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Criticality-Control Applications in the Nuclear Industry for Thermal Spray Amorphous Metal and Ceramic Coatings

J.C. Farmer, J-S. Choi

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Joseph Collin Farmer & Jor-Shan Choi
Lawrence Livermore National Laboratory, Livermore, California USA

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Abstract

Amorphous metal and ceramic thermal spray coatings have been developed that can be used to enhance the corrosion resistance of containers for the transportation, aging and disposal of spent nuclear fuel and high-level radioactive wastes. Iron-based amorphous metal formulations with chromium, molybdenum and tungsten have shown the corrosion resistance believed to be necessary for such applications. Rare earth additions enable very low critical cooling rates to be achieved. The boron content of these materials, and their stability at high neutron doses, enable them to serve as high efficiency neutron absorbers for criticality control. The high boron content of $Fe_{49.7}Cr_{17.7}Mn_{1.9}Mo_{7.4}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ (SAM2X5) makes it an effective neutron absorber, and suitable for criticality control applications. Average measured values of the neutron absorption cross section in transmission (Σ_t) for Type 316L stainless steel, Alloy C-22, borated stainless steel, a Ni-Cr-Mo-Gd alloy, and SAM2X5 have been determined to be approximately 1.1, 1.3, 2.3, 3.8 and 7.1 cm^{-1}, respectively.

Introduction

The outstanding corrosion resistance that may be possible with amorphous metals was recognized several years ago [1-3]. Compositions of several iron-based amorphous metals were published, including several with very good corrosion resistance. Examples included: thermally sprayed coatings of Fe-10Cr-10-Mo-(C,B), bulk Fe-Cr-Mo-C-B, and Fe-Cr-Mo-C-B-P [4-6]. The corrosion resistance of an iron-based amorphous alloy with yttrium (Y), $Fe_{48}Mo_{14}Cr_{15}Y_2C_{15}B_6$ was also been established [7-9]. Yttrium was added to this alloy to lower the critical cooling rate. Several nickel-based amorphous metals were developed that exhibit exceptional corrosion performance in acids, but are not considered in this study, which focuses on iron-based amorphous metals. Thermal spray coatings of crystalline nickel-based alloy coatings have been deposited with thermal spray technology, but appear to have less corrosion resistance than comparable nickel-based amorphous metals [10].

A family of iron-based amorphous metals with very good corrosion resistance has been developed that can be applied as a protective thermal spray coating. One of the most promising formulations within this family was found to be $Fe_{49.7}Cr_{17.7}Mn_{1.9}Mo_{7.4}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ (SAM2X5), which included chromium (Cr), molybdenum (Mo), and tungsten (W) for enhanced corrosion resistance, and boron (B) to enable glass formation and neutron absorption [11-15]. The parent alloy for this series of amorphous alloys, which is known as SAM40 and represented by the formula $Fe_{52.3}Cr_{19}Mn_2Mo_{2.5}W_{1.7}B_{16}C_4Si_{2.5}$, has less molybdenum than SAM2X5 and was originally developed by Branagan [16-17]. In addition to SAM2X5, yttrium-containing SAM1651 ($Fe_{48}Mo_{14}Cr_{15}Y_2C_{15}B_6$) has also been explore

Possible Applications

SAM2X5 may have beneficial for applications such as the safe long-term storage of spent nuclear fuel. A standard container for the disposal of a 21-PWR fuel assembly in Yucca Mountain is shown in Figure 1.

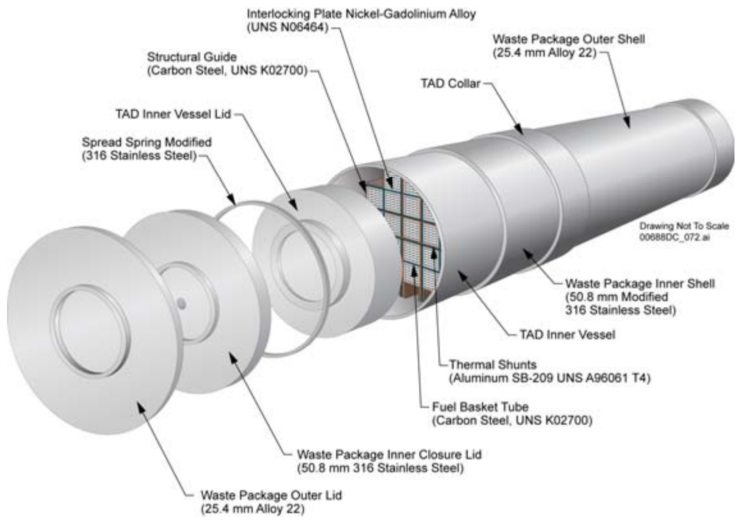

Figure 1 – Spent-Nuclear-Fuel (SNF) Container with Criticality-Control Structure (Basket Assembly) for 21-PWR Fuel Assembly.

These new iron-based amorphous metals have exceptional neutron absorption characteristics, and are stable at high dose. The absorption cross section in transmission for thermal neutrons for SAM2X5 coatings is three to four times (3 to 4×) greater than that of borated stainless steel, and twice (2×) as good as nickel-based Alloy C-4 with additions of Gd (Ni-Cr-Mo-Gd) [18-20]. The hardness values for Type 316L stainless steel, nickel-based Alloy C-22, and HVOF SAM2X5 are 150, 250 and 1100-1300 VHN, respectively. These materials are extremely hard and provide enhanced resistance to abrasion and gouges. In fact, successful tests have been conducted for applications as disk cutters for the tunnel boring machines. It may be possible to achieve substantial cost savings by substituting these new Fe-based materials for more expensive Ni-Cr-Mo and Ni-Cr-Mo-Gd alloys. Thermal spray coatings of Fe-based amorphous metals are predicted to cost ~ $7 per pound, whereas plates of Ni-Cr-Mo are expected to cost ≥ $37 per pound, based upon actual purchase costs of Alloy C-22 (UNS # N06022), without additions of gadolinium.

Thermal Spray Coatings

The coatings discussed here were made with the high-velocity oxy-fuel (HVOF) process, which involves a combustion flame, and is characterized by gas and particle velocities that are three to four times the speed of sound (mach 3 to 4). This process is ideal for depositing metal and cermet coatings, which have typical bond strengths of 5,000 to 10,000 pounds per square inch (5-10 ksi), porosities of less than one percent (< 1%) and extreme hardness. The cooling rate that can be achieved in a typical thermal spray process such as HVOF are on the order of ten thousand Kelvin per second (10^4 K/s), and is high enough to enable many alloy compositions to be deposited above their respective critical cooling rate, thereby maintaining the vitreous state. However, the range of amorphous metal compositions that can be processed with HVOF is more restricted than those that can be produced with melt spinning, due to the differences in achievable cooling rates. Both kerosene and hydrogen have been investigated as fuels in the HVOF process used to deposit SAM2X5 and SAM1651. Type 316L stainless-steel cylinders and plates were coated with SAM2X5, and served as half-scale models of containers and baskets for the storage of spent nuclear fuel. Figure 2 shows a prototypical half-scale half-length basket assembly, sized to fit inside a half-scale container. The photograph shown on the left was taken after fabrication by water-jet cutting, and the photograph on the right was takent after thermal-spray coating with SAM2X5.

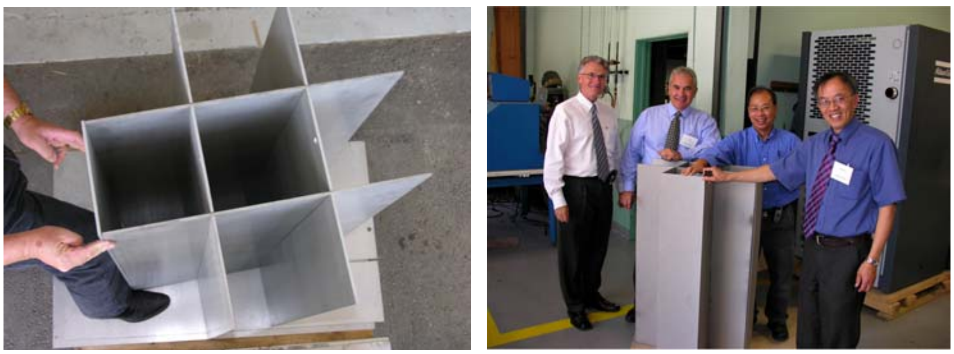

Figure 2 – Half-Scale Criticality-Control Modules (Basket Assemblies) Before and After SAM2X5 Coating.

Neutron Absorption

The high boron content of $Fe_{49.7}Cr_{17.7}Mn_{1.9}Mo_{7.4}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ (SAM2X5) makes it an effective neutron absorber, and suitable for criticality control applications. Average measured values of the neutron absorption cross section in transmission (Σ_t) for Type 316L stainless steel, Alloy C-22, borated stainless steel, a Ni-Cr-Mo-Gd alloy, and SAM2X5 have been determined to be approximately 1.1, 1.3, 2.3, 3.8 and 7.1 cm^{-1}, respectively [19-20]. Data are sown in Table 1 and Figure 3. This material and its parent alloy have been shown to maintain corrosion resistance up to the glass transition temperature, and to remain in the amorphous state after receiving relatively high neutron dose.

Materials used in criticality control applications must be relatively stable during irradiation with thermal neutrons. Melt-spun ribbon samples of various iron-based amorphous metals were subjected to high neutron dose in the 1.5 MW TRIGA reactor at McClellan Nuclear Radiation Center (MNRC) [20]. The neutron flux was 1.6×10^{10} n cm^{-2} sec^{-1}. Samples were irradiated for three different times: duration of 1st irradiation was 44 minutes; duration of 2nd irradiation was 132 minutes; and duration of 3rd irradiation was 263 minutes. The corresponding neutron doses were: 4.3×10^{13} n cm^{-2}, 1.3×10^{14} n cm^{-2} sec^{-1} and 2.6×10^{14} n cm^{-2}, respectively. These doses are equivalent to approximately 670, 2000 and 4000 years inside the waste packages designed for emplacement at Yucca Mountain. As shown in Figure 4, an exposure corresponding to a 4000-year service life does not cause any detectable, deleterious phase transformations.

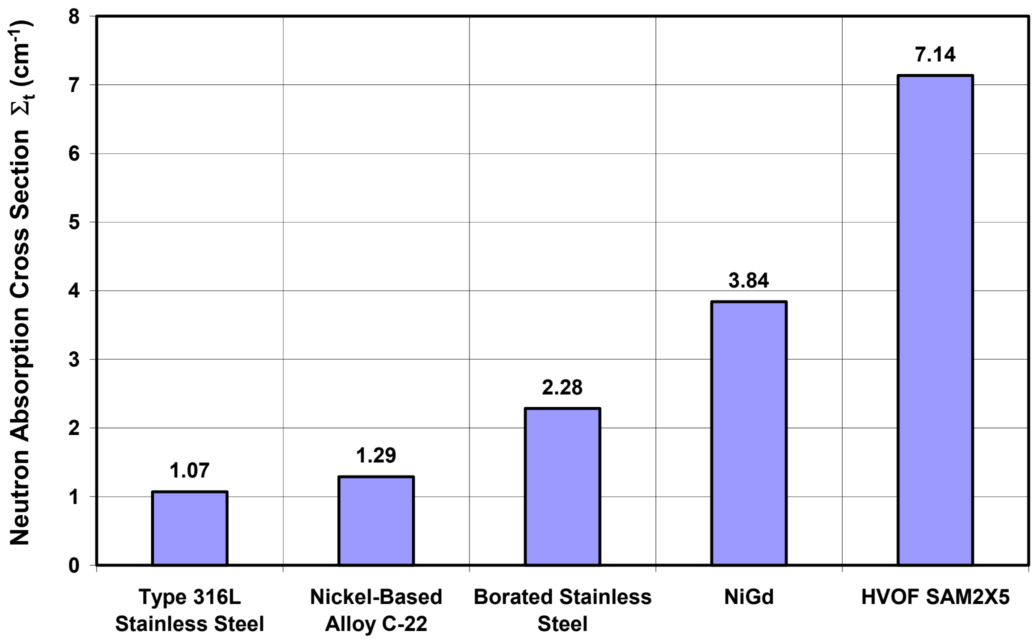

Figure 3 – Average measured values of the thermal-neutron absorption cross-section in transmission (Σ_t) for Type 316L stainless steel, Alloy C-22, borated stainless steel, a Ni-Cr-Mo-Gd alloy, and SAM2X5.

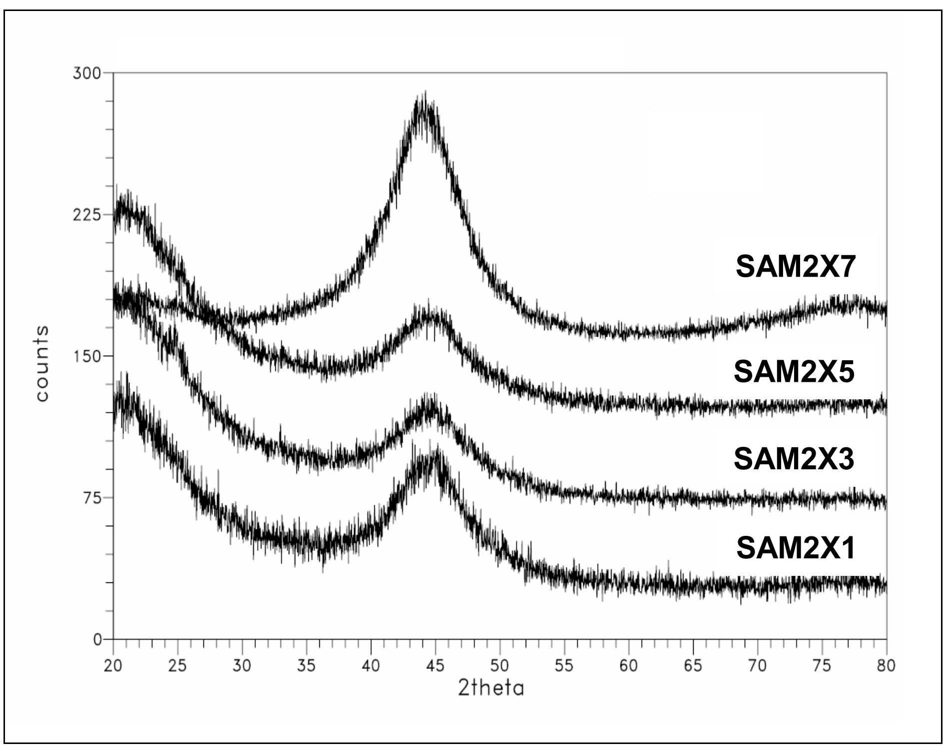

Figure 4 – XRD of High-Boron SAM2X-Series Alloys After 3rd Irradiation.

Conclusions

SAM2X5 may have beneficial for applications such as the safe long-term storage of spent nuclear fuel. These materials have exceptional neutron absorption characteristics, and are stable at high dose. The absorption cross section in transmission for thermal neutrons for SAM2X5 coatings is three to four times (3 to 4×) greater than that of borated stainless steel, and twice (2×) as good as nickel-based Alloy C-4 with additions of Gd (Ni-Cr-Mo-Gd). It may be possible to achieve substantial cost savings by substituting these new Fe-based materials for more expensive Ni-Cr-Mo and Ni-Cr-Mo-Gd alloys. Thermal spray coatings of Fe-based amorphous metals are predicted to cost ~ \$7 per pound, whereas plates of Ni-Cr-Mo are expected to cost ≥ \$37 per pound, based upon actual purchase costs of Alloy C-22, without additions of gadolinium.

Simulations and design calculations at LLNL show that k-effective can be lowered by at least ten percent (10 %) with the application of 1-millimeter thick coating of SAM2X5 to SNF support structure (basket) in a 21-PWR container. Even better performance is possible through the use of enriched boron for the synthesis of the Fe-based amorphous metal. The Fe-based amorphous metals have already been produced in multi-ton quantities and should cost less than \$10 per pound, while relatively few (three-or-four) 300-pound heats have been made of the Ni-Gd Material, which may cost nearly \$40 per pound.

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Acknowledgments

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