Neutron irradiation and high temperature effects on amorphous Fe-based nano-coatings on steel – A macroscopic assessment

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Abstract

The study revealed that loss of ductility in an amorphous Fe-alloy coating on a steel substrate composite structure was essentially prevented from occurring, following radiation with modest neutron doses of $\sim 2 \times 10^{18}$ n/cm². At the higher neutron dose of $\sim 2 \times 10^{19}$, macroscopic stress-strain analysis showed that the amorphous Fe-alloy nanostructured coating, while still amorphous, experienced radiation-induced embrittlement, no longer offering protection against ductility loss in the coating-substrate composite structure. Neutron irradiation in a corrosive environment revealed exemplary oxidation/corrosion resistance of the amorphous Fe-alloy coating, which is attributed to the formation of the Fe₂B phase in the coating. To establish the impact of elevated temperatures on the amorphous-to-crystalline transition in the amorphous Fe-alloy, electron microscopy was carried out which confirmed the radiation-induced suppression of crystallization in the amorphous Fe-alloy nanostructured coating.

1. Introduction

Nanostructured materials, especially amorphous ones, are expected to exhibit radiation resistance stemming from their inherent lack of long range order (a.k.a. translational symmetry) that offer sites to which radiation-induced defects could migrate. Such a process may enable nanostructures amorphous materials to resist loss of ductility (an important property for nuclear materials), and also possess oxidation and corrosion resistance while operating in aggressively corrosive and oxidizing environments. Capitalizing on anticipated good radiation performance of nanostructured amorphous materials in the form of protective coatings deposited on nuclear materials, i.e. nuclear steels, is a challenge albeit with significant technological implications. Of primary interest is the functionality of the composite system (coating-steel substrate), and its collective response to stimuli consisting of irradiation fluxes, elevated temperatures and corrosive/oxidizing environment, all of which may occur simultaneously. The objective here is to extend the lifetime of nuclear steels with the protection provided by nanostructured coatings by enhancing the effective resistance of the composite system to embrittlement (or equivalently loss of ductility), while providing a barrier to environmental surface attacks such as oxidation and corrosion.

R. Gerling, et al. [1, 2, 3] reported on the thermal annealing of various amorphous metallic alloys such as Fe₄₀Ni₄₀P₂₀, Fe₄₀Ni₄₀B₂₀, Cu₆₄Ti₃₆, etc., and the ductility restoration achieved with low-dose neutron irradiation. It was deduced from the studies in [1, 2, 3] that amorphous alloys, whether already brittle in the as-quenched state such as Fe₄₀Ni₄₀B₂₀ or ductile in as-quenched state but thermally embrittled afterwards, regained full ductility upon irradiation. This, in turn, indicating the embrittlement-crystallization process was reversible at temperatures below the onset of crystallization. In [4] neutron irradiation effects on amorphous and nanocrystalline Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉ alloys were studied by exploring structural, magnetic and mechanical properties following thermal embrittlement, which attributed the observed changes in properties to the generation of excess free volume (irradiation-induced swelling). X-ray diffraction studies on as-quenched and thermally relaxed samples at temperatures up to 400 °C showed typical diffraction patterns for amorphous alloys. Specifically, a broad diffuse intensity

maximum was observed, while crystalline α -Fe(Si) appeared after annealing at 545 °C, and iron borides formed at 650 °C. The results of the study, as reported in [4], found that the fraction of amorphous phase increased at the expense of crystalline phases upon neutron irradiation, indicating that partial re-amorphization in the nanocrystalline alloy and the restoration of ductility therein are the result of radiation-induced swelling. The amorphous and nanocrystalline $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloys were also studied in [5] by the Mössbauer spectroscopy, revealing that the formation of nanocrystals in the amorphous alloy can be triggered by thermal annealing at ~520 °C. By the use of standard thermal analysis methods, the Curie temperature of the as-quenched amorphous alloy was determined as $T_c = 329$ °C.

The effect of electron irradiation on crystallization and phase stability of boron-containing amorphous alloys such as Fe-Zr-B was studied in [6]. Observed in [6] was that the amorphous phase is not stable under irradiation, and that crystallization is accelerated by electron irradiation. Also reported in [6] is that the crystallization process was very sensitive to boron concentration. Irradiation effects in amorphous and crystalline sputter-deposited Mo-Ni were explored in [7], where it shown that ion bombardment of crystalline Mo-Ni at temperature <570 °K caused complete transformation to amorphous state, and that irradiation at elevated temperatures accelerated thermally activated processes. Amorphous-to-crystalline phase transformation by neutron irradiation in $\text{Fe}_{83}\text{B}_{17}$ alloy was studied in [8]. A series of studies on irradiation effects in amorphous and crystalline Fe-based alloys and the corresponding irradiation-induced changes in density, ductility, and Curie temperature were also reported in [8]. In [9] the thermal embrittlement of amorphous Fe-based alloy ribbons were studied, wherein it was reported that such amorphous alloys became brittle after annealing to temperatures significantly lower than their crystallization temperatures.

The Curie temperature and the crystallization behavior of the $\text{Fe}_{80}\text{B}_{15}\text{Si}_{5-x}\text{Ge}_x$ amorphous system was studied in by Kabacoff et al. [10], who concluded that crystallization initiates by precipitation of α -Fe, followed by crystallization of the remaining amorphous material. The effect of the substitution of Ge by Si on the Curie temperature of $\text{Fe}_{80}\text{B}_{15}\text{Si}_{5-x}\text{Ge}_x$ was studied as well. In [11] Fe-based amorphous composite coatings, which were prepared by plasma re-melting, were studied using DSC to confirm the presence of amorphous phase, and revealed that the coating has an exothermic crystallization peak in the range 492.2~569.1°C, and undergoes an amorphous to crystalline transition in the vicinity of 511.2 °C. Such singularities in the thermal analyses indicated the presence of amorphous phases in the coatings. At temperatures exceeding 569.1°C a phase transition was observed. Following plasma re-melting, X-ray diffraction patterns were generated, which revealed the presence of a nanocrystalline phase that is dispersed in the amorphous matrix.

Reported in this study are effects of temperature, environment and spallation-induced neutron irradiation on amorphous Fe-alloy nanostructured coatings on alloy steel substrates. Specifically, ~240 μm thick amorphous Fe-alloy coatings, which were deposited on 4130 alloy steel, are characterized for their alloying composition using electron microscopy/EDS spectroscopy and X-ray diffraction. The DSC/TGA thermal behaviour of such nanostructured amorphous coatings were studied in terms of phase transitions and oxidation, and reported herein. Moreover, the amorphous-to-crystalline evolution up to 1000 °C was studied. The effects of neutron irradiation (primarily fast neutrons) on dimensional stability of the coating-substrate system, and the potential role of the amorphous coating in resisting ductility loss, as observed during stress-strain mechanical testing, are explored in depth. Neutron irradiation experiments were conducted at varying fluence and conditions: (a) 2×10^{18} n/cm² at ~70 °C, and water and (b) 2×10^{19} n/cm² at ~210 °C under vacuum. Post-irradiation results are based on dilatometry, mechanical testing and X-ray diffraction using 67 keV monochromatic X-rays at the XPD beamline of NSLS II, and 200 keV polychromatic X-rays at the X17-B1 beamline of NSLS. Furthermore, the ability of the amorphous Fe-alloy coatings to resist corrosion and oxidation is explored to assess their potential application as protective barrier role with the designed experiment. A combination of optical assessment and X-ray characterization provides a clear picture of the mechanochemical properties of such amorphous Fe-alloy coatings in nuclear applications.

2. Experimental

2.1 Amorphous Fe-based nanostructured coating SEM/EDS and X-ray based characterization

The synthesis of amorphous Fe-alloy coating is based on feedstock melted in a plasma torch with the molten metal sprayed by rastering a nozzle over the surface of the steel substrate which is at a temperature significantly lower than that of the molten metal. Upon contact, the liquid iron is splat-quenched and solidified suppressing the crystallization and phase decomposition of the molten iron whereby amorphous Fe is obtained as a single phase solid. The resulting Fe-based coating is a highly alloyed material that imparts great oxidation resistance in comparison to even stainless steels. The non-equilibrium nature of the process (splat-quenching) and the high concentration of alloying elements results in an amorphous solid which is thermodynamically metastable but kinetically well stabilized [12, 13].

To understand the evolution of the amorphous Fe-based coating with temperature and/or environment in the absence of irradiating neutrons, out of beam studies characterizing the coating and its thermal response were conducted at the BNL Center for Functional Nanomaterials (CFN). These studies consisted of thermal annealing, differential scanning calorimetry, and thermogravimetric analysis (DSC/TGA), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectra (EDS). The microscopy-based characterization was augmented with energy dispersive X-ray diffraction analysis at the X17-B1 beamline of the NSLA and XPD of NSLS II, respectively. Understanding of the thermal response and amorphous-to-crystalline transition in the absence of irradiating beam is of paramount importance towards the delineation of the effects, i.e. irradiation-induced vs. temperature-induced.

Figure 1 depicts micrographs of the as-received, deposited Fe-based ~240µm-thick coating on 1.4mm-thick 4130 alloy steel generated using a JEOL 7600F Analytical High Resolution SEM. The presence of pre-existing micro-crack networks developed during the deposition process is evident. Figure 2 shows energy dispersive spectroscopy (EDS) data and the identified elements in the coating such as B, Mo, W, Cr, Cu and Aluminium generated using an INCA instrument for the X-ray analysis. The presence of oxygen and carbon indicates that oxides and carbides have formed during deposition which typically takes place in air. The variation of the chemical composition of the coating over two (2) selected sites is listed in Table 1. The variation of the chemical composition of the coating over two (2) selected sites is listed in Table 1. It should be noted that boron was found to vary considerably throughout the coating. Listed in Table 1 are two sites with elevated boron levels. One may observe the elevated levels of carbon that should be in the form of carbide phases in the coating. The present alloying elements are expected to be partitioned in Fe-based phases depending on the solubility limit, e.g. Fe vs. (Fe,Cr,Mo)₃O₄.

Figure 1: SEM micrographs of as-received ~240 µm amorphous Fe-based coating on 4130 alloy steel.

X-ray diffraction patterns using both polychromatic and monochromatic high-energy X-rays were used, in conjunction with the EDS spectra, to identify the resulting phases in the coating. An understanding of the developed phases present in the coating will help provide anticipated behaviour either with regards to temperature or environment such as corrosive or oxidizing. Figure 3 presents X-ray diffraction patterns along with identified phases within the amorphous Fe-based coating as well as at the

interface with the bcc-steel substrate. The patterns were produced using 200 keV X-rays in the energy dispersive mode (EDXRD) at the X17-B1 beamline. Figure 4 depicts X-ray diffraction patterns and shows identification of phases developed during coating deposition, including the presence of alloying elements such as Mo.

Figure 2: EDS spectra of as-received amorphous Fe-based coating generated using a JEOL-7600/INCA

Table 1: Chemical composition and variation of as-received amorphous Fe-based coating

<u>Element</u>	<u>Site 1</u>		<u>Site 2</u>	
	<u>Weight%</u>	<u>Atomic%</u>	<u>Weight%</u>	<u>Atomic%</u>
B-K	10.23	26.67	10.6	30.83
C-K	11.16	26.19	8.4	22
O-K	8.44	14.87	2.82	5.54
Al-K	3.16	3.3	3.35	3.91
Si-K	0.32	0.32	0.3	0.34
Cr-K	9.25	5.01	12.18	7.37
Fe-K	31.76	16.03	40.68	22.91
Cu-K	0.19	0.08	0	0
Y-L	4.74	1.5	0	0
Mo-L	20.21	5.94	21.67	7.1
W-M	0.55	0.08	0	0

Based on the EDS spectra and X-ray diffraction patterns from the two experiments (polychromatic and monochromatic) it is assessed that the amorphous Fe-based coating under consideration is essentially a 4-phase system consisting of (1) BCC-Fe:Cr,Mo;W (metallic; crystalline solid solution), (2) (Fe,Cr,Mo)₃O₄ (ceramic; crystalline solid solution), (3) (Fe,Cr)₂B (ceramic boride; crystalline solid solution) and (4), amorphous-Fe:Cr;Mo;W (metallic; amorphous solid solution) plus amorphous (Fe-B-C) phases. Phase separation, crystallization, as well as oxidation are evident in the coating. Formation of oxide phases (Fe₃O₄-based) and borides (Fe₂B-based) is expected to contribute to coating's embrittlement (similar to temperature-induced embrittlement). It is also expected that the oxide phase will form at grain boundaries according to the oxidation mechanisms of polycrystalline metals. Poor corrosion (and oxidation resistance) of Fe is attributed to the redistribution of alloying elements among BCC-Fe, amorphous-Fe, (Fe,Cr,Mo)₃O₄ and (Fe,Cr)₂B [14-18]. On the other hand, corrosion resistance of the coating might very

well arise from the presence of Fe_2B . The coating is essentially a ternary CERMET with a ductile metal matrix (austenite), reinforced by a carbide and a boride.

Figure 3: X-ray diffraction patterns and identified phases in the amorphous Fe-based coating (left) and at the interface with the bcc-steel substrate using “white”, 200 keV X-rays and EDXRD technique.

Figure 4: D-spacing and identified phases in the amorphous Fe-based coating at the interface with the substrate (left) and identification of alloyed elements (right) using monochromatic, 67 keV X-rays at the XPD beamline of NSLS II.

2.2. Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM) Studies of Crystallization prior to Irradiation

Studies based on DSC/TGA were conducted on amorphous Fe-alloy coatings up to 1000 °C using a Perkin-Elmer Diamond TG/DTA (Thermo-gravimetric/Differential Thermal Analyser). A JEOL 7600F SEM, which was equipped with an integrated energy dispersive spectrometer (EDS), was brought to bear for microstructural analyses at the Center of Functional Nanomaterials (CFN) and BNL. The coating was meticulously removed from the 4130 alloy steel surface and subjected to analysis to identify (a) the onset of crystallization, (b) phase transitions that occur at elevated temperatures, and (c) the Curie temperature of the coating as obtained under nonequilibrium conditions from the deposition process. Such thermal characterization is crucial in discerning the effects of neutron irradiation from those resulting from temperature and environment. The thermal analysis results were assessed in conjunction with SEM

analyses to confirm the onset of amorphous-to-crystalline transitions. Figure 5 shows the identified Curie temperature occurring for this amorphous Fe-based system at $\sim 405^\circ\text{C}$. Also shown in Figure 5 is a phase change occurring at $\sim 485^\circ\text{C}$. The onset of crystallization, which has been reported by other studies (340°C) is depicted in Figure 6, following annealing under vacuum and SEM characterization. The DSC-based study confirms the amorphous-to-crystalline transition in Figure 6b.

Figure 5: a) DSC-based identification of Curie temperature, and b) phase change at $\sim 485^\circ\text{C}$ of amorphous Fe-alloy used in this study. Specimen obtained from the thermally sprayed coating. Heating rate is $1^\circ\text{C}/\text{min}$.

Figure 6: a) SEM-based identification of onset of crystallization if the amorphous coating on the steel substrate at 340°C , and b) confirmation of the process using DSC analysis.

To confirm the finding in [11] regarding the acceleration of the crystallization processes in amorphous Fe-alloys such as the one used in this study for the ~ 490 – 515°C temperature range, studies were conducted to establish whether the present coating exhibits similar behaviour. Figure 7 depicts SEM micrographs following annealing under vacuum for 3 hours. Crystallization of the amorphous Fe-based structure is evident from the fibrous crystallites at 480°C (Fig. 7a), faceted grains at 510°C (Fig. 7b) and crystallites forming on primary particles at 520°C (Fig. 7c). Figure 8 depicts DSC results over the same temperature range with isotherms at 504°C , and 514°C on heating and on cooling. The peak temperature in the thermal cycle was 535°C . While over the 504°C isotherm a phase transition is observed, crystallization is seen over the 514°C isotherm, both in the heating and the cooling phases of the thermal cycle while the heat flow slope for the two isotherms remains the same. Microstructures observed $< 480^\circ\text{C}$ are typical of thermally sprayed amorphous Fe-alloy coatings. The heterogeneous nature of the

microstructure is indeed very desirable from fracture mechanics perspective as it promotes crack blunting, increasing the effective toughness of the coating thereby.

Figure 7: Progressive crystallization of the amorphous Fe-based nanostructured coating on the steel substrate: a) 480 °C; b) 510 °C and c) 520 °C.

Figure 8: DSC based analysis of phase transitions and crystallization from 504 to 535 °C.

Annealing at higher temperatures (640 °C, 700 °C, 900 °C and 1000 °C) was conducted and the resulting SEM microstructures are depicted in Figure 9. In the micrographs pertaining to annealing at temperatures >640 °C, the small faceted features can be described as crystalline second phases which are the product of the decomposition and crystallization. The coating however remains mostly amorphous as can be verified from the morphology, i.e. no extensive faceting. The observed micro-cracking is due to differential shrinkage during deposition/solidification processing as well as differential thermal expansion upon second phase formation during annealing. The coating remains intact despite the crack network, protecting the substrate thereby. Here, the multiplayer coating deposition approach is very beneficial as it promotes crack blunting. Not observed is any substantial scaling of Fe due to oxidation attributed to the alloying elements a large fraction of which remained in solid solution during annealing. Temperatures >700 °C promote accelerated crystallization due to substantially enhanced diffusion rates. The observed dendritic growth of second phases is an indication of nucleation and growth phenomena associated with phase decomposition which, in turn, is a thermodynamic necessity as the amorphous phase is a metastable supersaturated (but kinetically stabilized) state of matter. The SEM micrographs show phase decomposition via nucleation and growth whereby crystalline second phases form. Here, the higher the temperature, the faster the nucleation and growth whereby crystalline second phases form.

Figure 9: SEM images of amorphous Fe-alloy coating on 4130 alloy steel substrate following annealing in vacuum for 3 hours at a) 640 °C, b) 700 °C, c) 900 °C, and d) 1000 °C.

Furthermore, the higher the temperature the faster the mass transport and hence the more pronounced is the phase decomposition kinetics in this metastable system. Upon further increasing the annealing temperature, one observes grain growth and Ostwald ripening which is a thermodynamic necessity to maximize the stability of the secondary phases.

The oxidation kinetics of the amorphous Fe-alloy coating was studied using thermogravimetric analysis (TGA). Figure 10a depicts heat flow and % change in weight, while Figure 10b depicts phase transitions occurring at high temperatures. The Curie point is similarly identified as at ~405°C in Fig. 5. Transition from α -Fe (ferromagnetic) to β -Fe (paramagnetic) is observed at 771°C as well as the body centered cubic (BCC) $\rightarrow$ face centered cubic (FCC) allotropic transition at 912 °C. The formation of Fe-oxides is clearly shown to occur in the temperature range of 820-850 °C.

Figure 10: TGA analysis of oxidation in amorphous Fe-alloy coating: a) time resolved trace, and b) temperature resolved trace.

The microstructural evolution of the amorphous Fe-alloy coating in at 700 °C in air is shown in Figure 11. It is seen that thermally activated processes at 700 °C cause the formation of crystallites (see Fig. 11a), and grain boundary formation among crystallites (see Fig. 11b) and crystalline inclusions in amorphous patches (see Fig. 11c).

Figure 11: SEM micrographs following annealing in air at 700°C. Noted is the contrast between nm-size and μ -size crystalline phases.

2.3 Irradiation Experiment

Spallation-generated fast neutrons were used to conduct two (2) irradiation damage experiments and reported herein. The irradiations were conducted at BLIP using the mixed spectrum generated by the 118 MeV protons of 110 μ A beam current that are stopped by an array of isotope producing targets upstream of the coating-substrate array. The first irradiation, which reached an integrated flux of $\sim 2.0 \times 10^{18}$ n/cm², was conducted with both amorphous Fe-alloy coating and the 4130 alloy steel in contact with the circulating cooling water at the target station. The irradiation temperature was estimated to be ~ 70 °C. The second irradiation experiment, which reached a fluence of $\sim 2.0 \times 10^{19}$ n/cm², was conducted with coating/substrate samples that were encapsulated within specially designed vacuum capsules. The neutron flux for both irradiation phases was $\sim 2.2 \times 10^{13}$ n/cm²/s. The irradiation temperature under vacuum was estimated to be ~ 210 °C. Strip-like specimens (42x 4x1.43 mm) and “dog-bone” shaped samples of similar dimensions were used in the irradiations (see Fig. 25a). The dog-bone tensile specimens were used in post-irradiation evaluation for mechanical tensile tests and in situ four-point bending work in conjunction with X-ray diffraction. The strip samples were also used for post-irradiation dimensional stability analysis.

Figure 12: (a) Spallation neutron profile and b) neutron energy spectra at the amorphous Fe-based coating/substrate irradiation location generated using the FLUKA [19, 20] transport code

Figure 12a depicts the configuration of the irradiated array downstream of the isotope producing targets, while Figure 12b depicts the neutron energy spectra at the different irradiating locations. The mean energy of the irradiating neutrons for the configuration shown here was ~ 10 MeV. Combined with

the neutron fluence, the coatings received a secondary proton fluence of $\sim 3.2 \times 10^{15}$ p/cm² with 23 MeV mean energy, a photon fluence of $\sim 3.0 \times 10^{18}$ γ/cm² with mean energy of 1 MeV, and $\sim 2.4 \times 10^{16}$ e/cm² with mean energy of 1 MeV. The effect of neutrons however is expected to be dominant.

3. Post-Irradiation Evaluation

3.1 Photon Spectra of Irradiated Amorphous Fe-alloy coatings on alloy steel substrates

Following each of the two irradiation experiments, photon spectra of the irradiated samples were collected using the high sensitivity ORTEC Ge detector for isotopic composition. The primary objective here was to observe the evolution of the isotopic map as a function of the fluence, and also verify the presence of alloying elements by identifying isotope signatures. Figure 13 depicts actual photon spectra that were collected from irradiated coating/substrate sample. While the cooling times between the end-of-bombardment (EOB) and photon spectra analysis for the two irradiation experiments are different, it is clear from Figure 13 that the relative amplitude of isotopes had evolved. The alloying elements that were present in the coating were detected by EDS and identified from their isotopic signatures.

Figure 13: Photon spectra of amorphous Fe-based coating on 4130 alloy steel for the two neutron fluences of the irradiation experiment: a) 2×10^{19} n/cm², and b) 2.0×10^{18} n/cm²

3.2 X-ray Diffraction Assessment of Amorphous Fe-alloy Coating

Using the 67 keV X-rays at the XPD beamline of NSLS II, the effect of neutron irradiation on the amorphous Fe-alloy coating was evaluated. The objective of the experiment was to assess whether

radiation-induced phase separations and amorphous-to-crystalline transitions have occurred in the coating as a result of the bombardment. Observations based on X-ray diffraction and the coating microstructure evolution is used herein to explain macroscopic mechanical behaviour (strain-strain response) and dimensional stability. Figure 14 depicts phase maps in a quarter-segment of the 2D detector at XPD beamline for the unirradiated and irradiated amorphous Fe-alloy coating-steel substrate system. For the comparison, the highest neutron fluence ($2 \times 10^{19} \text{ n/cm}^2$) sample was used in conjunction with the unirradiated state. The images shown correspond to the coating-substrate interface but not exactly at the same location on the interface. The dominant phase in the amorphous Fe-alloy coating and the diffraction patterns of α -Fe (BCC) substrate near the interface are clearly depicted. Figure 15 shows a direct comparison of the d-spacing map of the unirradiated state and following irradiation to $2 \times 10^{19} \text{ n/cm}^2$. It is evident that the Fe-based coating remains amorphous following irradiation to this fluence level and no separation of phases has occurred. One also observes an increase in peak intensity and reduction in peak width which implies that there is some increase in crystallite size in the system.

Figure 14: 2D X-ray diffraction images of a) unirradiated and b) neutron-irradiated coating-substrate interface.

Figure 15: Comparison of X-ray diffraction patterns of unirradiated and neutron irradiated amorphous Fe-alloy coating on steel in D-space, showing the unaffected amorphous state of the coating by irradiation and coating-substrate steel interface.

3.3 Dimensional Stability and Crystallization

By utilizing a high sensitivity LINSEIS dilatometer, the changes in dimensional stability and annealing of the irradiated amorphous Fe-alloy coatings on steel substrates were observed in air. Specifically, isochronal annealing consisting of multi-isotherm cycles was conducted to observe the dimensional changes in the composite structure, and to correlate it with DSC and TGA results. Shown in Figure 16 is post-irradiation thermal analysis of an irradiated sample to the fluence of $2.0 \times 10^{18} \text{ n/cm}^2$. Here, the thermal process consists of several isotherms up to 700°C with particular emphasis on about 500°C where crystallization of the amorphous coating was observed in DSC analysis of the unirradiated coating. What one observes in Figure 16a, and in more detail in Figure 16b (see the vicinity of 500°C), is that no noticeable crystallization occurred, as there is no evidence of thermally-induced contraction, indicating that neutron irradiation has delayed the crystallization process.

Figure 16: Thermally induced dimensional change in neutron irradiated amorphous Fe-alloy coating on 4130 alloy steel for $2 \times 10^{18} \text{ n/cm}^2$ fluence.

The thermally induced dimensional changes in the amorphous coating/steel substrate samples irradiated at the higher fluence ($2 \times 10^{19} \text{ n/cm}^2$) over two successive thermal cycles (TC1 and TC2) are depicted in Figure 17, and compared with its unirradiated counterparts that followed the identical thermal path. It is observed that the unirradiated structure undergoes significant contraction at temperatures/isotherms above 600°C that is accelerated over the 700°C isotherm. Crystallization of the unirradiated structure ceases during the cooling phase and over isotherms that are lower than the

maximum temperature of the experiment, i.e. 700 °C. During the second thermal cycle (TC2) with identical profile, it is observed that over the 700 °C isotherm the coating continues to contract which is indicative that crystallization is continuing. A drastically different behaviour of the irradiated amorphous Fe-based coating is observed over the 600°C and 700°C isotherms as demonstrated in Figure 17. Over the first thermal cycle (TC1) and for the isotherm succession (600°C, 700°C and 600°C) the composite structure is dimensionally stable (no contraction and so no crystallization occurs) even during heating and cooling between 600°C and 700°C at the rate of 2°C/min. During the second heating cycle (TC2) and during the 700°C isotherm the irradiated structure appears to experience a faint contraction indicating onset of some crystallization. To gain a better understanding of the ensuing processes, the behaviour over temperature ranges that were identified through DSC/TGA analysis as crystallization and phase transitioning ranges were studied.

Figure 17: Comparison of thermally induced dimensional change and crystallization in neutron irradiated amorphous Fe-based coating on 4130 alloy steel for $2 \times 10^{19} \text{ n/cm}^2$ fluence.

Figure 18 depicts the dimensional behaviour of the irradiated composite structure over the 400°C isotherm. One observes the similarity of the TC1 isotherm with the Curie temperature observed for the unirradiated amorphous coating, but the temperature is ~5 °C lower.

Figure 18: Dimensional stability in neutron irradiated amorphous Fe-alloy coating on 4130 alloy steel ($2 \times 10^{19} \text{ n/cm}^2$) over the a) 400 °C isotherm, and b) Curie temperature of unirradiated coating.

The comparison of the behaviour in the temperature range 400-600 °C is depicted in Figure 19, where clearly at ~500 °C, the unirradiated coating undergoes a significant contraction/crystallization which is in line with DSC/TGA and SEM observations made previously. Of significance is the fact that the neutron-

irradiated ($2 \times 10^{19} \text{ n/cm}^2$) structure exhibits no contraction indicating resistance to crystallization. Figure 20 is a closer look of the dimensional changes and crystallization process of the unirradiated structure over the 600-700 °C range depicting the onset of a “delayed” faint crystallization over the 700 °C isotherm of the second heating cycle. Important to note on Figure 20b is the upward trend during the 600 °C isotherm of the cooling phase.

Figure 19: Dimensional change comparison between unirradiated and neutron irradiated amorphous Fe-alloy coating on 4130 alloy steel ($2 \times 10^{19} \text{ n/cm}^2$) in the range a) 400-600°C, and b) 600-700°C.

Figure 20: Dimensional change and crystallization of neutron irradiated amorphous Fe-alloy coating on 4130 alloy ($2 \times 10^{19} \text{ n/cm}^2$) steel in the 600-700 °C range over a) successive thermal cycles, and b) close-up showing the changes during thermal cycle 1 (TC1).

3.4 Post-irradiation mechanical behavior of irradiated Fe-based coatings on alloy steels

Following the completion of the first irradiation to fluence of $\sim 2.0 \times 10^{18} \text{ n/cm}^2$, tensile tests were performed on the special dog-bone type samples to assess the mechanical response. Some very intriguing results were obtained regarding the ability of the composite structure (coating-substrate) to resist ductility loss from irradiation. Figure 21 compares the stress-strain behavior of unirradiated samples with that of the irradiated to $2.0 \times 10^{18} \text{ n/cm}^2$. The stress-strain response of the two unirradiated samples demonstrate the repeatability of the data, which ensures that any observed changes in the stress-strain curve will be attributed to external stimuli, i.e. temperature and/or irradiation. It is evident that while the overall strength experiences a reduction, contrary to what is expected for irradiated structures, there appears to be no loss in ductility, and even some slight enhancement. Such observed increase in ductility, or resistance to its loss confirms previous studies for low dose irradiation of amorphous ribbons [1]. Embrittlement in these amorphous structures induced by thermal treatment is the direct result of the decrease in the excess volume which is retained from quenching. Neutron irradiation induces swelling, or irradiation-induced

excess volume, which restores or even enhances the ductility of the amorphous Fe-alloy-steel substrate structure. Given the fact that irradiation during this experiment was conducted at $\sim 70^\circ\text{C}$, no loss of excess free volume was attributed of temperature. Shown on Figure 21b is a close-up view of the yield zone and the influence of neutron irradiation.

Figure 21: a) Comparison of stress-strain behaviour of unirradiated and neutron-irradiated amorphous Fe-based coating on steel for fluence $2 \times 10^{18} \text{ n/cm}^2$, and b) detailed view near the yield zone which is more clearly delineated following irradiation-induced changes and deformation in the coating.

Following the completion of the second irradiation to a fluence that is one order of magnitude higher ($2 \times 10^{19} \text{ n/cm}^2$), and at a slightly higher irradiation temperature while in vacuum (210°C instead of 70°C), mechanical tensile tests were performed to assess the higher neutron dose effects. Figure 22 demonstrates that at the higher dose and temperature, the lower the ductility of the coating-substrate system with simultaneous increase in strength as in typical metals. It can be deduced that the decrease in excess free volume in the amorphous coating, resulting from the higher irradiation temperature, compensates for the radiation-induced excess volume which is expected to be higher as compared to the one in the first irradiation experiments.

Figure 22: Stress-strain behaviour of unirradiated and neutron-irradiated amorphous Fe-alloy coating on steel substrate for fluence up to $2 \times 10^{19} \text{ n/cm}^2$.

To further explore the effect of temperature on the stress-strain behaviour of the coating-substrate system and to correlate it with the evolution of crystallization in the coating, samples were annealed to temperatures up to 1000 °C, and tested under tension. Figure 23 depicts results of the stress-strain tests as a function of the annealing temperature, and is compared with the unirradiated and irradiated to low neutron dose specimens ($2 \times 10^{18} \text{ n/cm}^2$). As shown in Fig. 23a, the ductility in the unirradiated and treated at 640 °C is enhanced indicating that the “softening” in the steel substrate overtakes the crystallization and embrittlement of the amorphous coating. With increasing temperature, as noted in Fig. 23, the ductility loss increases (though not monotonically due to the counteraction of processes in the amorphous coating and the substrate). At 1000 °C, where large scale crystallization was observed in the coating with SEM, the effective ductility is greatly reduced. Two different tests at 1000 °C are shown confirming repeatability of the experimental data.

Figure 23: Stress-strain behavior of amorphous Fe-alloy coating on steel substrate comparing fast neutron irradiated and unirradiated cases: a) Overall behavior and b) close-up of the yield point

3.5 Corrosion of Fe-based coatings on steel

Questions regarding the ability of amorphous Fe-alloy coatings to resist corrosion in harsh nuclear reactor environments while under the influence of neutron irradiation effects are of great technological relevance that requires both qualitative and quantitative assessment. Coating characterization studies have assessed that there exist phases within the amorphous coating structure that will, in theory, help protect the coating against corrosion. Following the first of the two irradiations that occurred with both amorphous Fe-alloy coating and substrate steel in contact with the circulating cooling water, it was observed that the substrate suffered from corrosion effects, the Fe-alloy coating remained completely unaffected. This is depicted in Figure 24a showing an irradiated tensile (dog-bone) sample after irradiation and Figure 24b-d for Fe-alloy coating under irradiation as well. To further study the corrosion-resistance of the amorphous coating under higher neutron doses than the original $2 \times 10^{18} \text{ n/cm}^2$, a special irradiation test was conducted where only the coating was exposed to both the cooling water and the neutron flux. The experiment configuration is shown in Figures 24b-c. Specifically, a disk with the coating on the water side and the substrate on the vacuum side was welded in vacuum over a cavity preventing the substrate is in contact with water. Following irradiation to $2 \times 10^{19} \text{ n/cm}^2$, the coating was visually examined (shown in Figure 24d). No corrosion was evident over the amorphous coating with only signs of corrosion effects on the seam of the electron beam welding which had inevitably disturbed the steel substrate.

Figure 24: (a) Corrosion in steel substrate after $\sim 10^{18}$ n/cm² in water, (b, c) experimental set up of corrosion test of amorphous coating, and (d) coating after $\sim 10^{19}$ n/cm² in water.

X-ray diffraction characterization was performed to substantiate the optical (visual) assessment of corrosion resistance of the amorphous Fe-alloy coatings. Figure 25 compares X-ray diffraction patterns of amorphous coatings on steel under different environmental conditions during irradiation (water vs. vacuum). These patterns were obtained collecting data across the thickness of the substrate and coating by spatially resolved X-ray diffractometry. Shown clearly in Fig 25b is the appearance of phases in the substrate which are not attributed to irradiation since no such phases appear under higher neutron dose in vacuum as shown in Fig. 25c.

Figure 25: EDXRD 3-D phase map of 240 μ m thick amorphous Fe-alloy coating on steel substrate of a) as-received unirradiated, b) neutron irradiated to 2×10^{18} n/cm² in water, and c) irradiated to 2×10^{19} n/cm² in vacuum.

A closer view of the combined effect of the environment and dose on the amorphous coating is shown in the diffraction patterns of Figure 26. As demonstrated by the X-ray diffraction analysis, the coating remains amorphous under irradiation to fluence 2.0×10^{19} n/cm², while no new phases were observed that would otherwise indicate large scale decomposition or corrosion/oxidation.

Figure 26: 2D EDXRD traces of 240 μm thick amorphous Fe-alloy coating on steel substrate of as-received unirradiated, neutron irradiated to $2 \times 10^{18} \text{ n/cm}^2$ in water, and irradiated to $2 \times 10^{19} \text{ n/cm}^2$ in vacuum. Patterns were obtained in the middle of the coating across its thickness.

It is assessed that the corrosion resistance of the coating observed here is due to the formation of the Fe_2B phase. That is so because boron is not water soluble, and neither is Fe_2B in which iron is bound to boron at a fixed stoichiometry. Furthermore, the amorphous Fe-alloys considered in this study contain over 20% alloying elements, which impart corrosion resistance to the base ferrous phase. It also contributes to suppress crystallization. Similar conclusions were reached by Xiao et al. [21], who carried out a quantitative phase analysis of amorphous-Fe thermal spray coating and assessed the stability, electronic and mechanical properties of Fe_2B . In a study by Kartal et al. [22], who investigated the morphology and corrosion behaviour of electrochemically borided steel, a similar behaviour was observed and it was assessed that the presence of boron and its alloying is behind the corrosion resistance. It was postulated that the boron atoms diffuse through the surface of the sample, creating borides with the base alloy substrate. And at the end of the boriding process, different boride phases are formed depending on the amount of diffused boron atoms from surface into matrix as follows: FeB_x ($x > 1$), FeB , Fe_2B , Fe_3B , Fe_yB ($y > 3$) Fe. Diffraction studies and characterization of the amorphous Fe coating have revealed that such boride phases are found in the composition of the coatings considered in this study.

It follows from the preceding considerations that the exemplary resilience of the Fe-based amorphous nanostructured coatings against corrosion stem from the high concentration of alloying elements that suppress crystallization in the first place, and impart oxidation resistance at the same time. The alloying elements which add up to 30% of the nominal composition are mostly stable oxide formers providing a protective native oxide barrier. In addition, the presences of Fe-B compounds, which inevitably form to some degree, also contribute to amorphous Fe-alloy's resilience against corrosion.

4. Summary & Discussion

Amorphous Fe-alloy nanostructured coatings, which were deposited on alloy steel substrates via plasma spraying, were exposed to spallation-generated fast neutrons under different conditions (water environment and vacuum) to evaluate their potential as protective barriers [23]. Post-irradiation evaluation aiming to understand the macroscopic behaviour of the coating-substrate structure under stress, and its dimensional stability was conducted. X-ray diffraction experiments using high energy X-rays and advanced diffraction techniques augmented the macroscopic observations.

The effect of temperature on the amorphous-to-crystalline transitions in the Fe-based coating up to 1000 °C, and, consequently, on the stress-strain response and dimensional stability was explored using differential scanning calorimetry/thermo-gravimetric analysis, and scanning electron microscopy. Such studies revealed that the Curie temperature of amorphous structure is lower than what was observed for other amorphous metals (~405 °C). The onset of amorphous-to-crystalline transition in the unirradiated coating was at ~340 °C, while above 900 °C the coating completely crystallizes.

Specially designed samples of the composite structure (coating-substrate) were originally subjected to modest irradiation doses ($\sim 2 \times 10^{18}$ n/cm²) in combination with oxidizing-corrosive environment. For this dose level, the amorphous Fe-alloy coating exhibited remarkable resistance against corrosion, and oxidation while during mechanical tensile tests it provided the substrate steel, or the composite structure, with effective ductility under irradiation -a feature resulting from the amorphous character of the coating that promotes the generation of excess free volume. Post-irradiation EDXRD work confirmed that the coating exhibited resistance to crystallization and maintained its ductility. The amorphous→crystalline phase transformations appear to be brought to a halt due to the mutually counteracting effects of temperature (favouring crystallization) and neutron irradiation favouring amorphization.

Irradiation experiments at fluences higher by a factor of 10 (2×10^{19} n/cm²), and subsequent post-irradiation examination revealed that the amorphous coating, while it retained its amorphous structure, underwent embrittlement, and was no longer contributing ductility to the composite structure. The significantly higher excess free volume generated by the higher fluence of fast neutrons (primarily), and to lesser extent by thermal neutrons that are captured by the boron, influence dramatically the dimensional behaviour of the coating-substrate system at temperatures >600 °C during post-irradiation thermal annealing. The study also confirmed the radiation-induced suppression of crystallization in the amorphous Fe-alloy based nanostructured coating.

The exemplary corrosion/oxidation resistance of the Fe-alloy amorphous coating was attributed to the formation of the Fe₂B phases and the apparent suppression of crystallization along with the resistance to ductility loss to neutron fluence $< 2 \times 10^{19}$ n/cm² were deemed as encouraging attributes of such coatings to play the role as protective coatings on steels used in nuclear technology. Envisioned future experiments will aim to address the operating envelope of such structures in the nuclear environment [24].

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facilitated the EDXRD experiments; H. Zhong developed numerical processes for analysis of diffraction data, F. Camino facilitated the scanning electron microscopy; E. Dooryhee, S. Ghose, and S. Gill played critical roles in various data collection and processing aspects of this study; E.K. Akdoğan and İlyas Şavklıyıldız participated in the EDXRD experiments, performed X-ray diffraction data collection and analysis. E.K. Akdoğan made major contributions to interpreting key diffraction and microstructural data.

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