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**INTERFACIAL PRECIPITATION, SEGREGATION
AND DEFORMATION IN ALLOY 600:
IMPLICATIONS ON PRIMARY-SIDE IGSCC**

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Interfacial Precipitation, Segregation and Deformation In Alloy 600: Implications on Primary-Side IGSCC

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A great many unknowns still exist concerning the mechanisms controlling intergranular stress corrosion cracking (IGSCC) of alloy 600 in high-temperature, deaerated water environments. Any proposed mechanism must involve the microstructure, microchemistry and mechanical properties of grain boundary regions. To facilitate basic understanding, specific aspects of alloy 600 metallurgy are reviewed and discussed in the following sections. Interfacial carbide precipitation, chromium depletion, impurity segregation and local deformation characteristics are examined and related to IGSCC behavior. The purpose of this paper is to provide information, and prompt discussion, on these various issues for the EPRI Alloy 600 Experts Meeting.

Carbide Precipitation

Chromium carbide precipitation occurs readily in alloy 600 because the carbon solubility is quite low even at very high temperatures, e.g., 0.03 wt% at 1000°C. This low solubility and the resulting high driving force for precipitation help explain the significant heat-to-heat variations in mill-annealed (MA) tubing microstructures and SCC resistance that have been observed. Carbide distributions can vary from predominately IG to predominately transgranular (TG) among heats within a given steam generator. These variations result from differences in bulk composition (C content) and thermomechanical history during processing and fabrication. The final processing temperature has a critical effect on the amount of carbon taken back into solution and the amount of carbide precipitation that occurs during cooling. A high-temperature anneal (>1000°C) tends to put more carbon into solution, produce a higher density of intergranular precipitates and is more resistant to SCC.

Mill-processing conditions also have an important effect on microstructures of thermally treated (TT) tubing. The ability to produce a favorable microstructure depends on the carbon remaining in solution and available to precipitate. A low-temperature final anneal and a slow-cooling rate may result in a high density of intragranular precipitates and an insufficient supply of carbon for subsequent intergranular precipitation. Thus, additional thermal treatments may not significantly modify material microstructure and cracking resistance.

Precipitates present in alloy 600 include M_7C_3 and $M_{23}C_6$ carbides as well as titanium nitrides and carbonitrides. The predominant precipitate forming during processing treatments and subsequent thermal treatment is the M_7C_3 (M>95% Cr) carbide. Grain boundary precipitates can be produced ranging from small (or large) discrete particles to a semi-continuous array of particles. Maximum improvement in SCC resistance is observed for alloys with a semi-continuous array of IG carbides. This indicates that SCC resistance is dependent on the distribution of IG carbide precipitates. However, the mechanism by which this occurs remains open to some debate.

Chromium Depletion

The precipitation of chromium-rich carbides at grain boundaries in alloy 600 also promotes the formation of a chromium-depleted region for certain time-temperature conditions. Because of the low carbon solubility and a fast chromium diffusion, this depletion occurs much more rapidly (i.e., at shorter times at

temperatures between 500 and 750°C and for faster cooling rates from higher temperatures) in Alloy 600 than in unstabilized austenitic stainless steels. A significant heat-to-heat variation in grain boundary chromium depletion is present in MA materials. Isolated carbide precipitates can produce localized regions of chromium depletion which is not continuous along boundaries.

The relatively high diffusivity of chromium in alloy 600 enables the chromium content to be replenished at interfaces during heat treatments at temperatures greater than 650°C. As a result, thermal treatment can produce a desensitized microstructure (i.e., semi-continuous carbide precipitation without chromium depletion). The exact time-temperature dependence of chromium depletion and desensitization will again be dependent on the material bulk composition and prior thermomechanical history.

Although chromium depletion can be present in MA tubing and may be increased during long exposures at steam generator operating temperatures, depletion is not a controlling factor in the SCC of alloy 600 in deaerated water or caustic environments. Chromium depletion does appear to accelerate cracking in oxygenated tests, but the opposite is more consistent with the data for deaerated water tests. Since it is difficult to produce significant chromium depletion without semi-continuous carbide precipitation, the effect of chromium depletion on SCC resistance has not been isolated. If chromium depletion is detrimental, its effect appears to be minor compared to the beneficial effect of intergranular carbides.

Grain Boundary Segregation

Impurity segregation promotes SCC in a number of alloy systems. Sulfur segregation induces IG corrosion and hydrogen embrittlement in nickel alloys, while phosphorus causes IG corrosion and SCC when tested in low-temperature acidic environments. Impurities such as sulfur have also been suggested to be important in the alloy 600 cracking mechanism. However, there is no direct evidence that impurity segregation promotes IG attack or SCC in high-temperature water.

Phosphorus is the primary segregant to grain boundaries in alloy 600. This segregation results from an equilibrium process and could be modeled using surface adsorption analogues. Grain boundary phosphorus segregation increases sharply with decreasing temperature until the solubility limit is exceeded (i.e., at about 700°C for a 100 ppm heat). Below this temperature the amount of phosphorus available to segregate decreases with decreasing temperature, and segregation increases at a much slower rate. Phosphorus levels at grain boundaries in MA commercial alloy 600 are typically on the order of several atomic percent and increase to ~10 at% after several hours at 700°C. There is no indication that these levels of phosphorus segregation promote IGSCC in high-temperature water. However, phosphorus-induced IG cracking is observed at lower temperatures in alloy X750 when hydrogen is available. Very little information is available concerning the influence of phosphorus segregation without the presence of GB chromium carbides.

Several other impurities identified at the grain boundaries of alloy 600 include boron, sulfur, nitrogen and titanium. Grain boundary segregation of boron and sulfur has been observed, even when bulk contents are only several parts per million. Boron may be particularly important since it is often observed at grain boundaries of MA specimens. Contrary to the effects of sulfur or phosphorus, boron segregation has not been shown to induce IG corrosion or SCC. Boron additions appear to improve the resistance of nickel to hydrogen embrittlement and has been noted to improve IGSCC resistance of alloy X750. Low levels of boron retard chromium carbide precipitation, while higher levels accelerate precipitation in stainless steels. Boron's effect on SCC may be related to its influence on IG chromium carbide formation kinetics.

Sulfur has not been shown to consistently segregate to grain boundaries in alloy 600 due to the presence of sulfide formers such as magnesium, calcium and titanium. Significant segregation has only been documented in samples after extremely high-temperature anneals (>1300°C) where sulfur is released from

preexisting inclusions and is able to segregate to grain boundaries. Although sulfur has been proposed to play a role in primary-side IGSCC, it is unlikely based on the limited segregation that occurs in alloy 600 tubing under normal processing and fabrication conditions. However, sulfur strongly segregates in nickel alloys (when available in solution) and is a potent embrittling element at low- and high-temperatures. It is interesting to note that sulfur does not thermally segregate in low-alloy steels, but does enrich boundaries under creep conditions promoting IG embrittlement.

One alloying element not normally discussed as a segregant in alloy 600 is carbon. Its behavior in certain alloys is believed to similar to boron and nitrogen, i.e., increase IG cohesive energy and improve resistance to hydrogen embrittlement. Unfortunately, very little direct evidence is available for alloy 600. Carbon is known to strongly segregate in commercial-purity nickel leading to graphite precipitation at grain boundaries. It also segregates to boundaries in alloy 600 for nucleation and growth of chromium-carbide precipitates. In the solution-annealed (SA) and MA conditions, it is certain that some degree of interfacial carbon enrichment is present. However, inherent difficulties in grain boundary fracture and carbon composition analysis (contamination) have restricted accurate assessment. Significant segregation of elemental carbon may also be limited by competitive phosphorus segregation. Interstitials such as carbon, boron and nitrogen may be the only elements (besides hydrogen) with reasonable mobility at ~300°C and may interact with the dynamic effects occurring at GBs at this temperature.

Interfacial Microdeformation

The observation that a semi-continuous distribution of IG carbide precipitates improves SCC resistance suggests that the carbides may be affecting grain boundary mechanical behavior. Interfacial deformation and cracking is directly influenced by the presence of carbides. A semi-continuous distribution of carbides can promote IG fracture at low temperatures and IG creep cavities at elevated temperatures. However, direct studies of interfacial deformation processes have been limited. The following discussion summarizes the transmission electron microscopy (TEM) observations of Bruemmer, Charlot and Henager on MA, SA and TT alloy 600 deformed at 300°C. This work examined grain boundary dislocation activity as a function of plastic strain for various interfacial and matrix microstructures.

Microstructural Effects on Dislocation Activity

Initial dislocation activity in the alloy 600 matrix is confined to planar arrays along (111) slip planes. Sites present at grain boundaries that block the ability of grain boundary dislocations to glide within the boundary plane result in a pile up at the site and a stress concentration. To relieve these local stresses, such sites emit dislocations into the grain. Carbides and ledges both act in this manner. Grain boundary ledges are apparently more effective sources than triple points at low strains. Few dislocation emissions could be traced back to triple-point regions, even after a high density of other sources were activated. Microstructural features identified as sources of dislocation activity in alloy 600 include grain boundary ledges, grain boundary precipitates and matrix precipitates.

Mill-processing procedures have a significant effect on tubing microstructure and on microdeformation characteristics. The comparison of microdeformation behavior in a SCC-susceptible material (LMA) and a SCC-resistant material (HMA) illustrated these effects. Low-mill-anneal temperatures for LMA tubing produced a microstructure with few IG, but many TG, carbides. This material required a large plastic strain before general dislocation activity in the matrix was realized. Dislocation emission from grain boundary ledges produced short planar arrays into the matrix, encountered more matrix obstacles, and developed a high local dislocation density at grain boundaries. High-mill-anneal temperatures (HMA material) produced a microstructure with many IG, and few TG, carbides. Much smaller strains were required to promote dislocation activity. Boundary carbides emitted much longer planar arrays and did not develop a preferential dislocation structure at grain boundaries.

Planar dislocation activity is typical in moderate-to-low stacking fault energy materials since dislocation cross slip is difficult. Retention of dislocations in arrays (resulting from lack of cross slip) causes large back stresses on the dislocation source. The back stress is proportional to the number of dislocations in the array divided by the length of the pile up. During deformation a given source may operate and shut off many times as the dislocation microstructure evolves. A wide spectrum of dislocation sources is activated as deformation proceeds and the material work hardens.

The ease of source operation depends on the nature of the boundary and the discontinuity. The effectiveness of a discontinuity as an emission site is influenced by its orientation and access to matrix slip planes. For example, in a face-centered cubic (FCC) material source activity into the grain will be favored if the dislocation line within the boundary has direct access to one of the matrix (111) planes. (It is interesting to note that grain boundary carbide growth in alloy 600 is along (111) planes and $\langle 110 \rangle$ directions.)

Second-phase particles are a good source of dislocations because of the presence of an elastic discontinuity at the particle-matrix interface. This leads to dislocation loop punching at incoherent interfaces. Misfit dislocations (along coherent interfaces) are additional sources of dislocations, either by being directly incorporated into the lattice or by acting as renewable sources. Little distinction has been made between coherent and incoherent particles as dislocation sources, and the importance of the interface orientation relationship with the matrix is unknown.

In summary, grain boundary precipitates are effective sources because they block dislocation movement within the boundary during sliding, produce a large local stress concentration, and may have better access to matrix slip planes for easy emission into the lattice. This allows grain boundary precipitates to emit dislocations at lower macrostresses and strains and also to continue to operate against higher back stresses than other sources. The influence of carbides to restrict boundary sliding may play a dominant role on SCC behavior and will be discussed in a following section.

Microdeformation Effects on Crack-Tip Stress State and Fracture

Mechanisms by which a normally ductile material fails in a brittle manner have been studied and attempts made to explain this brittle behavior using dislocation models of deformation. Rice and Thomson proposed such an explanation by developing an energy balance argument for dislocation emission from cracks (blunting) vs crack propagation by interface decohesion (cleavage). Based on the Rice-Thomson analysis, the tendency for ductile behavior restricting brittle crack advance increases with the ease of dislocation emission at the crack tip. If the stress required for dislocation emission is greater than that for interfacial cleavage, crack advance will occur.

Dislocation sources operating at or near crack tips can therefore influence crack propagation. With IG fracture, grain boundary dislocation sources may determine whether the crack propagates by cleavage or by ductile rupture. The ability to produce an IG crack in a cleavage-like manner requires that a sharp crack tip be maintained. Dislocation sources operating near the crack tip on grain boundaries provide a means for crack blunting, thereby promoting ductile rather than brittle behavior. This concept is discussed in detail in EPRI NP-5192 and an attempt was made to quantify microstructural effects on the crack tip stress state, independent effects of dislocation sources, and the overall tendency for brittle vs ductile behavior.

Current microdeformation results can be used to indicate potential effects of alloy 600 grain boundary and matrix microstructure on the crack-tip stress state. Susceptible to resistant microstructure (in order of decreasing crack tip stress state) are: (1) transgranular (TG), no IG carbides; (2) no IG or TG carbides; (3) IG and TG carbides; and (4) IG, no TG carbides. IG carbides promote easy source activity, while TG carbides (and other pinning sites) restrict source activity. Consequently, microdeformation becomes more localized at grain boundaries as microstructure reverse from (4) back to (1).

Stress Corrosion Cracking Resistance

Any model proposed to explain the mechanism(s) of primary-side IGSCC in alloy 600 steam generator tubing must be consistent with the following observations:

1. MA tubing is more susceptible to cracking than SA, furnace-sensitized (FS), and TT tubing.
2. IGSCC susceptibility decreases with increasing grain boundary carbide precipitation.
3. Presence of matrix precipitates is apparently detrimental.
4. Significant chromium depletion or impurity segregation at grain boundaries is not essential for IGSCC.

These observations are consistent with the microdeformation behavior and susceptible to resistance microstructure summarized above. Materials with TG, but no IG carbides tend to be the most susceptible to IGSCC and those with IG, but no TG, carbides the most resistant. The variability in SCC resistance of MA material results from the fact that, depending on processing treatment and tubing chemistry, MA microstructures have been observed resembling all of the above. This also points out that a HMA treatment, which precipitates most carbides along grain boundaries, may be superior to a HMA + TT or SA + TT treatment, which gives both IG and TG precipitates.

Until now, the tendency for brittle fracture has been discussed without considering the environmental component in the SCC process. This environment component is required for IG cracking to occur. Slip dissolution and hydrogen embrittlement models of SCC depend on similar rate-controlling parameters. Microdeformation characteristics directly influence the IG crack tip stress distribution and thereby the crack tip strain rate, oxide rupture rate, crack tip dissolution or hydrogen adsorption and, as a result, SCC. Thus, the previous discussion of microstructure/microdeformation effects on the crack-tip stress state are pertinent to environmentally assisted cracking.

Hydrogen effects on brittle behavior can be described by the relationships among dislocation nucleation, crack shape, and interfacial decohesion. The balance between interfacial cohesive energy and the energy to nucleate dislocations can still control cracking susceptibility. Hydrogen can have a significant effect on both of these energies and promote intergranular crack advance. If hydrogen is involved in the SCC process, it must have a different effect at elevated temperatures than has been seen at lower temperatures. The tendency for IG fracture at room temperature (or below) in hydrogen environments is inconsistent with a microstructural effect on primary-side SCC.

Dissolution-controlled SCC often results from the presence of an electrochemically active region which causes localized dissolution. This localized dissolution can sharpen the crack tip to enable mechanical advance or prompt cracking by rapid corrosion of the more active region. A common example of localized corrosion and SCC is for sensitized austenitic stainless alloys (and alloy 600) in oxidizing environments. Crack growth can be ascribed mostly to a dissolution process.

This is not true for primary-side SCC of alloy 600 tubing. However, localized dissolution to sharpen the crack tip may occur. The grain boundary region may be more electrochemically active than the matrix because of structural or microchemical differences. Present results show increased local microdeformation at grain boundary regions in IGSCC-susceptible tubing (LMA) than resistant tubing (HMA). These regions, with higher dislocation densities, may promote sufficient attack to sharpen the crack. The corrosion process at the tip may also produce local hydrogen available to assist crack propagation.

Both hydrogen ingress and metal dissolution events may possibly help create conditions for brittle crack

advance. Hydrogen may locally lower the cohesive strength and destabilize the passive film, while dissolution at the tip sharpens the crack and increases Mode I crack opening stress. Consequently, even though the crack opening stress is typically much less than the theoretical cleavage stress for a ductile material like alloy 600, both can attain similar values because of specific microstructural, microchemical, environmental, and crack lip conditions. Some method of reducing the IG cleavage stress does appear necessary to promote cracking. This suggests that hydrogen and/or grain boundary chemistry have roles in the SCC mechanism.

Creep Deformation, Grain Boundary Sliding and IGSCC

Recent research has indicated that creep deformation plays a role in the susceptibility of alloy 600 to IGSCC. Bulk creep rate differences appear to explain the increased cracking resistance of high-chromium alloy 690. Work at the University of Michigan has demonstrated that increasing the bulk chromium content in a high-purity Ni-Cr-Fe alloy sharply decreases the creep rate and IGSCC. The high-temperature water environment has been shown at the Electricite de France to accelerate the creep rate over that in air. This suggests that hydrogen in the metal may be enhancing bulk dislocation activity or the water environment degrades any benefit of the surface film on resisting creep deformation. If creep plays an important role in the IGSCC, it is likely that grain boundary sliding (GBS) is an essential part of the cracking mechanism. Grain boundary sliding is discussed below in relation to the microstructure and microchemistry of alloy 600.

Grain boundary sliding does not typically become a significant deformation mode at temperatures above ~ 0.4 of the melting temperature. Interestingly, this is approximately the temperature ($\sim 360^\circ\text{C}$) where IGSCC is reproduced in the laboratory and where sliding has been observed in MA alloy 600 tubing. It is well founded that sliding contributes to the overall strain during dislocation creep and is necessary for diffusion creep. Sliding occurs by the movement of extrinsic grain boundary dislocations (GBDs) along the boundary plane and can explain many aspects of GBS including:

- A threshold stress is often observed for GBS analogous to matrix slip since a friction stress has to be overcome. IG precipitates (carbides) will provide effective barriers to GBD movement and increase the observed threshold stress.
- Grain boundary hardening results during dislocation creep primarily due to the pile-up of lattice dislocations. Steps in the boundary are created by impingement of matrix dislocations and impede interfacial dislocation movement.
- A relationship commonly exists between matrix strain and GBS strain, since boundary sources are critical in the bulk deformation process.
- Grain boundary migration often accompanies GBS because interfacial dislocations (depending on the local Burgers vectors and boundary plane) can produce both events simultaneously.
- The activation energy for GBS is typically between the extremes for GB and matrix diffusion resulting from the mechanisms controlling the rate of sliding, i.e., interfacial diffusion required for the climb of boundary dislocations or matrix diffusion required for accommodation processes in the adjacent grains.

Diffusional mass transport along grain boundaries controls many metallurgical processes under certain stress-temperature conditions including diffusional creep. Fast diffusion in the boundary plane appears to occur by a vacancy mechanism with atoms jumping between various sites in the boundary core. The strong influence of structure and solute segregation on interfacial diffusivity may be partially explained by differences in the core sites. Specific impurity segregants such as boron in iron and sulfur in copper have been shown to have very large effects on grain boundary diffusivity. It is possible to increase or decrease interfacial diffusivity by modifying the boundary composition. Very little is known concerning segregant (i.e., carbon, nitrogen, boron and phosphorus) effects on interfacial diffusivity or GBS in alloy 600. Local hydrogen effects must also be considered. Hydrogen-enhanced plasticity definitely occurs and may play

a dominant role in promoting GBS through its effect on the climb of GBDs and on local matrix accommodation processes. Second-phase particles obstruct GBD migration and restrict GBS until higher local stresses are produced or tests are performed at higher temperatures.

Creep cavities can nucleate at stress concentrations which arise at inhomogeneities in sliding grain boundaries and can be assisted by a vacancy condensation (diffusional) mechanism. Solute segregation effects noted above can control the nucleation and growth of grain boundary cavities in several ways. Segregants which decrease cohesion at the grain-to-grain or particle-matrix interface will reduce the stress required for wedge cracks or cavities to form. In addition, segregation at the newly formed cavity may reduce its surface energy, and thereby reduce the critical size for a stable cavity. Cavity nucleation will also be determined by grain boundary sliding which again is dependent on local composition. The largest influence on cavity growth will stem from segregation effects on diffusional mass transport along grain boundaries and on newly formed surfaces.

The resistance of a material to creep embrittlement depends on the mechanisms of interfacial deformation, cavity nucleation and cavity growth. Grain boundary chemistry resulting from segregation events before or during deformation must be considered. The enrichment of certain impurity elements has been shown to increase the susceptibility to creep and stress-relief embrittlement. Solute segregation can modify grain, and particle-matrix, interface cohesive energies, influence cavity surface energies and control the resultant mechanical properties. However, direct investigations linking solute segregation to cavity nucleation and growth have been limited, and no research has addressed the complexities of the particle-matrix interface nor the interfacial deformation processes leading to cavity nucleation.

The general concepts discussed above for GBS do not answer the specific questions concerning IGSCC of alloy 600 in high-temperature water. Based on the information at hand, it appears that a material's resistance to GBS scales consistently with its resistance to IGSCC. Similar to the discussion in the microdeformation section, the influence of the environment remains unknown. Hydrogen could reduce the threshold stress for GBD movement and enable sliding to occur at lower temperatures. Crack propagation could result from small cavity formation immediately ahead of the crack tip at boundary inhomogeneities such as slip step. If this is the case, segregants may play an important role in the formation of stable cavities. Mobile elements within the boundary may enrich and stabilize the newly created surface produced during sliding. High-resolution scanning electron microscopy combined with interfacial microchemical analysis (e.g., by scanning Auger) of samples with existing IGSCC cracks is required to determine if small interfacial voids are formed and if a particular segregant is involved in the process. It is possible that preferential GB dissolution of chromium ahead of the crack tip assists in crack advance. High-resolution microchemical analysis of GB regions will also clarify whether this does occur.

Summary

Specific grain boundary microstructural, microchemical and mechanical issues related to the IGSCC of alloy 600 in high-temperature water have been discussed. Interfacial carbide precipitation, chromium depletion, impurity segregation and local deformation characteristics are examined and related to IGSCC behavior. Grain boundary carbide precipitation has a dominant effect improving IGSCC resistance, while chromium depletion and impurity segregation have secondary effects at most. The key to cracking susceptibility remains focussed on the local microdeformation behavior at grain boundaries with recent results indicating an important effect of matrix and interfacial creep processes. Hydrogen appears to be a necessary component for crack propagation either by an interfacial decohesion or by an enhanced plasticity mechanism. Detailed experimentation and modeling is needed to elucidate the complex interactions among grain boundary deformation, solute segregation, hydrogen and IG crack propagation.

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