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Characterization of Removable Coatings for Graphite-moderated Nuclear Reactors Decommissioning

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In this study the behavior and characteristics of two removable coatings to be deposited on a nuclear grade graphite substrate were analyzed, with the aim to evaluate their possible application on graphite bricks during dismantling operations of graphite-moderated nuclear reactors.Indeed, nowadays many shut-down reactors are still in decommissioning phase, and effective measures should be taken to guarantee safe dismantling operations. One option could be the use of coating application techniques, which mitigate the risk of graphite dusts spreading and loose contamination, protecting clean surfaces.Tested coatings, both polymeric mixtures, were selected according to their previous application history, availability in commerce and easiness in handling, whereas substrates used were non-irradiated nuclear Virgin Atcheson Graphite Ordinary Temperature (AGOT) graphite samples from L-54M Politecnico di Milano research reactor, which is in decommissioning phase.

Thermal characterization of the coatings was carried out before deposition using a Thermogravimetric and Differential Thermal Analysis (TGA-DTA) equipment, tests were performed to obtain a preliminary estimation of the drying time and degradation conditions.

After deposition, mechanical properties, such as hardness, of the coating were assessed.

The preliminary experimental campaign showed that coating painting could be a feasible option to prevent the spread of highly contaminated graphite dusts during decommissioning of graphite components of nuclear reactors, thus ensuring clean and safe working conditions.

1. Introduction

The present study is in the scope of graphite-moderated reactors decommissioning, since nowadays many of them are shut down, and tools for graphite components safe dismantling are being developed.

Worldwide there are around 250.000 tonnes of irradiated graphite, mainly from reactors moderators and reflectors, and the majority must be disposed of (Wickham et al., 2017).

Two examples of issues are the components manipulation and transportation; indeed, neutrons modify graphite crystal structure causing components shrinkage, distortion, and possible fracture. In addition, graphite can be further damaged by ionizing radiation and chemical attack by gaseous coolants and thermal neutrons that could generate further radioactive isotopes from graphite (e.g. ^{14}C) and impurities (Wickham et al., 2017).

Therefore, coating painting could be a useful tool that could ensure safe decommissioning operations, preventing the spread of graphite dusts and airborne contamination, generated by component damage or accidental breaking during handling operations outside the core reactors.

Fixatives in nuclear industry were first used in 1950s to bind contaminants to surfaces, and further developed at the end of the cold war with the decommissioning of facilities at nuclear weapons sites (Lee et al., 2022).

During 1980s fixatives were used also in other industrial fields, for instance, as encapsulants for asbestos (Demmer et al., 2017), and, in the following years, continue to develop for decontamination, e.g., after nuclear reactors accidents (Yang et al., 2018) and RDD (radiological dispersal devices) (Kaminski et al., 2016).

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Since, nowadays, reactors dismantling is one of the main challenges in nuclear industry, coating painting could be a ready and promising technique that could be integrated in decommissioning and decontamination phase, and it has the advantage to be more environmentally friendly and easier to dispose of than treating contaminated liquids (Guidi et al., 2010).

Fixative technique was successfully used, to control dust and loose contamination, during Brookhaven Graphite Research Reactor decommissioning operations, completed in 2014 (US DoE, 2019). The core was dismantled in air with the use of a coating painting, which was sprayed on the graphite pile by a remote-controlled tool placed on the excavation crane (Kirby, 2011).

Two types of coatings are typically applied for short term dust or contamination fixation:

- Strippable coatings: removable and with a few weeks duration;
- Permanent coatings: not removable and with a longer duration than strippable ones, depending on their composition and properties (Demmer et al., 2017).

In both cases, coatings are usually constituted by a mixture of polymeric or other organic components, for instance, polyacrylates, polyvinyl esters, polyisobutylene (Pulpea et al., 2020). Typical composition of a strippable coating, in the simplest form, is: 3-30 % polymer, 1-10 % plasticizer, 0-1.5 % additives (Pulpea, 2018).

The preliminary experimental campaign described in this paper is in the scope of EU H2020 Inno4Graph Project, and it aims to select, if feasible, a commercially available coating, suitable for porous materials, to be used to ease irradiated graphite retrieval. After characterization, the most promising coating could be implemented in decommissioning procedure.

In the following sections, testing procedure and results related to two investigated coatings are described.

2. Materials and methods

Details about materials and procedure used for preliminary tests are provided in 2.1 and 2.2.

2.1 Materials

For the preliminary experimental campaign, two coating paintings were chosen:

- Cemblok base (Venber)
- DeconPeel Nuclear 5000 (General Chemical corp.)

Criteria for selection included: applications history, availability in commerce, easiness in handling, non-toxicity, and compositions suitable for a temporary application.

Cemblok is designed to incapsulate asbestos containing-materials and avoid dispersion of asbestos fibres, whereas DeconPeel is already used for decontamination of floors, walls and equipment in nuclear facilities.

According to the products technical data sheets, available information about properties and composition of the two coatings are reported in Table 1.

Table 1: properties and composition of the investigated coating products

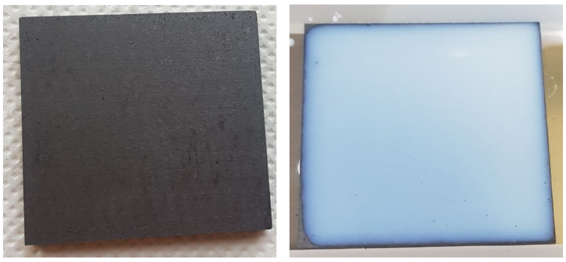
Coating	Cemblok base	DeconPeel Nuclear 5000
Composition	Synthetic polymer emulsion	Water-based polymeric solution
Colour	Transparent	Clear dry film
Volumetric mass [g/L]	1,050	1,114
Viscosity [cP]	200±50	8,000-14,000
pH	8	8

Substrate used for preliminary tests was non-irradiated AGOT graphite from Politecnico di Milano L-54 M research reactor, which was shut down in 1979 after 20 years of operation, with a nominal power output of 50 kW_{th}, and it is now in decommissioning phase.

For the experimental tests, samples of graphite bricks were machined into parallelepipedal coupons of basis 1 cm x 1 cm and 5 cm x 5 cm and thickness 0.5 cm.

2.2 Methods

Prior to application, thermogravimetric analysis on the coating were carried out to evaluate the drying time and thermal degradation of the coatings using a TGA-DTA horizontal furnace (sample quantity: 30-40 mg); drying time was evaluated by isothermal tests at 30-40°C for 12 h in air.
Coating decomposition and thermal stability was analysed in non-isothermal mode reaching a temperature of 500°C with a heating rate of 5°C/min in N_2 or air.
Coating paintings were applied by pipette or blade on graphite coupons; these application methods were used on a laboratory scale for a preliminary assessment of drying and peeling ability of the selected coating.
Specimen surface, after cleaning with compressed air, was covered with the fixative and the weight of the coated specimen was recorded after the application and also after 24 h in air at environment temperature. Then peeling of the coating was realised with the aid of tweezers or spatulas.
After coating drying, hardness tests were carried out in compliance with ISO 14577-4 standard, which is suitable for coating thickness in micro/nano range. Specimens were graphite coupons of dimension 5 cm x 5 cm and coating was applied with a blade equipped with a micrometric ruler, set coating thickness was 250 µm (Figure 1).



a b

Figure 1: Sample before (a) and after (b) application of Cemblok

3. Results and discussion

3.1 TGA

Thermogravimetric analysis for drying assessment (Figure 2) showed that Cemblok, after drying, loses around 80% of its initial weight, the plateau is reached after about 3 ¾ h at a temperature of 40°C.
Concerning DeconPeel, weight loss extent after drying is about 50 wt% and complete drying is achieved after about 6 h.

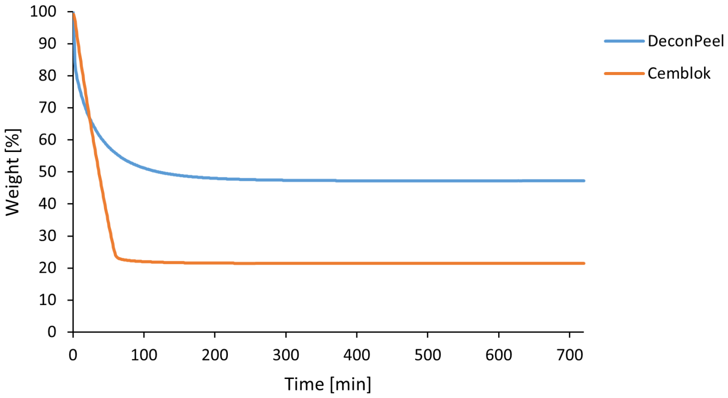


Figure 2: TGA profile of drying - Cemblok and DeconPeel coatings

In Figure 3, degradation trends for the two coating paintings are shown, after drying plateau, it can be observed that Cemblok starts to degrade at 350°C, whereas DeconPeel at about 300°C.

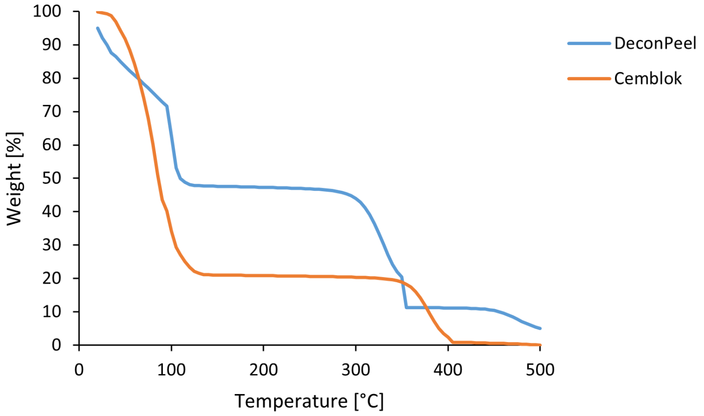


Figure 3: TGA profile of degradation - Cemblok and Deconpeel coatings

3.2 Coating application and peeling

Coating paintings were applied by weight and uniformly distributed (blade or spatula) on graphite coupons, tests were carried out using different amounts of product, varying from 50 mg (1cm x 1cm coupons) to 500 mg (5 cm x 5 cm coupons). Cemblok, after drying, in all cases, had a cracked and non-uniform appearance, due to shrinking. DeconPeel appearance, after coating was smooth (Figure 4). Weight loss was coherent with TG analysis.

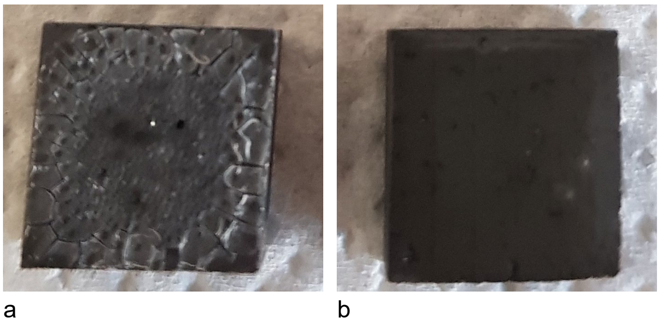

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Figure 4: Cemblok (a) and DeconPeel (b) after drying

After drying, easiness in peeling was assessed with the aid of spatula or tweezers. Cemblok did not peel off, while DeconPeel did; it was possible to easily peel off the coating created with an initial amount of 50 mg. In Figure 5, substrate and DeconPeel coating are shown after peeling. It can be observed that the entire film was separated from the substrate in a single piece, that seems to retain loose graphite particles, avoiding dispersion.

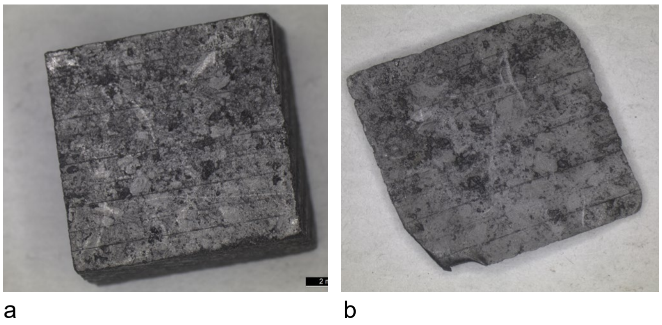
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Figure 5: substrate (a) and coating (b) after peeling test

Due to easiness in peeling and deposition on graphite substrate, DeconPeel represents probably a more suitable option to the specific application. Indeed, it seems to form a more uniform and durable coating on graphite, after drying. In addition, currently there are not established criteria for graphite repository (Fuks et al., 2020), and the coating could be efficiently separated from substrate in case it is not allowed to store graphite in the same waste container with other materials.

3.3 Micro-hardness assessment

After preliminary tests for coating paintings behaviour assessment, also mechanical properties of the two coating paintings were analysed by micro-hardness test, according to standard ISO 14577-4, that defines the test procedure for metallic and non-metallic coatings in micro and nano range.

In Table 2, mean values calculated for Vickers hardness (HV), elastic modulus (EIT), maximum penetration depth (hmax) and spring back (nIT), which represents the percentage of elastic return, are reported. Tests were performed in five different positions on the coated samples surface, in the case of Cemblok, the assessment was done in samples area in which coating appeared to be uniform.

From test results, it is possible to observe that HV, EIT and nIT values recorded for DeconPeel coated specimens are higher than the ones registered for Cemblok, while penetration depth is higher for Cemblok samples.

Table 2: results of hardness test - ISO 14577

	HV	EIT [GPa]	hmax [μm]	nIT [%]
Cemblok				
Mean value	8.63	3.49	7.11	23.74
DeconPeel				
Mean value	14.03	6.02	5.52	25.99

4. Conclusions and future work

The preliminary experimental campaign presented in this paper is in the scope of nuclear graphite components decommissioning operations, which represent a technological challenge. Coating paintings could represent an option that could ease handling of irradiated graphite, so two coating products available in commerce and suitable for porous materials were tested on a graphite substrate.

The preliminary thermal characterization showed that Cemblok, compared to DeconPeel loses a higher amount of weight after drying and exhibits a higher drying rate, indeed DeconPeel drying time is around 40% higher. Concerning thermal stability, DeconPeel appears to degrade at a lower temperature after drying, components decomposition reactions start at a temperature that is 50°C lower than Cemblok.

Regarding application of the coating, DeconPeel appears to be more suitable for the substrate since during tests was easier to distribute it evenly on sample surface and it had a smooth and uniform appearance after drying in air, whereas, Cemblok, after drying appeared cracked or did not uniformly coat the substrate. An option for application of this last product could be multiple application steps, but the issue in this case is that the removal of coating could be problematic, and irradiated graphite, on storage perspective, could not be segregated from coating material in waste containers. DeconPeel product appears to be easy to peel off and it could be possible to separate it from graphite waste; it also shows a higher hardness.

However, it should be considered that coatings were tested only on one kind of non-irradiated nuclear grade graphite. So, further experimental work should be done to assess coating properties on different graphite substrates, and, on irradiated specimens, since properties and structures can be much affected by irradiation. It would be also important to characterize the detached coating in order to understand its level of contamination to choose the disposal method.

Another future development of this research is the study of application method. Indeed, spray technique could be better implemented in decommissioning operations since it does not involve contact between tool and irradiated component. Future experimental campaigns could focus on spraying to investigate main parameters, such as speed, flow and distance between tool and substrate.

In addition, a challenge is to implement the optimized technique in real-scale decommissioning operations, developing an automated spraying system that could also separate coating from graphite.

Nomenclature

EIT – elastic modulus, GPa
hmax – maximum penetration depht, μm
HV – Vickers hardness
nIT – spring back, %

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