology:

Al_2O_3 and Al_2O_3 -13wt.% TiO_2 coatings were sprayed on steel (P265GH) substrate at atmospheric pressure using a direct current plasma torch, developed in Lithuanian Energy Institute [15]. The steel substrates (dimensions of 40 × 10 × 6 mm) were polished and chemically cleaned before the deposition process. The substrates were placed on the water-cooled sample holder. The plasma torch was moving in the x-axis direction back and forth, in order to prevent overheating. Air was used as primary and the powder carrier gas, and hydrogen was used as a secondary gas. The coatings were deposited using the plasma torch parameters, that are listed in the Table 1.

Current	200 A
Voltage	198 V
Spray distance	70 mm
Primary gas flow rate	3.7 g/s
Powder carrier gas flow rate	0.75 g/s
Secondary gas flow rate	0.06 g/s
Deposition duration	60 s

Two different compositions of powders were used in this research. Conventional 63–81 μm size (Fig. 1) Al_2O_3 (MOGUL PC15, purity 99.8) and the same size distribution Al_2O_3 – 13 wt.% TiO_2 (MOGUL PC12) powders were used as feedstock material, which were injected into the reactor nozzle (internal diameter of 7 mm) at 150 mm from the exit. Additionally, the bonding layer was formed from nickel-chromium powders (MOGUL M3, Ni/Cr ratio of 80/20) powders in order to increase the coating adhesion to steel substrate. Before the coating process, all powders were dried. Three different specimens were used in the research: uncoated steel (P265GH), Al_2O_3 and Al_2O_3 -13wt.% TiO_2 coatings.

In order to imitate the burning process of the straw pellets in the heating furnace the metallic tube was made (Fig. 2). The specimens were heat treated under identical conditions and were as following: the samples were placed into a metal cylinder (Fig. 2b) and filled with straw pellets (as shown in Fig. 2a). The cylinder had holes on each side and air was flowing through the bottom one at a constant rate. Then the cylinder was closed and inserted into the heating furnace (model TMH12/38/500–2416) and the temperature was set at 500 °C. The duration of the measurement was 60 minutes after the temperature in the furnace reached 500 °C. Additionally, the temperature inside the cylinder was measured using three thermocouples, placed inside the metal cylinder. The first thermocouple was placed below the samples, while the second and third were placed on the top of Al_2O_3 and Al_2O_3 -13wt.% TiO_2 coatings, respectively. The variation of the temperatures was measured using digital multimeter (Mitutoyo SurfTest SJ-210). After the heating was over, the specimens were left in the furnace to cool down for several hours. This sequence completed one cycle of heat treatment and when the five cycles were reached the surface morphology, phase and elemental composition were investigated.

The specimens were washed using ultrasonic cleaning after each five cycles before the characterization. The surface morphology of the coatings was characterized by scanning electron microscopy (SEM) using a Hitachi S-3400N, elemental composition by energy dispersive X-ray spectroscopy (EDS) using dispersive X-ray spectroscopy (Bruker Quad 5040 spectrometer, AXS Microanalysis GmbH). The measurements were performed from 1.05 mm² surface area at 4 different points for each sample and the mean values were calculated. Structure of the coatings was analyzed using X-ray diffraction crystallography (XRD) with Bruker D8 instrument whose main parameters were theta-theta configuration,

CuK α ($\lambda = 0.154059$ nm) radiation. The five cycles procedure was repeated, and the testing was finished when 20 cycles of heat treatment were reached.

Results:

Variation of the temperature during the burning of straw pellets is shown in Fig. 3. The temperature of the first thermocouple (below the samples) is quite lower, that is due to the constant air flow from the bottom of the cylinder, and the maximum temperature is considerably lower (450–480 °C), because the burning of straw pellets is happening on top of the samples. The rapid growth of temperature can be observed at 17 min., that is when the straw pellets start to burn, the peak temperature is reached after 25 min. and is between 520–600 °C. Meanwhile, the temperature on the surface was about 100 °C higher than on the bottom when the straw pellets were burning. Once the burning process is over the temperature starts to decrease and stabilizes at 430–470 °C range. The temperature obtained on the top surface of the coatings was about ~ 50 °C higher after burning process was finished.

Surface morphology of uncoated steel before the heat treatment and after 20 cycles is shown in Fig. 4. The surface of untreated sample (Fig. 4a) is relatively clean, although some particles can be observed. After 20 heat treatment cycles the change of the surface is evident. A lot more particles can be observed on the surface, that remained even after ultrasonic cleaning, these are mainly leftover products of burned straw pellets. In addition, the surface seems to be etched, this is the result of ongoing chemical reactions and oxidation during the burning of straw pellets. The SEM images clearly indicated that the surface of P265GH steel was changed and damaged.

Surface of sample with the Al₂O₃ coating is shown in Fig. 5. The surface of untreated sample (Fig. 5a) consists of splats and somewhat unmolten particles, also no defects, such as cracks or delamination, can be seen. Surface of the sample after 20 cycles (Fig. 5b) is similar, but the quantity of small particles is considerably higher. Much like in steel sample, a lot of those small particles are leftover products of burned straw pellets, that were not cleaned completely. Just as in steel sample, the surface is etched and cavities do form, but they are considerably smaller. This is due to the fact, that Al₂O₃ coating is a lot more resistant to chemical reactions, happening during the burning process of straw pellets, than steel.

The surface of Al₂O₃-13%wt.TiO₂ sample is shown in Fig. 6. As in previous sample, untreated coating (Fig. 6a) consists of splats and somewhat unmolten particles, also no cracks or delamination zones can be seen. But unlike in Al₂O₃ sample the surface after 20 cycles is relatively the same, roughly the same number of small particles and no formed cavities are observed (Fig. 6b). The addition of titania increased coatings resistance to chemical and thermal impact.

Elemental composition was determined using energy dispersive X-ray spectroscopy. Samples were tested before treatment, and after 5 and 20 cycles. Each sample was measured in 4 different spots, then mean values were calculated (deviation 1%). The first sample (uncoated steel) consisted mainly of iron (93 at.%), also a small amount of oxygen (4 at.%) and other materials, that came from elemental

composition of steel, were found. Even after 5 cycles the amount of oxygen dramatically increased to 46%, while iron lowered to 50%, and further increase of cycles had no effect to the amount of oxygen in the sample. This is due to absorbed oxygen during the combustion process, during the burning of straw pellets. Additionally, low traces of silicon, potassium, calcium and sulfur are found, that are leftover products of combustion reactions and were not completely removed with ultrasonic cleaning.

Al_2O_3 sample before treatment consisted of aluminum (31 at.%), oxygen (58 at.%), nickel (6 at.%) and chromium (2 at.%). Also, low amounts of other elements can also be found (carbon, iron, silicon etc.) and are attributed to impurities within the sample. Chromium and nickel originate from NiCr underlayer, that was applied before the coating in order to increase the adhesion of the coating. After 20 cycles aluminum decreased by 4% (to 27 at.%) and oxygen by 1% (to 57 at.%), nickel increased by 2% (to 8 at.%) and chromium remained the same (2 at.%). This happened due to the increase of other elements (iron, carbon, silicon etc.) during burning of straw pellets, and because the combustion products could not be completely removed.

Al_2O_3 -13wt.% TiO_2 sample consisted of aluminum (22 at.%), oxygen (57 at.%), titanium (4 at.%), nickel (9 at.%) and chromium (3 at.%). Much like in the Al_2O_3 sample, nickel and chromium are attributed to NiCr underlayer and small traces of other elements (carbon, iron, silicon etc.) are found due to impurities of the sample. However, after 20 cycles the amount of aluminum, titanium and chromium remained the same (22 at.%, 4 at.% and 3 at.% respectively), while oxygen increased by 2% (to 59 at.%) and nickel decreased by 1% (to 8 at.%). Also, just as in Al_2O_3 coating, number of other elements coming from combustion products increased. The data indicates that addition of titania did increase stability in elemental composition, since even after 20 heat treatment cycles only amount of oxygen altered by more than 1%.

Phase composition of the P265GH steel sample is shown in Fig. 7. Before the treatment there is only 2 peaks of Fe at $2\theta = 44.7^\circ$ and 65.1° , but even after 5 cycles several peaks of Fe_3O_4 appear and become the dominant phase. The further increase of heating cycles continues to increase the intensity of Fe_3O_4 peaks. These results support the previous statement, that steel sample was heavily damaged during the treatment cycles and protection is necessary under these working conditions.

There is noticeably less phase composition change in Al_2O_3 sample. Firstly, the dominant phase remains $\alpha\text{-Al}_2\text{O}_3$ with peaks when $2\theta = 25.6^\circ, 35.7^\circ, 43.5^\circ, 57.7^\circ$ and 63.1° . Secondly, another phase of alumina also apparent, that is $\gamma\text{-Al}_2\text{O}_3$ at $2\theta = 37.4^\circ, 38.9^\circ, 45.8^\circ$ and 67.1° . The ratio of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ most intense peaks before treatment is 1.16 but increases to 2.06 after 20 cycles. This is since $\alpha\text{-Al}_2\text{O}_3$ peak intensity increased, while $\gamma\text{-Al}_2\text{O}_3$ remained similar. This happens because the temperature is not high enough for phase transition reactions from $\alpha\text{-Al}_2\text{O}_3$ to $\gamma\text{-Al}_2\text{O}_3$ to occur. The temperature is only enough to initiate transition of amorphous Al_2O_3 to $\alpha\text{-Al}_2\text{O}_3$. Similar results were found by Dhakar et al [16] where Al_2O_3 coating were heat treated at 900°C . Thirdly, besides alumina there are two more peaks that are attributed to iron and nickel at $2\theta = 44.3^\circ$ and 51.6° , their intensities remained the same before and after 20 heat cycles.

Addition of titania in the final sample increased stability of phase composition of alumina coating, therefore even less changes can be observed (Fig. 9). There is a less peaks of $\alpha\text{-Al}_2\text{O}_3$: when $2\theta = 35.7^\circ$, 43.5° and 63.1° . Also, there are a few $\gamma\text{-Al}_2\text{O}_3$ peaks at $2\theta = 37.4^\circ$, 45.8° and 67.1° . The ratio of $\alpha\text{-Al}_2\text{O}_3$ to $\gamma\text{-Al}_2\text{O}_3$ the most intense peaks of the coating was 1.46. Meanwhile after 20 cycles of treatment the $\alpha\text{-Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ ratio increased very slightly up to 1.51, which confirms, that the resistance to heat treatment increased with the addition of titania. Just as in $\alpha\text{-Al}_2\text{O}_3$ sample there are two peaks of at $2\theta = 44.3^\circ$ and 51.6° attributed to the bonding NiCr layer. These results agree with the work of other authors [17], where no significant changes were observed for $\gamma\text{-Al}_2\text{O}_3$ phase during the annealing of up to 700°C of plasma sprayed NiCrAl/ Al_2O_3 -13wt.% TiO_2 coatings. The authors obtained only minor changes in the peak's intensities of alpha phase.

Conclusion:

Al_2O_3 , Al_2O_3 -3% TiO_2 and Al_2O_3 -13% TiO_2 coatings were formed using atmospheric plasma spray technology. Surface morphology was examined using scanning electron microscopy, and the result show that most damage was done to the uncoated steel sample, while the samples with both, alumina and alumina-titania coatings were almost intact. Elemental composition results done by energy dispersive X-ray spectroscopy indicate, that the steel sample was heavily oxidized after 5 heating cycles, since oxygen increased from 1–46%. The change of elemental composition in other samples was insignificant. In Al_2O_3 coating oxygen decreased from 58–57%, and aluminium decreased from 31–27%. In the Al_2O_3 -13% TiO_2 coating amount of oxygen increased from 57–59%, but aluminium and titanium fraction remained the same. It was determined that after 5 cycles of treatment the uncoated steel substrate is heavily oxidized and Fe_2O_3 becomes the dominant phase. The X-ray diffraction results show that even after 20 cycles of heat treatment at 500°C , the phase composition of Al_2O_3 coating greatly increased the thermal and chemical resistance of the P256GH substrate and the addition of titania increased its phase stability even further.

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Figures

Fig 1 SEM micrograph of Al₂O₃ powders

Figure 1

SEM micrograph of Al₂O₃ powders

Figure 2

a) samples in tube with grain pellets, b) metal cylinder with the samples, c) experimental setup.

Figure 3

Temperature graph measured by thermocouples in metal cylinder

Figure 4

SEM micrographs of steel sample, before a) and after b) 20 heating cycles

Figure 5

SEM micrographs of Al₂O₃ sample, before a) and after b) 20 heating cycles

Figure 6

SEM micrographs of Al_2O_3 -13% TiO_2 sample, before a) and after b) 20 heating cycles

Figure 7

X-ray diffraction pattern before and after 5 and 20 treatment cycles of steel sample. Fig 8. Al₂O₃ coating
Fig. 9 Al₂O₃ – 13%wt.%TiO₂ coating