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FIRST DO NO HARM: A WHOLISTIC APPROACH TO IDENTIFYING FEASIBLE COMMERCIAL CORROSION MITIGATION COATINGS FOR USE ON SPENT NUCLEAR FUEL STORAGE CANISTERS

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INTRODUCTION

In 2020, a literature review was performed to determine coating materials that would be able to survive the harsh conditions present during interim storage [1]. The materials surveyed included a range of polymer, ceramic, conversion, and sprayed metallic coatings. The report did not find any single coating technology that had been previously demonstrated in this application but identified the most feasible candidate materials for use as corrosion mitigation on spent nuclear fuel canisters were epoxies, polyethylene, some rubber compounds, cold sprayed metallic coatings, sol-gel ceramic coatings and phosphate conversion coatings. Three application scenarios were also identified for when a possible technology may be employed for use on an SNF canister; *ex situ* mitigation, *ex situ* repair, and *in situ* repair. *Ex situ* mitigation is defined as a situation in which mitigation coatings could be applied on new canisters before loading with SNF. This application scenario results in the highest thermal, radiological, and mechanical requirements that the coating must survive. *Ex situ* repair is an application scenario in which coatings could be applied to canisters that have been removed from their overpacks after having been in interim storage for a number of years. This application scenario subjects the coating to lower thermal and radiological stresses but could require a coating with good mechanical properties to be able to survive replacement into the overpack. In situ repair is an application scenario in which coatings are applied robotically in the annulus between the overpack and the outer surface of the canister (~6 in). Access restrictions in the overpack make this application scenario challenging and prevents the use of complicated cleaning or application processes [1].

Cold spray coatings have been studied for use on spent nuclear fuel canisters and been shown to be a promising option for future mitigation and repair needs [2]. Cold spray coatings have extremely high adhesion strengths and, due to their metallic nature, are inherently mechanically, thermally, and radiologically robust [3] which could make them ideal repair and mitigation coating systems. Robotic traversal of the overpack outlet vents and in situ application of cold spray coatings has been previously shown to be feasible [1, 4], which may be required when performing repair activities. Cold spray coatings applied to metallic substrates may be vulnerable to galvanic corrosion at the boundary of the repair patch where the coating meets the substrate [5]. The coating surface finish and density have also been shown to impact the corrosion resistance of the coating [5]. Results to date of cold spray studies have been previously summarized in Karasz et. al(2022) [6], thus the data presented herein will focus on the other aforementioned coating technologies.

RESULTS

Phase 1: Electrochemical and Mechanical Tests

In 2021, a collaborative working agreement between US commercial coatings vendors and Sandia National Labs was established to identify existing commercial coatings that were potential candidates for use in this application. The criteria for selection included ease of applicability (such as spray or roll-on coatings), curing temperatures, outgassing behavior, and the industrial maturity of the coating system. A multi-year, phased testing approach was developed in which more elaborate, expensive, or time-consuming tests would be performed on coatings that showed promise and were down selected into later test phases, thereby allowing concentration of experimental resources towards variants that had a high likelihood of performing well in the interim storage environment.

Four vendors were initially identified for Phase 1 tests including Luna Labs, Flora Coatings, White Horse R&D, and Oxford Performance Materials. These four vendors provided 11 candidate coating variants for initial evaluation (see Table 1).

Table 1. Coating variants provided by vendors and their alphanumeric nomenclature.

Vendor	Coating	Phase 1 Nomenclature	Phase 2 Nomenclature
EXAMPLE	EXAMPLE	VENDOR-YEAR-VARIANT-COUPON#	VENDOR-YEAR-VARIANT-COUPON#
Oxford Performance Materials	Polyetherketoneketone (dip cast)	OPM-21-01-XX	OPM-23-01-XX
Oxford Performance Materials	Polyetherketoneketone (solution cast)	OPM-21-02-XX	n/a
White Horse R&D	Modified Polyimide-Polyurea-Phenolic Resin (no filler)	WHRD-21-01-XX	n/a
White Horse R&D	Modified Polyimide-Polyurea-Phenolic Resin (filler)	WHRD-21-02-XX	WHRD-21-02-XX
White Horse R&D	Modified Polyimide-Polyurea-Phenolic Resin (most filler)	WHRD-21-03-XX	WHRD-21-03-XX
Luna Labs	Hybrid Ceramic V1	LUNA-21-01-XX	n/a
Luna Labs	Hybrid Ceramic V1 + Zn-Rich Primer	LUNA-21-02-XX	n/a
Luna Labs	Hybrid Ceramic V2	LUNA-21-03-XX	LUNA-23-03-XX
Luna Labs	Hybrid Ceramic V1 + Zn-Rich Primer	LUNA-21-04-XX	LUNA-23-04-XX
Luna Labs	Bare Zn-Rich Primer	LUNA-21-05-XX	n/a
Flora Coatings	Hybrid single-component inorganic/modified polyurethane with a quasi-ceramic structure	FC-21-01-XX	FC-23-01-XX
TDA Research	S-W Macropoxy 646N (polyamide epoxy) with an inhibitor package	N/A	TDA-23-01-XX
TDA Research	S-W Zinc Clad II with an inhibitor package	N/A	TDA-23-02-XX

The coatings were applied by each vendor on stainless steel coupons and returned to SNL for evaluation in simulated corrosion conditions. During Phase 1, Electrochemical Impedance Spectroscopy (EIS) tests to evaluate corrosion resistance in relevant brine (chloride) environments over time were performed. A qualitative summary of the EIS results pre and post exposure, namely the charge transfer resistance (R_{CT}), the pore resistance (R_{PO}), the coating capacitance (C_C), are provided in Figure 1. Additionally, a suite of mechanical tests (such as ASTM D4541 pull-off adhesion testing [7] and ASTM D7027 scratch testing [8]) were conducted and results are also presented in Figure 1. Each coating vendor had at least one candidate coating that performed well in these tests. After Phase 1 tests were completed, a qualitative comparison was performed to determine which coating variant would be down selected for additional testing in Phase 2 (Figure 1). The results and analysis were documented in detailed reports [9, 10].

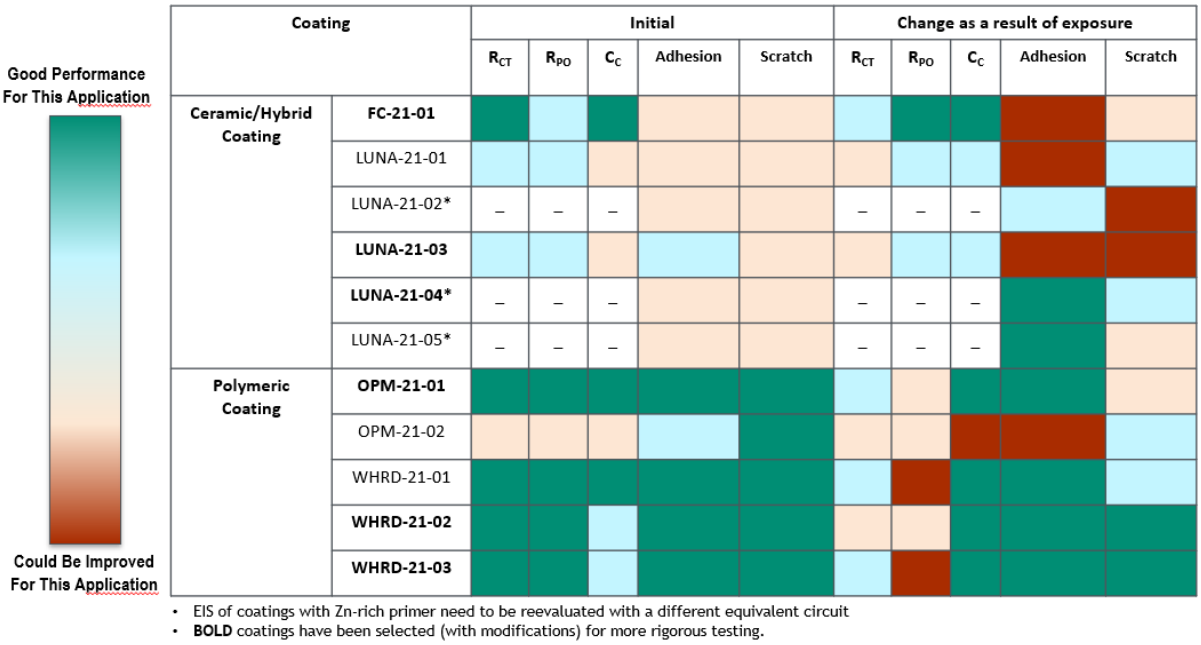

Figure 1 Qualitative comparison of coating performance before and after environmental exposure on Phase 1 coating variants. Variants selected for Phase 2 testing are bolded.

Phase 2: Radiation and Thermal Tests

During Phase 2 tests, the down selected coating variants were subjected to radiolytic and thermal exposures designed to simulate potential SNF storage relevant conditions that might influence the corrosion mitigation functions of the coatings (*i.e.* high doses of radiation up to>730 Mrad [11] and prolonged exposure to temperatures exceeding 220°C [12]). A new company was also added to the project; TDA Research which provided an epoxy coating and a zinc rich primer coating (TDA-23-01 and TDA-23-02 respectively). Sandia National Lab's Gamma Irradiation Facility was used to expose six sets of samples to five different radiation doses using two different dose rates. Two sets of samples were exposed to the same total dose of ~350 Mrad at two different exposure rates which allowed the simultaneous study of dose rate effects and total dose effects (Figure 2). A linear ^{60}Co array was used to achieve an exposure rate of 176 rad/sec (silicon) and a circular ^{60}Co array was used to achieve a higher rate of 1054 rad/sec (silicon). Expected dose rates on a loaded canister was calculated to be 2-3 rad/sec initially [11] thus dose rates used in this study were highly accelerated compared to the actual application.

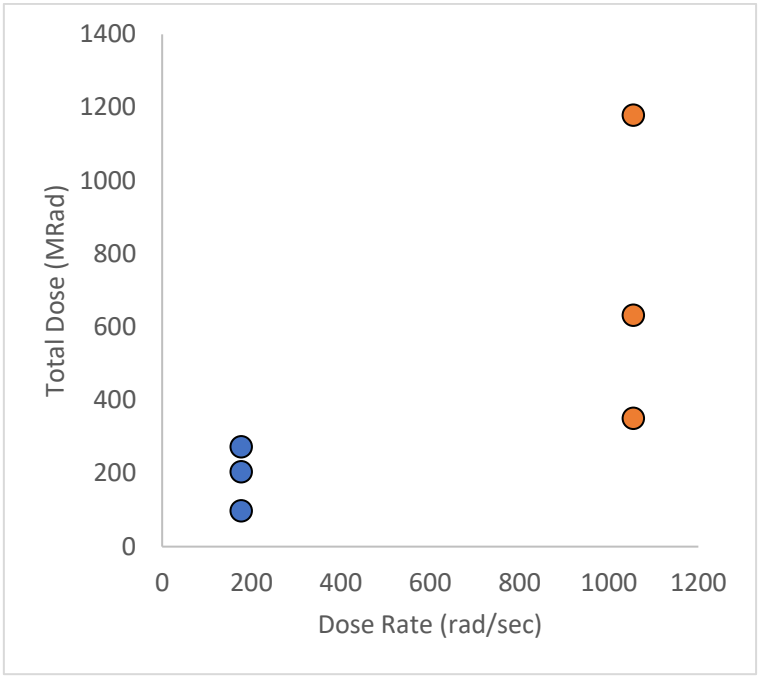

Figure 2 Total dose (Mrad) and dose rates (rad/sec (Si)) of study performed on coating variants at SNL's Gamma Irradiation Facility.

The total doses used in the irradiation study were selected based on calculations of gamma ray fluence at the surface of a canister storing commercial spent nuclear fuel with a burnup of 45-48 GWd/MTU (4% ^{235}U) [11]. They were also based on canister inspection intervals which would occur during the lifetime of a canister (such as the initial inspection after 20 years in interim storage). Depending on when a canister was coated, the total dose the coating would experience would vary. A coating applied to a new canister, before or immediately after placement into storage would experience the highest total dose. Conversely, a coating applied to a canister after decades of storage would receive a significantly lower dose. These intervals can be seen in Figure 3.

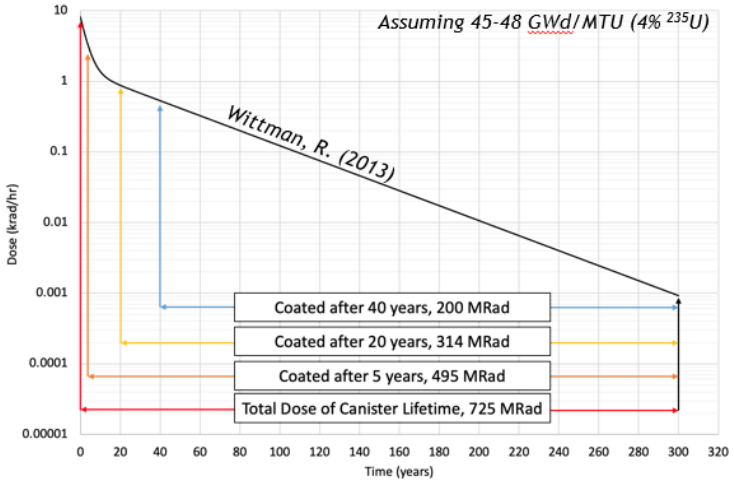

Figure 3 Calculated radiolytic dose rate as a function of time after loading with commercial spent nuclear fuel. Modified from [11].

The impact of radiolytic exposure on the mechanical integrity of the coating variants was evaluated using ASTM D4541 [7] adhesion testing (Figures 4 and 5) and nanoindentation (Figure 6 and Table 2). Previous studies have shown evidence of radiation interaction with polymeric materials resulting in of cross-linking (hardening) or chain scission (softening) [13] of the polymer chains.

These interactions should result in increasing or decreasing adhesion strengths as well. The high dose rates (especially compared to the actual fluence on the canister surface) may result in hardening or softening phenomena which may not occur on a canister due to the highly accelerated nature of this experiment. The implications of these effects have not yet been fully explored.

Figure 4 shows the average pull-off pressure as a function of radiolytic dose. Samples were also tested in baseline to measure the unirradiated adhesion strength. Overall, the adhesion pressure appears to decrease with increasing dose. This may be due to chain scission in the polymers that comprise the coatings [13]. WHRD-21-02 and WHRD-21-03 exhibited type 2 failure (failure within the coating) after radiolytic exposure. OPM-23-01 exhibited a type 3 failure mode (failure between the test dolly/epoxy and the coating surface). The decrease in OPM-23-01 pull-off values indicates that the adhesion of the epoxy to the coating surface is dependent on the radiolytic exposure, possibly meaning that chemical changes are occurring on the surface (such as reactions with ambient moisture or oxygen). The remaining datasets exhibited cohesive or adhesive failure modes.

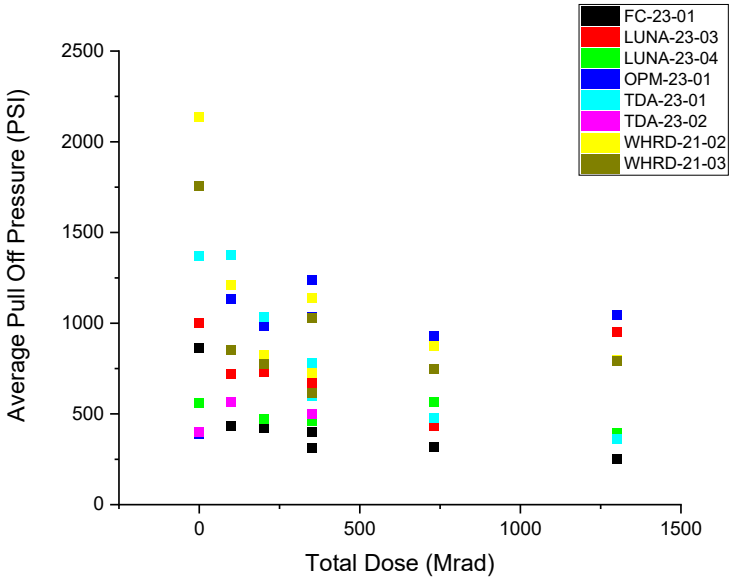

Figure 4 Average adhesion pull-off pressure (PSI) as a function of total dose in megarad. Samples with zero dose were baseline measurements. OPM-23-01 exhibited a type 3 failure mode while WHRD-21-02 and WHRD-21-03 exhibited type 2 failure mode.

Figure 5 shows a dose rate comparison of the average pull-off pressure on the coatings. Overall, there are no clear trends that indicate a strong dose-rate dependence for adhesion. OPM-23-01 exhibited a type 3 failure mode (failure between the test dolly and the coating surface) while WHRD-21-02 and WHRD-21-03 exhibited a type 2 failure mode (failure within the coating). The remaining datasets exhibited cohesive or adhesive failure modes.

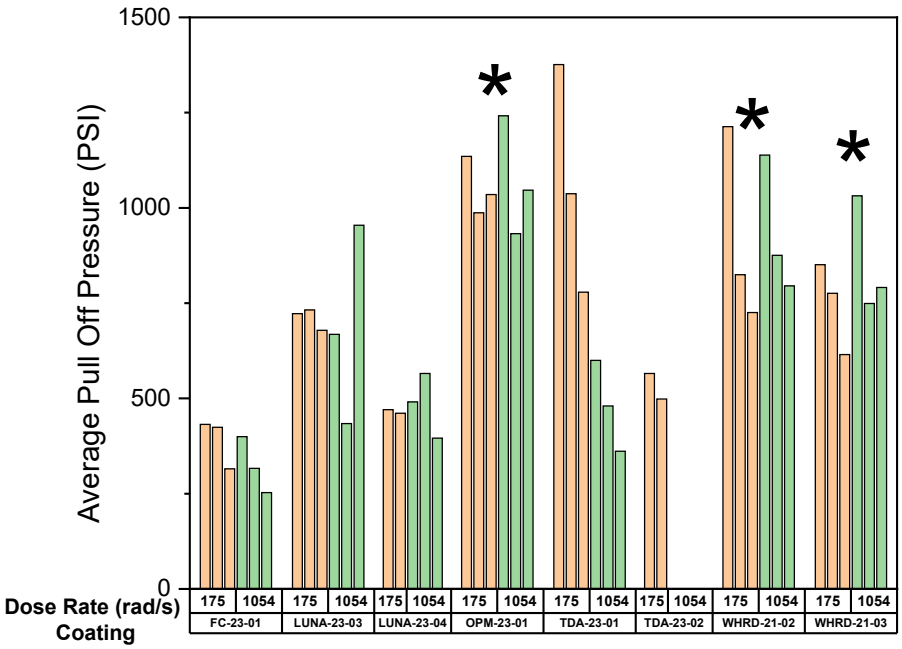

Figure 5 Dose rate comparison of average pull-off pressure for all coatings. Three datasets are marked (*) to denote that OPM-23-01 exhibited a type 3 failure mode while WHRD-21-02 and WHRD-21-03 exhibited type 2 failure mode.

Nanoindentation was performed on all coatings. Figure 6 shows the load-displacement curves of TDA-23-01 before and after exposure to 750 Mrad. After exposure, the stiffness of the coating decreased substantially likely as a result of chain scission [13] (also seen in Table 2).

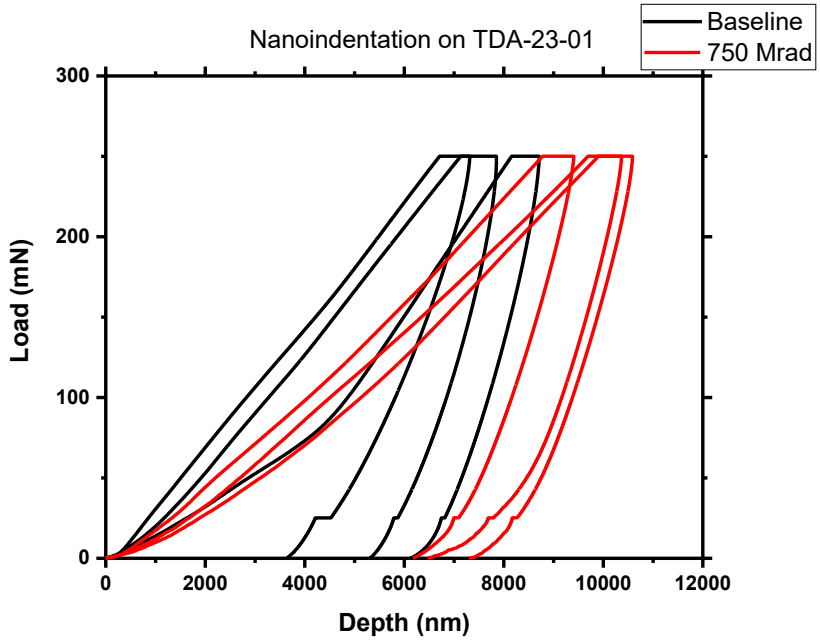

Figure 6 Load-displacement curves for baseline and irradiated TDA-23-01.

Table 2 Nanoindentation Average Hardness and Modulus for Coatings

Coating	Dose (Mrad)	Dose Rate (rad/s)	Modulus (GPa)	Hardness (MPa)
TDA-23-01	0	0	4.68	362
TDA-23-01	750	1054	3.498	200

The approximate temperature of the outer surface of canisters has been modeled for vertical and horizontal canisters in interim storage as a function of storage time. Canister surface temperatures can exceed 220°C immediately after loading. After 20 years, some locations on the canister still exceed 150°C in some locations on the canister [12]. Phase 2 coating variants were evaluated against these two application intervals and their respective calculated surface temperatures. The temperatures which a coating must be able survive is then highly dependent on when the coating is applied during the canister storage lifetime.
Thermogravimetric analysis (TGA) was used to determine the onset of thermal decomposition temperature of the Phase 2 coating variants (Figure 7). A small amount of coating (~10mg) was removed from the coating substrate and heated at 10°C/min to 500°C in air while measuring mass against an empty alumina crucible. Three coatings did not experience onset of thermal decomposition at the expected canister surface temperature of 230°C, while three coatings (WHRD-21-02, WHRD-21-03, and FC-21-01) did. While these did not survive higher heat loads, these coatings could still be of interest for ex-situ repair scenario in which coatings are applied to canisters which have cooled for at least 20 years. Additionally, further research is necessary to determine potential effects on coatings decomposition when examined at various thermal ramp rates and/or aging for prolonged periods at canister relevant temperatures.

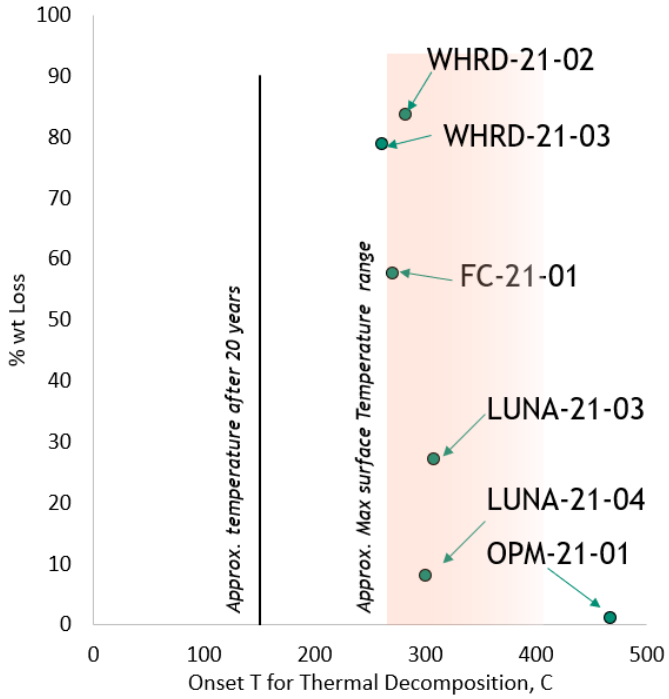

Figure 7 Thermogravimetric data expressed as weight loss (due to outgassing or decomposition) as a function of onset temperature.

CONCLUSIONS

Eleven candidate coatings were subjected to electrochemical and mechanical tests under environmental, radiological, and thermal exposure conditions to determine the feasibility of use on spent nuclear fuel storage canisters. After an initial round of electrochemical and mechanical tests on unexposed coupons, a small down selection was performed. The second round of testing included exposure to radiation which caused softening and a decrease in adhesion strength in some of the coatings. Three coatings showed lower onset of thermal decomposition but generally all materials displayed good thermal resistance under the conditions examined. Future work will include further investigation of mechanical properties after thermal and radiological exposures.

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