Nanomaterials of Fe, Al and Ti, in the reduction of potentially reactive basalt aggregate in Portland cement dosages: deposition of coatings by plasma

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Abstract The mitigation of the effects of the alkali aggregate reaction (AAR) in cement mortars and concretes, with the addition of nanomaterial based on Fe, Al and Ti, on reactive aggregates was investigated. The coatings were prepared by the plasma technique. For this purpose, a rotational system was designed to obtain continuous nanometric films. The addition of metal-based nanomaterials and their metallic oxides (Fe, Al and Ti) helped in the reduction of the AAR process, by the formation of nanoclusters with potential reduction of the effects of the aggregated alkali reaction. This occurs by the modification of the degree of wettability of the interface or even a possible chemical interaction of the deposited films with the reactive components of the rock, eliminating the contact of the alkalis of the cementitious paste with the reactive silica of the aggregates.

1. Introduction

Nanomaterial technology has been applied in various areas of science and its effectiveness is no longer dependent on the type or design of the base material or substrate, but on the interaction of nanomaterials with this medium and the parameters of its manufacture. Thus, it is possible to produce altered surfaces, of greater or lesser wettability, self-cleaning, which is explained by the hysteresis of the contact angle of the substrate with the drop and its low adhesion, and with continuous films, from low to high roughness [1, 2].

There are several industrial and laboratory processes for the production of altered surfaces on the most diverse substrates, such as the use of organic and inorganic materials and the alteration of surface roughness and the deposition of lower energy materials. Examples of these processes are the CO₂ laser, chemical etching, lithography, processing by sol-gel, Layer by layer and colloidal assembly, electro spinning, and the technique described in this research which is the plasma generated by magnetron-sputtering, in this specific case, the pulsed dc plasma [3].
Plasma has its greatest importance when using high power and higher energy density and its main benefits are low energy consumption and a reduction of environmental pollutants by reducing or extinguishing toxic gases and/or sub-products, less use of raw material for coating (nanometric layers), and it is possible to obtain final products that are compatible with the environment and at lower cost [4]. Plasma technology can be defined as thermal (high electron density) or cold (low electron density). Thermal is characterized by the thermodynamic equilibrium of electrons and particles, and the gas is completely ionized. The cold or non-equilibrium plasma is characterized by low energy density and ionization and has as examples those of low pressure, with application of direct current, RF, fluorescent discharges (neon) and corona effect [5].

The advantage of using plasma is in the interaction of its components, either by the ionization process, dissociation, or even, of excitation, which can attack the reactor surface with energy ions, causing corrosion or sputtering. In this case, its reactive particles and ions are directed to the substrate as deposit material, forming the film of desired dimensions and characteristics, by manipulation of the parameters of its operation [4-6]. Thus, by the characteristic of the plasma formed, its geometry, source (radio frequency, microwaves (2.45 GHz), direct current (DC) and pulsed direct current), power supply systems, the flow and the type of gas involved, the angle of incidence of the ions and the surface of the substrate (more or less rough or with greater or lesser wettability), determine the intensity of this superficial interaction or not [7]. Sources based on pulsed direct current, such as the one used in this research, have in their output for plasma generation a pulse width modulation (PWM). Thus, the pulsed characteristic and the geometry of the magnetron-sputtering system are determinants to define the deposition rate. As transcribed by Portella et al. (2017), high quality films on certain substrates can be obtained with nanomaterials by sputtering deposition, with magnets connected to the target, which promote an accumulation of charges in their surroundings and favor a greater sputtering of local species [8]. In this research, the application procedures of pulsed plasma, on building materials and the performances obtained in their applications are presented.

2. Material and Method

2.1. Basalt aggregates.
Aggregate samples had an average size of 6 mm and were obtained from the region of Pinhão and Telêmaco Borba, Paraná - Brazil. Initially, the aggregates were washed in running water to remove impurities that could possibly affect and contaminate the vacuum system. After washing, the aggregates were taken to a drying oven at a temperature of 105 °C for 3 h in order to reduce the local humidity.

2.2. Plasma system.
The plasma system used in this work and previously published in previous works [8, 9] is of the pulsed magnetron sputtering plasma type. The vacuum system consisted of a mechanical and a diffuser pump. After the vacuum formation process, the argon working gas (99.999% purity) at a pressure of $10^{-3}$ mbar was inserted with the aid of needle type valves. When the system was stable, the plasma was started with a pulsed direct current voltage source, with a peak voltage of 800 V, 1.3 A of peak current with pulse cycles of 50%. A titanium metal target (99.999 % purity) was used as a nanomaterial precursor in a magnetron-type magnet system with dimensions of (80 x 245) mm. The magnetron-type system was of the balanced type. The distance from the plasma source to the targets was approximately 140 mm with 5 RPM rotation. Figure 1 shows the main constituent parts of the plasma system. For more details of the system, see other published works [9].
2.3. Morphological and elementary chemical analysis of the aggregates.

Images of the surface of the aggregate were obtained with the FEG (Field emission gun) system, Tescan brand, MIRA 3 model of the multiuser laboratories of the UEPG (Universidade Estadual de Ponta Grossa). The equipment has an EDS - Energy-dispersive X-ray spectroscopy system.

3. Results and discussion

3.1. Effect of AAR mitigation on basaltic aggregate by deposition of Fe, Al and Ti nanomaterials.

Figure 2 shows the effect of AAR mitigation on basaltic aggregate by deposition of Fe, Al and Ti nanomaterials from pulsed dc plasma targets. In petrographic analysis [8], the rock was identified with fine granulation, consisting of ripiform crystals of plagioclase (50%), pyroxenium (40%), and metallic minerals anahedral (basalt rock). Rock considered potentially reactive. By EBSD [8], were identified the mineral chemical phases of the aggregates, as plagioclase anorthite (Ca0.1Na0.1Al2Si2O8), corresponding to 42.77%; augite in 32.41% (green totality); and the phases in a lower proportion to albite-mon, in 5.33% (whitish), and the others 4.52% which is more difficult to visualize due to visualize due to the percentage of phase present [8]. Other phases (20.30%) have not been identified with possible of amorphous regions, pores and imperfections on the sample surface. The chemical reactivity of the aggregate for AAR was verified from the ABNT NBR 15577-5:08 standardized test [10]. It can be noticed by different physical-chemical techniques that the films generated produced a process of mitigation of the reaction in accelerated mode, by the test ABNT NBR 15577-1 to 5:08 [10]. It is inferred that such results may have been the result of a total coverage of the surface of the aggregate exposed to
the alkalis, a modification of wettability or even a possible chemical interaction of the deposited films with the reactive components of the rock, eliminating the contact of the alkalis of the cementitious paste with the reactive silica of the aggregates.

![Graph showing expansion over time]  
**Figure 2.** Effect of AAR mitigation on basaltic aggregate by deposition of Fe, Al and Ti nanomaterials from pulsed dc plasma targets.

### 3.2. Micrographic analysis by FEG-SEM.

To show the thin film deposit effect in Figure 3 are shown micrographic images of the surface of a diabase aggregate, also analyzed for its physical properties, on which nanomaterial from the Ti target was deposited. The aggregate showed grain diameters with an average size of 6 mm (Figure 3(a)). In Figures 3(b - c) are indicated the regions of semi quantitative surface analysis of elements by EDS. In Figure 3(c). It is possible to verify the titanium dispersion in the whole analyzed surface. A percentage of Ti (d) of approximately 2.49% was observed for the proposed deposition conditions.

Plasma systems that use a magnetron-sputtering present a directional deposition of films on a surface [7]. In a previous work, a rotational system was developed (image shown in Figure 1 c) for the deposition in aggregates in order to treat the entire surface exposed to the plasma by continuous rotation [7]. Due to this, specific information was obtained regarding its heterogeneity in the composition of the film formed, where the particles grow and coalesce until the formation of a continuous thin film on the surface [7]. Thus, it was possible to verify regions with varied Ti contents and whose values varied from approximately 22.11 % of Ti to 7.02 %.

In order to better characterize the surface effect of the film formed, the results of the water absorption coefficient of the aggregates without and with the surface thin film based on Ti varied up to 81% with its deposit, with a final increase of 2.9% in water absorption. However, the addition of metal-based nanomaterials and their metallic oxides (Fe, Al and Ti) helped in the reduction of the AAR process, in accelerated and standardized testing. This may be related to the barrier effect caused by the films to the contact of reactive silica with the alkalis of the cementitious layer [8, 10]. The presence of nano compounds Fe, Al and Ti reduced the effects of AAR.
Figure 3. (a) Image, by FEG-SEM/EBSD, of aggregate submitted to nanotitanium deposition treatment. (b) Magnification of the region to obtain images of the morphology of the aggregate and the deposited film. (c) Analysis of elementary mapping of the titanium dispersed in the surface of the aggregate. (d) Table with the main constituents of the aggregate used in this work.

Other investigations of the effects of superficial gel formation are necessary to understand the physical mechanisms involved in this interaction of the nanomaterials with the studied aggregates, once it was observed variation in the water absorption coefficient with its deposition.

4. Conclusion
The deposition of nanomaterials by pulsed dc plasma in potentially reactive aggregates for AAR showed a tendency to mitigate the reaction in Portland cement material, with three different targets, Fe, Al and Ti, in accelerated and standardized test. From the results obtained, it was inferred that such results may have been the result of a total coverage of the surface of the aggregate exposed to alkalis, a modification of the wettability of the interface or even a possible interaction of the deposited films with the reactive components of the rock, eliminating the contact of the alkalis of the cementitious paste with the reactive silica of the aggregates. Also, by the determination of the water absorption coefficient, it was noticed the influence of the deposited film, perhaps, by the larger exposed surface area of the nanomaterial.

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