Transactions of the Korean Nuclear Society Autumn Meeting
Jeju, Korea, October 21-22, 2010

Role of Grain Boundary Carbides in PWSCC Behavior of Ni Base Alloys

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1. Introduction

Primary water stress corrosion cracking(PWSCC) of alloy 600 in a PWR has been reported in the control rod drive mechanism (CRDM)[1], In original PWRs, the SCC was not considered appropriately. Beginning in the mid seventies the world's PWR plants suffered from a sequence of SCC events mostly confined to S/G tubes, initially ODSCC then PWSCC. In forged alloy 600 materials, PWSCC was first reported in the Bugey 3 vessel head penetration in September 1991. All reactor vessel heads(RVH) with alloy 600 penetrations (54 VH out of 58) were replaced in France. Other PWRs experienced cracking attributed to PWSCC of major primary side welds made from Alloy 182 at the end of the year 2000. The three events concerned dissimilar metal butt welds between the main austenitic stainless steel primary circuit piping and the outlet pressure vessel nozzles of Ringhals 4 and V. C. Summer and some J-groove welds of the CRDM of the RVH at Oconee 1. [2]

In addition to the RVH, PWSCC of Alloy 182/82 has been reported at Bottom Mounted Instrumentation (BMI) nozzle J-welds, Steam Generator (SG) drain J-welds drain nozzle and SG tube sheet cladding [3]. As of the year 2006, 344 PWSCC incidents of Alloy 600/82/182 were reported in RVH, SG, Pressurizer, and other primary side pipings.

The objective of the present work is to study a role of grain boundary carbides in PWSCC behavior of Ni Base alloys.

2. Carbide Precipitation

2.1 Carbide Precipitation in Stainless Steels and Ni alloys

Sensitization is the precipitation of chromium carbides along the grain boundaries of stainless steel. This precipitation depletes the Cr content near the grain boundaries in solution, thereby diminishing its corrosion resistance. In austenitic stainless it occurs at a maximum rate around 815 °C (1500 ^{o}F)and more slowly down to 482 °C (900^{o}F). Consequently the material shows Cr depleted region as shown in Fig. 1. The sensitization rate is a complex function of a number of factors. In austenitic stainless steels, it is avoided by keeping carbon below 0.03% (Type 304L, 316L). Austenitics can be quenched from above 871 °C (1600^{o}F), which prevents the precipitation, but ferritics

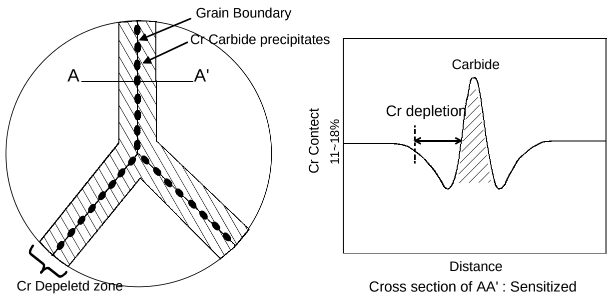

Fig. 1 Schematic of Cr depletion in sensitized 304 stainless steel

cannot be quenched rapidly enough.

In the mid 1970's, serious intergranular stress corrosion cracking problems appeared in the heat-affected zones of type 304 stainless steel welded piping used in boiling water reactors. One of the main causes of these failures was the presence of chromium carbide precipitates with chromium depleted zones at grain boundaries of austenitic stainless steel, i.e., sensitization.

Ni alloys also show Cr depletion near grain boundaries when they are slowly cooled to room temperature or exposed to certain temperature depending on carbon content of the materials as shown in Fig. 2.

These sensitized Ni alloys exhibit high intergranular corrosion rate in acidic oxidized solution (for example, sodium tetrathionate $Na_2S_4O_6$ solution).

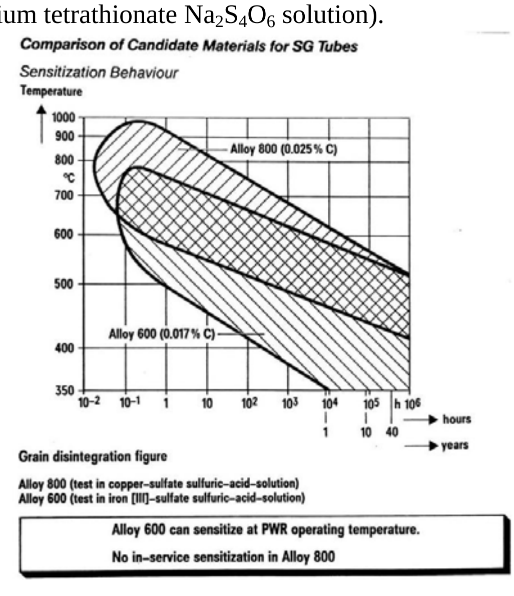

Fig. 2 Carbide precipitation in Ni alloys (TTT curve) [1]

2.2 Mechanism of intergranular or intragranular carbides in Ni alloys[2]

The main fabrication variables which control carbide morphology in Alloy 600 material are the final forming and annealing conditions. Those significant factors affect material PWSCC susceptibility.

Chromium carbides exist within grains and at grain boundaries prior to final forming and annealing as a result of previous forming and heat treating operations. Material is cold worked during final forming operations. Recrystallization during the final annealing treatment results in new grain boundaries being formed upon cooling. Solubility of the carbides during annealing is a strong function of the annealing temperature. At a low annealing temperature, carbides do not go fully into solution such that large amounts of carbides remain within the new grains after cooling and there are few grain boundary carbides.

Fig. 3 shows a final feature of carbides with different heat treatment history. Material with high enough final anneal has intergranular carbides during cooling, whereas low temperature final annealed material shows intragranular carbides.

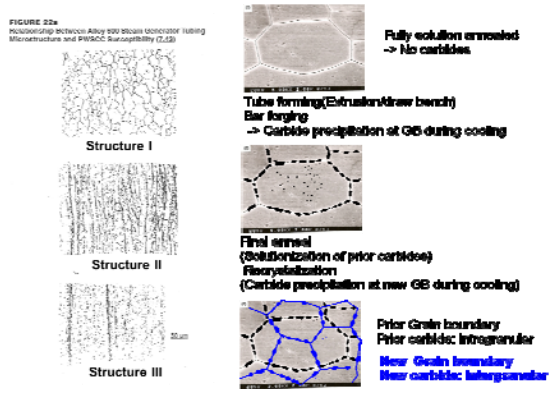

Fig. 3 Carbide Precipitation in Ni alloys

At a high annealing temperature, carbides go into solution more completely, the grains grow in size which reduces the grain boundary surface area, and carbides precipitate at the new grain boundaries upon cooling. Therefore, a high annealing temperature results in large grains, copious grain boundary (intergranular) carbides and few intragranular carbides.

2.3 Beneficial effect of intergranular carbides on PWSCC resistance

The occurrence of PWSCC of Alloy 600 strongly depends on the absence of intergranular carbides. High mill-annealing at temperatures (1065°C) during final heat treatment or thermal treatment at 705°C for 15 hrs produces intergranular carbides, which make Alloy 600 tubes resistant to PWSCC. In contrast, low mill-annealing temperatures produce intragranular carbides, which make tubes susceptible to PWSCC.

The most widely accepted hypothesis model has been proposed by Bruemmer. Bruemmer proposes that grain boundary carbides promote crack blunting due to their effectiveness as dislocation sources. The greater the number of carbides at the grain boundaries, the more dislocation sources there will be to blunt the crack.

Fig. 4 shows a comparison of different microstructures which have different carbon content or different thermal history.

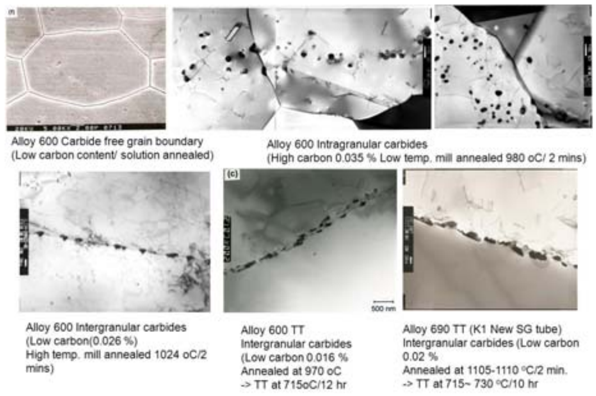

Fig. 4 Different Carbide Precipitation in Ni alloys depending on carbon contents or thermal history

3. Conclusions

A role of grain boundary carbides in PWSCC behavior of Ni Base alloys was reviewed.

- Sensitized Ni alloys exhibit high intergranular corrosion rate in acidic oxidized solution
- The main fabrication variables which control carbide morphology in Alloy 600 material are the final forming and annealing conditions and those significant factors affect material PWSCC susceptibility.
- High temperature (1065 C)mill annealed materials or thermally treated at 705C for 15 hrs produces intergranular carbides, which make Alloy 600 tubes resistant to PWSCC.
- Grain boundary carbides promote crack blunting due to their effectiveness as dislocation sources. The greater the number of carbides at the grain boundaries, the more dislocation sources there will be to blunt the crack.

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