GRAIN BOUNDARY ISSUES IN ENVIRONMENTALLY ASSISTED CRACKING

Michael B. McNeil
Materials Engineer
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

ABSTRACT:

In recent years a great deal of research has been done on grain boundaries, and studies have shown that geometrically different grain boundaries behave quite differently during environmentally assisted cracking. This paper will review some of these recent advances in relation to ways in which the results of grain boundary research can contribute to improved understanding of, and mitigation of, intergranular cracking of reactor components, and survey "grain boundary engineering", by which the resistance of some types of components to cracking can be markedly increased. The emphasis throughout is on face centered stainless steel and nickel alloys.

INTRODUCTION:

A major concern in many nuclear reactor components is environmentally assisted intergranular cracking, whether conventional stress corrosion cracking or irradiation-assisted stress corrosion cracking. Recent advances in the study of grain boundaries and of the effect of hostile environments and radiation on them is contributing to significant improvements in an understanding of intergranular cracking and to the development of mitigative approaches.

This paper will first describe the structure and basic energetics of grain boundaries, then review recent work on the effect of irradiation on the grain boundaries, and finally describe some recent applications to reactor component cracking. The focus throughout will be on face-centered cubic lattices, which are the most studied and include not only austenitic stainless steels but also most common high-nickel alloys. The same qualitative arguments apply to body-centered cubic and other lattices, however.

GRAIN BOUNDARY STRUCTURES:

A grain boundary has five macroscopic degrees of freedom describing the overall orientation change across the boundary. These can be described in two ways:

1. One can specify the normal of the boundary plane in the coordinate system of each of the two grains (this requires four independent parameters), and then specify the rotation angle between the lattices. This is the easiest specification to imagine:

one imagines cutting free surfaces on two grains and then sticking them together, using the fifth degree of freedom to specify a rotation of one lattice with respect to the other around a normal to the boundary plane (Figure 1).

2. One can use three degrees of freedom to specify the misorientation between the two lattices and then the remaining degrees of freedom to specify the normal to the boundary plane in the coordinate system of one of the lattices.

The second way of describing planes is the more commonly used, although it is less easy to visualize physically, because the misorientation across the boundary is the parameter which is most easy to measure. The relationships between these two descriptions, and their advantages and disadvantages in addressing different types of problems, are described in [1]

It is possible, using a technique called orientation imaging, to examine a sample using a scanning electron microscope with suitable detection equipment and data analysis software, and collect data on grain boundary misorientation for very large numbers of boundaries. These data are commonly expressed in terms of the coincidence site lattice (CSL) parameter Σ [2,3].

To see how Σ is defined, consider Figure 2. If one superimposes the lattices of the two crystals, imagining them to be extended across the grain boundary, one can define a new coincidence site lattice consisting of those points which are lattice points in both lattices (Figure 2). The ratio of the volume of the smallest unit cell of this CSL to the volume of the crystal unit cell is defined as Σ [4].

$\Sigma = 1$ means that the grain boundary is a low-angle misorientation between equivalent planes in the two crystals; for face-centered cubic lattices coherent twins have $\Sigma = 3$; other types of grain boundaries have $\Sigma = 5, 7, 9, 15, 25$, etc. for the face-centered cubic lattice. For other lattices, of course, other values of Σ are possible.

It was long ago observed that grain boundaries having low values of Σ (conventionally $\Sigma<29$) tend to have special properties in a number of ways: in particular, the tend to have lower energy, to be less susceptible to impurity and defect segregation, to have greater resistance to grain boundary sliding, and to have greater resistance to grain boundary degradation of all sorts (corrosion, cracking, cavitation, etc.) More recent studies have shown that the special boundaries in this sense are particularly those on planes with high atomic density, but statistically speaking low Σ planes tend to be special, high-Σ planes are rarely special, as shown from work on pure Ni in Figure 3 [5].

SPECIAL GRAIN BOUNDARIES:

All grain boundaries involve local distortions. If one regards the atoms as spheres, face-centered cubic is a closest-packing arrangement, and any grain boundary will involve some excess volume. One can think crudely of the grain boundary as a region of metal which has been expanded to less than normal density. Simple elasticity indicates that the extra energy would be roughly proportional to the volume of distorted metal and the degree of expansion. This is a gross oversimplification, but what is true is that the worse the fit across the grain boundary the less energy is required to split the component along the plane of the grain boundary and create new surfaces [6].

Environmentally assisted cracking often involves impurities acting on the grain boundary [7]. While there is often disagreement about what impurities act and how they act [8], it is clear that in predicting susceptibility to any cracking process which involves impurities (whether from the aqueous solution or the material), it is important to be able to assess the tendency of different grain boundaries to collect the impurities, and consider this in conjunction with the grain boundary distributions.

During irradiation, grain boundaries act as sinks for the point defects created. In addition the increased defect populations and fluxes associated with radiation damage lead to radiation induced segregation (RIS) at the grain boundaries; RIS in turn contributes to IGSCC.

SPECIAL GRAIN BOUNDARY EFFECTS OBSERVATIONS:

In most common engineering materials, it is not necessary to consider the populations of grain boundaries of various types, because the great majority of grain boundaries are nonspecial high-angle. Analysis of the characteristics of grain boundaries from the fracture standpoint became significant practically only in recent years when it became practical to produce materials with sizeable fractions of special grain boundaries.

As an intergranular crack propagates through a part, it tends to follow nonspecial grain boundaries, and observations have indicated that cracks rarely propagate along special grain boundaries [9,10].

It is possible to produce metal components with only special grain boundaries, but this is not practical for commercial alloys. What is practical (at least for some geometries) is to produce metal with varying fractions of special grain boundaries, and this has been done by a number of workers [11, 12]. Most components without special heat-treatment have special grain boundary fractions around 15%, but it is possible to produce materials with much higher fractions and they show greater resistance to cracking (figure 3). To understand how populations of special boundaries affect cracking, one must consider cracking as a percolation process [13, 14]. If the grain boundaries were completely randomly distributed, one could predict that at a certain fraction of special grain boundaries, a material would change from being quite vulnerable to cracking to being highly resistant.

The situation is much more complicated. For one thing, special grain boundaries are not randomly distributed. For another, coherent twin boundaries (an important subset of Σ=3 boundaries) tend to be internal to grains, and so must be discounted in the grain-boundary population counting (failure to consider this led to unfortunate consequences in an important study several years ago). However, the data does indicate that higher special boundary populations correlate with greater resistance to intergranular cracking.

Special boundaries also have special properties with regard to segregation of impurities and defects. In studying intergranular cracking of materials in nuclear applications, there are three types of such segregation which must be considered:

A. Equilibrium segregation. It has long been known that some types of impurities preferentially accumulate on or near grain boundaries under equilibrium [15,16].

B. Nonequilibrium thermal segregation. Industrial alloys, as placed into service, are rarely near equilibrium with regard to internal distribution of impurity atoms. Some segregation is inevitable during solidification, and subsequent heat treating does not normally eliminate it.

G. Radiation-induced segregation. Radiation damage in the lattice produces vacancies and self-interstitials. Some of these defects migrate to grain boundaries and annihilate there. This produces segregation by two different mechanisms. The inverse Kirkendall effect [17,18] arises from the fact that, as vacancies migrate to the grain boundaries, they preferentially remove more mobile atoms from the grain boundaries; this is responsible for the depletion of Cr from the grain boundaries in irradiated stainless steel. Point defects also bind to impurity atoms and drag them toward grain boundaries.

GRAIN BOUNDARY ENGINEERING:

The production of materials with controlled distribution of grain boundaries, generally with an increased proportion of special grain boundaries, has been the subject of extensive research in recent years. The term "grain boundary engineering" is commonly applied to this production technology.

Grain boundary engineered materials are produced by applying a series of working and annealing steps to the material in question. Much of the optimized technology is proprietary and at present, grain boundary engineering is primarily applied to relatively thin components. In principle, if fluidized or salt bath heat treatment facilities and appropriate working facilities were applied, it should be possible to grain-boundary engineer quite large components (e.g., 100cm thick plate). However, grain-boundary engineering of samples more significant than 1 cm thick is cutting-edge technology and is available in only a few places.

The components which would be hardest to produce in a grain-boundary engineered condition are those which are cold worked and then not heat-treated because the hardening effect of the cold work needs to be preserved (e.g., screws). Integran Technologies, a firm spun off by Ontario Hydro to facilitate development of grain boundary engineering applications in areas disjoint from the electricity generation, have developed a new technique which may permit the conversion of surface layers to a grain-boundary engineered condition without altering the bulk structure[19]. This may offer the prospect of extending grain boundary engineering to such applications as baffle bolts.

Grain boundary engineering has a number of practical applications. First of all, it can be used to make inherently brittle materials more ductile, in some cases greatly increasing the ductility by suppressing intergranular fracture in favor of transgranular fracture. This has been demonstrated in both Mo and Ni_3 Al [11], and might well be applied (e.g. to highly irradiated stainless steel). This application goes simply to the question of making a brittle material more ductile.

But there is another way in which grain boundary engineering can find application in nuclear power systems, and that is in producing components which are inherently less vulnerable to cracking. Boiling water reactor internals are subject to irradiation assisted stress corrosion cracking through the inverse Kirkendall effect, in effect radiation-induced sensitization. The essential cause of this is that vacancies created by irradiation migrate toward the grain boundaries instead of annihilating within the grains. A component where the grain boundaries were less efficient sinks for vacancies would be less affected. The nature of the form of irradiation-assisted stress corrosion cracking which affects pressurized water reactors is much less well understood, but it appears to involve defect accumulation at grain boundaries and there also GBE might have a mitigative role. Outside the core, cracking of steam generators appears to be associated with the accumulation of impurities on the grain boundaries [7,8,20]

CONCLUSIONS:

The use of components with controlled grain boundary characteristics offers promise for reducing environmental cracking problems, in water reactors. There are, however, several practical problems. The most important of these is that grain-boundary controlled materials are not yet easily available commercially even in thin sections, and are not available at all in thick sections. Solution of this problem will probably come gradually, as increasing understanding and acceptance of grain boundary engineered materials expands the general market.

A second significant issue is that there are as yet no generally accepted standards for characterization of grain boundary engineered materials; there are even different ways of specifying the fraction of special boundaries in a material. This is where standards bodies could contribute by taking a proactive stance and setting up subcommittees to address the problems of standardization and materials specification.

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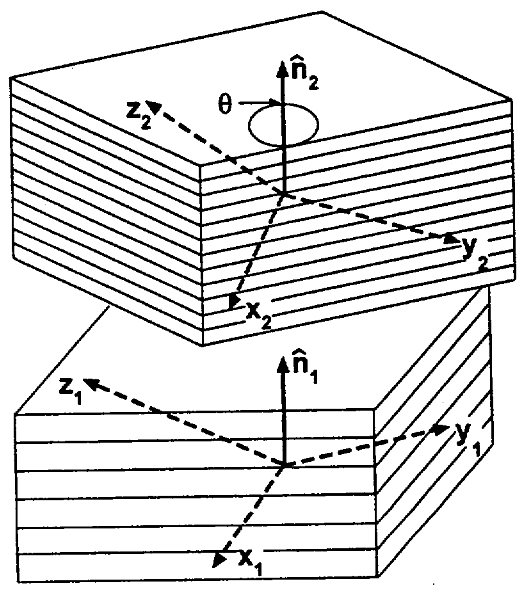
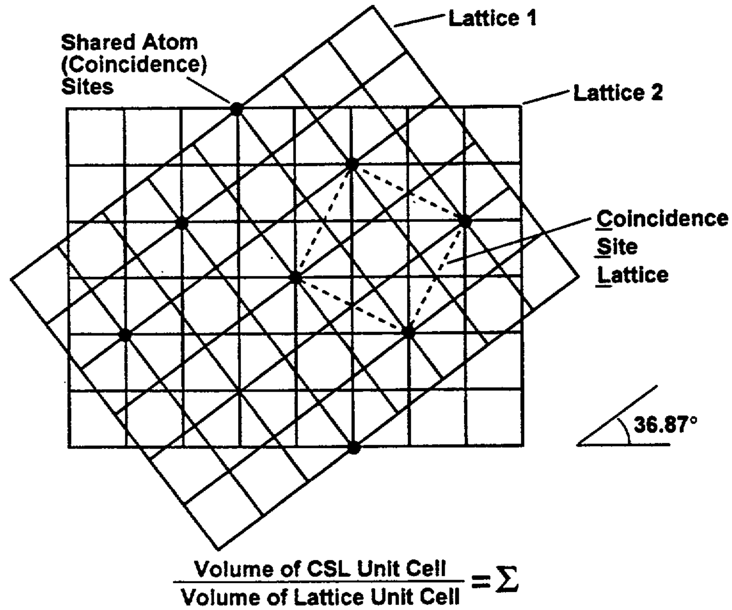


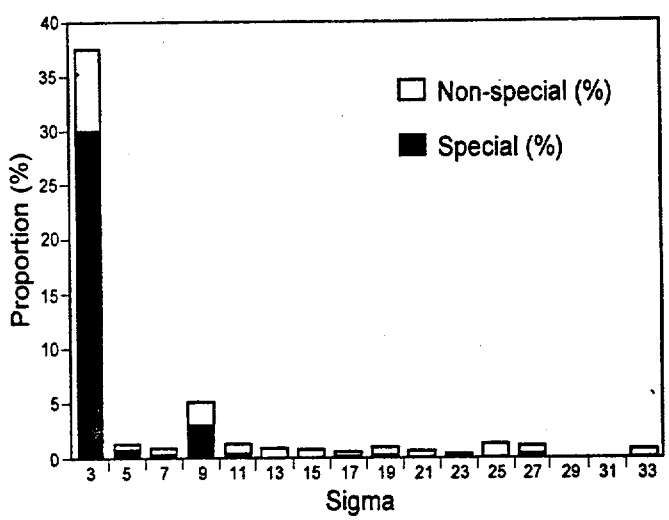
PARAMETERS OF A GRAIN BOUNDARY

Figure 1



SCHEMATIC REPRESENTATION OF THE COINCIDENCE SITE LATTICE GEOMETRY FOR A Σ5 INTERFACE FORMED BY A 36.87° [100] MISORIENTATION OF TWO ADJOINING LATTICES

Figure 2



PROPORTIONS OF 'SPECIAL' AND 'NON-SPECIAL' CSLs IN THE COMBINED DATA SET

Figure 3