Interfacial Materials for Nuclear Component Reliability and Plant Life Extension Initiatives

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ABSTRACT

Interfacial materials technologies, (comprised of grain boundary engineering - GBE™ and nanocrystalline materials - Electrosleeve™, Nanoplate™), are rapidly finding application in enhancing nuclear component reliability, providing opportunities for nuclear plant life extension, and reducing the costs associated with routine plant maintenance and inspection. In this paper, an overview of the metallurgical concepts associated with grain boundary engineering and nanocrystalline metallic materials is presented. These advanced materials concepts are further discussed in the light of specific nuclear power plant applications and opportunities, including: (1) advanced GBE™ microstructural characterization and stochastic modeling techniques for improved maintenance, repair and replacement scheduling, (2) GBE™ mill/fabrication processing of replacement nuclear components for minimizing the risk of intergranular cracking and corrosion failures during operation (e.g., reactor head penetrations, steam generator tubes, baffle bolts etc.), (3) in-situ GBE™ processing for the potential repair and/or preventive maintenance of critical components (e.g., top of tubesheet steam generator tubing PWSCC, SCC of reactor head penetrations, etc.), (3) electrodeposition of high strength nanocrystalline materials for in-situ component repair (e.g., Electrosleeve™ repair of nuclear steam generator or heat exchanger tubes, Nanoplate™ valve repair etc.), and (4) eddy current and ultrasonic inspection probes with nanocrystalline coatings on polymer spacers and centering feet for enhancing probe life, minimizing probe replacement, and reducing the time and cost associated with inspection outages.

INTRODUCTION

The GBE™ technology focuses on the optimization of grain boundary structure by thermomechanical processing to obtain materials that are, for all practical purposes, immune or extremely resistant to intergranular degradation processes (stress corrosion cracking, intergranular attack, creep, etc). These materials are ideal for applications in thermal electricity generation (nuclear and fossil), oil refineries, oil drilling, and many process industries.

The Nanoplate™ technology involves the synthesis of nanocrystalline metals and alloys (grain size approximately 100 nm or less) using electrodeposition techniques. With this approach a fully dense material with highly improved properties (high strength combined with high ductility) can be obtained at very competitive prices since the electrosynthesis of nanostructures only requires small modifications of existing electroplating equipment and processes. Of the technologies presently available to produce nanostructured metals, electrodeposition is the only one that yields a fully dense structure. Other technologies usually involve agglomeration techniques that lead to high intrinsic porosity in the material and, consequently, poor mechanical properties.

This paper briefly describes the physical principles on which GBE™ and Nanoplate™ are based and several applications which are relevant to CANDU.

GRAIN BOUNDARY ENGINEERING - GBE™

Intergranular degradation processes, (e.g., corrosion, stress corrosion, cracking, creep cracking) are a frequent cause of premature and unpredictable service failure of nuclear components (e.g., nuclear steam generator tubing, reactor head penetrations etc.). As these processes occur exclusively at grain boundaries, and lead to component failure via propagation through the intercrystalline network, they are ultimately governed by (1) specific grain boundary structure, (2) grain boundary chemistry (i.e., solute segregation and precipitation), and (3) grain size and shape (i.e., connectivity).

Previous studies (see review [1]) have shown that grain boundaries crystallographically described by low ∑ Coincidence Site Lattice (CSL)[2] relationships (∑≤29) possess more ordered structures, are less prone to solute interaction, and can often selectively display a high resistance (and sometimes immunity) to corrosion, intergranular sliding, cavitation, and fracture.

Recent advances in automated crystallographic orientation determination techniques [e.g., 3] have now made it possible to readily evaluate the distributions of these 'special' low ∑ grain boundaries in conventional polycrystalline materials and allow for (1) the stochastic evaluation of the intrinsic reliability of components and structures, and (2) the optimization of materials processing techniques in order to enhance the overall population of low ∑ grain boundaries to effect intergranular-degradation resistant microstructures.

GBE™ RELIABILITY ASSESSMENT

Geometric models have been previously formulated [4] which quantify the effect of average grain size and 'special' grain boundary (i.e., ∑≤29) frequency on bulk intergranular cracking processes. Increasing the fraction of 'special' grain boundaries, and decreasing grain size, can considerably reduce the maximum attainable intergranular crack length in a material.

Figure 1 [5] shows how this model [4] can be utilized to evaluate the probability of further propagation of identified cracks (e.g., by eddy current inspection) in a component, and be potentially incorporated in 'fitness for service' evaluations. As shown in Figure 1, the probability of a crack propagating

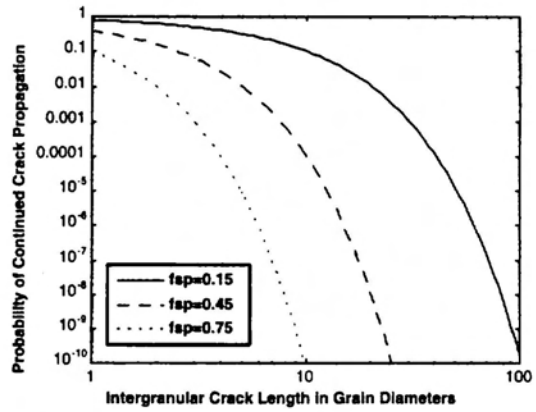

Fig. 1. Probability of continued intergranular crack propagation as a function of crack length and 'special' boundary frequency [5].

beyond 10 grain diameters is approximately 35% in a material having 15% special grain boundaries; the probability is reduced to approximately 1% in a material containing 45% 'special' grain boundaries, and to less than 0.001% in a material containing 75% 'special' grain boundaries.

Figure 2 shows the effect of reducing grain size on the probability of continued propagation of a preexisting intergranular crack of approx. 0.004 in. length.

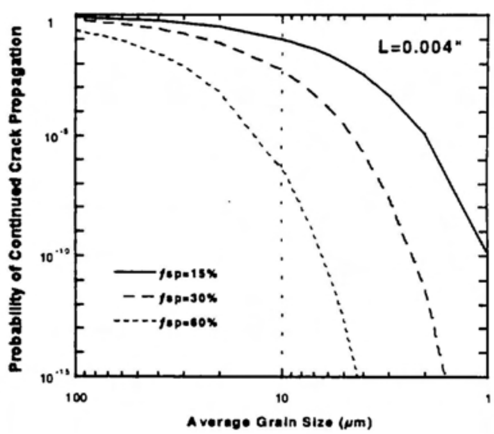

Fig. 2: Probability of continued intergranular crack propagation as a function of grain size and special grain boundary frequency.

Decreasing grain size significantly reduces the probability of continued propagation for all values of 'special' grain boundary frequency. By evaluating the prevalent microstructure (average grain size) and microtexture (special grain boundary content) in a component, either through the examination of archive materials or extracted sections combined with the evaluation of existing crack length distributions by NDE or forensic examination, the probability of further crack propagation, and the maximum extent of intergranular degradation can be predicted.

Figure 3 illustrates how this stochastic model [4] can be utilized to evaluate the overall reliability of an operating nuclear steam generator. As shown in this figure, increasing special grain boundary content significantly reduces the likelihood of steam generator tube dispositioning (and ultimate derating) as a result of tube degradation via intergranular cracking.

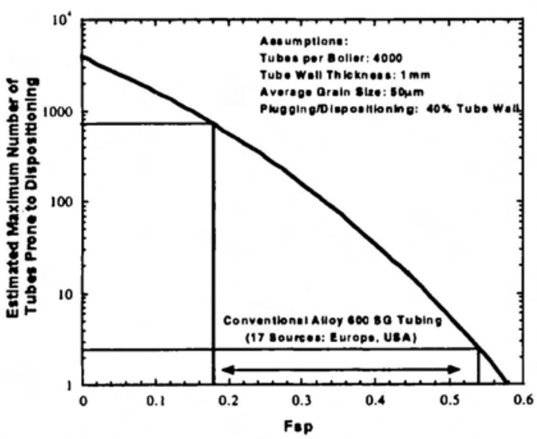

Figure 3. Effect of Special Grain Boundary Content on Nuclear Steam Generator Tubing Reliability

Also shown in this figure is the range of microstructures experimentally determined for Alloy 600 steam generator tubing investigated from 17 sources in the USA and Europe. A wide range of special grain boundary contents, from 18% to approximately 54%, has been identified.

These microstructures are representative of boilers in which hundreds of tubes would be considered susceptible, to installations in which only few tubes would be prone to dispositioning/plugging during the operating life of the plant.

It should be noted that, in general, only a small variability in microstructure is evident within a given boiler, as a result of the fact that tube manufacturing processes tend to be similar or identical for a given installation. An analysis of microstructure and microtexture can thus be invaluable to repair/replace decisions for aging installations.

GBE PROCESSING AND IN-SITU REPAIR

A proprietary thermomechanical processing methodology [6] for enhancing the frequency of special grain boundaries in austenitic chromium-bearing alloys has been developed. This treatment [6], which involves repetitive deformation - recrystallization steps and principally utilizes the formation of annealing twins to generate other low Σ CSL's in their wake [7], has been shown to increase the frequency of special grain boundaries from as low as 15% in conventional wrought Cr-bearing alloys to values usually in excess of 60%. It should be noted that commercial wrought stainless products, as a result of variations in metallurgical processing, usually display significant 'lot to lot', and 'heat to heat' variations in 'special' grain boundary content.

Figure 4 summarizes the increases in special grain boundary content achieved with several nuclear steam generator tubing materials through bulk 'grain boundary engineering' (GBE). Comparison values for 'conventional' wrought products shown in Fig. 4 represent the average special grain boundary populations encountered through random sampling of commercially available products. It is interesting to note that the average special grain boundary fractions encountered in the conventional alloys tend to fall in the order in which the nuclear industry generally ranks their overall resistance to SCC: Alloy 690 > Alloy800 > Alloy 600.

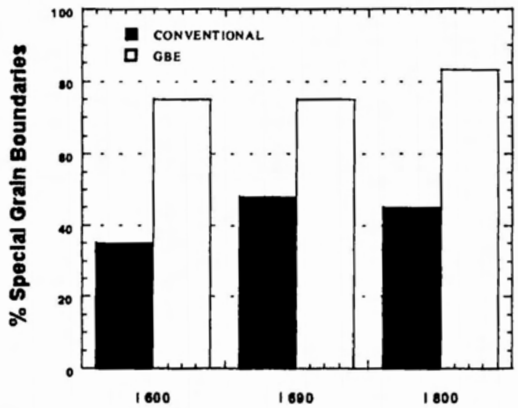

Fig. 4: Grain boundary character distributions for conventional and GBE-processed nuclear alloys.

More recently, a proprietary process has been developed [8] which allows for the application of GBE as a near-surface treatment (approx. 0.1 to 1mm depth) to finished and semi-finished components. This process (GBEST) can also be applied in-situ to installations where susceptibility to intergranular attack may be in a localized region (e.g., top of tubesheet SCC, reactor head penetrations etc.). Enhancements in special grain boundary content similar to that noted in Fig. 4 have been achieved with Alloy 600 using the GBEST treatment. This treatment is currently being evaluated SCC studies by Framatome (France).

NANOCRYSTALLINE MATERIALS

When the grain size of a crystalline material decreases, the intercrystalline component [9,10] starts playing an important and even dominant role in the properties of the material.

Some properties of nanocrystalline metals are associated with an increase in the frequency density of grain boundaries. An example of this is the Hall-Petch relationship between the mechanical strength of a material and its grain size.

Nanomaterials produced by electrodeposition have virtually zero porosity as has been determined, for example, by density measurements [11]. The properties of a fully dense electrodeposited nanomaterial are those that are truly attributable to the interfacial properties of the material with no interference from defects and voids deriving from agglomeration processes.

APPLICATION OF METALLIC NANOSTRUCTURES FOR COMPONENT REPAIR

Steam Generators and Heat Exchangers

Replacement of components in power plants can be a costly proposition in parts and downtime. In-situ repairs are often a desirable alternative that can bring about substantial savings. In nuclear plants, the degradation of steam generators has been one of the most important causes of downtime and is still one of the main reliability concerns. Although many nuclear operators have chosen replacement to address future reliability requirements, repair may be a viable alternative in cases in which the tube degradation is located in accessible regions in the tube bundle and only a limited number of tubes may be affected.

Electrosleeving is a nuclear steam generator tube repair that involves the in-situ electrodeposition of a nanostructured microalloyed sleeve on the tube inside diameter at the location of the damage.

Because of the properties of the nanostructured microalloy (high strength, acceptable ductility, and thermal stability) the repair is fully structural and long term. Compared to other repairs (laser welded sleeves, TIG welded sleeves, pressure fit sleeves), the obstruction in each tube repaired is minimal since there is a fully metallurgical bond along the full length of the Electrosleeves. Less thickness is required as a consequence of the high strength of the nanomaterial. A detail description of this repair is presented elsewhere in this conference[12].

Although the Electrosleeve^{TM} has been qualified for nuclear steam generators, it could be easily applied to other heat exchangers in the power industry. For example, the process could be easily adapted to pre-heaters in nuclear units that feature a separate vessel for this component or to other heat exchangers.

Electrosleeve™ is virtually immune to stress corrosion cracking in aqueous environments. Certain combination of acidic and oxidizing environments, not encountered in nuclear plants, may be detrimental to nickel. For these applications other nanostructured nickel based alloys can be electrosynthesized with enhanced corrosion resistance. These alloys can contain one of the elements tungsten, molybdenum, copper, and chromium, for example.

Wear Resistant Coating Repair

By controlling grain size, nanostructured nickel electrodeposits have been shown to possess high hardness (up to 650 VHN), yield strength and wear resistance. The latter property is accompanied with a reduction in the coefficient of friction, almost by a factor of two [13]. These properties make nanostructured nickel and many of its nanostructured alloys ideal materials for wear resistant coatings. Other electrodeposited materials, for example hard chromium and cadmium, have been used for this purpose but these electrodeposits are normally exceedingly brittle for some applications and they also represent serious environmental hazards. The properties of nanostructured cobalt for example offer an interesting alternative to hard chromium in applications in which improved strength and ductility are desirable. These properties are shown in Table 1.

Table 1. Mechanical properties of nano-cobalt and electrodeposited chromium.

Material	Ultimate Tensile Strength, (MPa)	Elongation, %
Wrought Poly Cobalt	900	23
Electrodeposited Nano Cobalt, 20 nm	1950	7.5
Electrodeposited Chromium	100-550	<0.1

The considerable ductility that high hardness nanostructured nickel alloys has, when combined with the properties listed above, makes this family of materials very attractive for wear resistant applications.

Table 2 shows several mechanical properties for polycrystalline conventional nickel, and nanostructured nickel with grain sizes of 100 nm and 10 nm, respectively.

Since Electrosleeve™ has proven that in-situ electrodeposition of nanostructures is a viable repair technology, a similar approach could be easily developed to repair wear resistant coatings of the type of hard facing alloys used in valve components.

This approach has the advantage that it would minimally affect the properties of the substrate material and would require minimal surface finishing.

Table 2. Mechanical properties of nickel with different grain sizes.

Property	Nickel		
	Poly	100nm	10nm
Yield strength, MPa (25°C)	103	690	>900
Yield strength, MPa (350°C)	N/A	620	N/A
Ultimate tensile strength, MPa (25°C)	403	1100	>2000
Ultimate tensile strength, MPa (350°C)	N/A	760	N/A
Tensile elongation, % (25°C)	50	>15	1
Elongation in bending, % (25°C)	N/A	>40	N/A
Modulus of Elasticity, GPa (25°C)	207	214	204
Vickers Hardness (HVN), kg/mm^2	140	300	650
Wear rate (dry air pin on disc) $\mu m^3/\mu m$	1330	N/A	7.9
Coefficient of friction (dry air pin on disc)	0.9	N/A	0.5

N/A – Not Available

APPLICATION OF NANOSTRUCTURED COATINGS IN CANDU NDE HARDWARE

Eddy current and ultrasonic tube inspection probes require sliders (feet) that allow proper centering of the probe inside the tube. The nuclear industry has usually employed feet with a petal design that achieve the centering objective. These feet are made of polymeric materials, normally Delrin of Nylon.

The experience of this design in CANDU steam generator tube inspection has been successful; however, the durability of the centering feet has been limited because of the presence of sharp crystals of magnetite on the internal diameter of the tubes. The roughness of this deposit wears out the soft polymeric material very rapidly. Also, the complex design of the feet makes it difficult to replace it with a metallic part. Coating the polymer with a thin layer of nanostructured nickel alloy offers an effective alternative for increasing the wear resistance of the component. The low coefficient of friction and wear rate of nanostructures makes them ideal for this application.

The approach that has been used involves a preliminary metallizing step, usually a thin coating of amorphous nickel/phosphorus, and a final electrodeposition of the nanostructured nickel alloy, its hardness being in the range of 600-650 VHN. The finished product should enhance feet durability and minimize probe replacement thus reducing time and cost associated with inspection outages.

CONCLUSIONS

Interfacial metals can be used to enhance CANDU component reliability, provide alternatives for unit life extension, and reduce maintenance costs.

The metallurgical concepts derived from interfacial properties and the advent of automated crystallographic orientation determination techniques have provided the basis for stochastic models that can be used to predict alloy performance in nuclear components, specifically in nuclear steam generator tubes.

Two material fabrication techniques GBE™ and GBEST have been developed that increase the resistance of the material to intergranular degradation processes either in the bulk of the material or in a 0.1 to 1 mm surface layer, respectively.

Nanostructured metals produced by electrodeposition, Nanoplate™, have found use in tube repair technologies such as Electrosleeve™, and are being considered for wear resistant coatings, environmentally friendly substitutes to Cr and Cd coatings, and improved hardfacing alloys of the type used in valve components. Other potential applications include those that require low coefficient of friction and wear resistant coatings such as in centering sliders for NDE inspection probes in CANDU systems.

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