## Stress Corrosion Cracking Growth Rate of Cold Rolled Thermally Treated Alloy 690 and Solution Annealed Alloy 690 and their Mechanisms in Simulated PWR Primary Water

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#### Abstract

The Stress Corrosion Cracking Growth Rate (SCCGR) measurement tests and high-resolutional scanning electron microscopy, etc., were conducted on the many level of cold rolled (CR) Thermally Treated (TT) or solution annealed (SA) Alloy 690 and mill annealed (MA) Alloy 600 using commercial heats and laboratory heats, to clarify the mechanism on the large SCCGR for heavily CR TT Alloy 690.

The number of micro-cavities near grain boundary (GB) carbides is strongly affected by the CR ratio. They are not detected in  $\leq 10\%$  CR commercial TT Alloy 690, in CR SA Alloy 690 and in  $\leq 20\%$  CR

MA Alloy 600 (no or small number of GB carbides). No stress dependency for their formation was observed. The formation of micro-cavities in CR TT Alloy 690 is unrelated to creep damage.

However, the number of micro-cavities near GB carbides in heavily CR TT Alloy 690 increased with increasing of time or temperature heated in air or exposure at 360°C in simulated PWR primary water and with increasing of Hydrogen concentration in simulated PWR primary water.

The SCCGRs of CR TT Alloy 690 at 360°C in simulated PWR primary water show the good correlation with the number of micro-cavities near GB carbides in CR TT Alloy 690.

Micro-cavities ner GB carbides in the TT Alloy 690 are deduced to be generated by shear strain due to CR. A high density of lattice defects is observed near GB carbides after CR and they agglomerate near GB carbides during heating at temperatures where lattice defects are sufficiently mobile. New micro-cavities or coarse cavities can be generated by heating and stabilized by Hydrogen absorbed from simulated PWR primary water. Nevertheless, in case of  $\leq 10\%$  CR (the likely upper limit of effective CR in practical components), the generation of micro-cavities near GBs is negligible.

#### Keywords

" cold rolling ratio," " stress corrosion cracking growth rate," " micro-cavities," "Hydrogen concentration in simulated PWR primary water," "grain boundary carbides"

#### **Introduction**

The fully solution annealed (FSA) and thermally treated (TT) Alloy 690 was developed as an alternative material to mill annealed (MA) and TT Alloy 600, for Steam Generator (SG) tube materials of Pressurized Water Reactors (PWRs), about 34 years ago, by the first author of this study, his co-workers and those of Sumitomo Metals. This FSA TT Alloy 690 was based on its excellent resistance to stress corrosion cracking (SCC) in simulated PWR primary water and also in highly caustic, acidic and other high temperature aqueous environments [1, 2]. The FSA and TT conditions in combination with the actual carbon content in the Alloy 690 were particularly selected based on inter-granular (IG) SCC resistance in highly caustic solutions and an optimum microstructure such as semi-continuous coherent Type B  $M_{23}C_6$  carbides precipitation[3].

However, D.J.Paraventi and W.C.Moshier [4] and K.Arioka et al. [5] reported that the primary water SCC growth rate (PWSCCGR) in heavily cold rolled (CR) TT Alloy 690 increased to high values about 1/5 to 1/10 of those observed in heavily CR Mill Annealed (MA) Alloy 600, in recent years. In addition, K.Arioka et al. reported that the cracks and cavities were observed at or near grain boundary (GB) carbides in advanced area of the IGSCC tip after long term exposure at 360°C in simulated PWR primary water and those cracks and cavities were observed at or near GB carbides in advanced area of the creep cracks that developed at 435 to 465°C in heavily CR TT Alloy 690 [6]. K.Arioka et al. estimated that the cavities were formed during stress corrosion crack or creep damage advance and seemed to be involved in the crack growth process as crack embryos ahead of the actual crack tip. These embryos were considered to have nucleated by the condensation of vacancies [6].

However, in the authors' previous study [7], it was concluded that PWSCCGRs in CR TT Alloy 690 were different for each heat and fabrication process examined, and that microcracks at carbides and cavities were observed at or near eutectic  $M_{23}C_6$  GB carbides ( $M_{23}C_6$  primary GB carbides) after CR. In addition, the presence and number of the microcracks and cavities in the  $M_{23}C_6$  primary GB carbides strongly depended on the chemical composition and fabrication process [8].

Other researchers have also indicated that the relatively high SCCGRs in heavily cold worked TT Alloy 690 immersed in simulated PWR primary water depends on the formation of creep cavities [9, 10, 11].

In order to verify the involvement of "the creep mechanism" for SCC of austenitic alloy in high temperature water, it is essential to prove that it is not only a necessary condition, but also a sufficient condition. That is to say, not only that the cavities could be detected after a SCC test, but also that the cavity generation must demonstrate stress dependence. If the SCCGR in heavily cold worked TT Alloy 690 depends on creep damage, the residual stress in heavily cold worked TT Alloy 690 must reduce concomitantly. Indeed, since residual stress is the driving force of most in-service SCC, creep relaxation should then reduce susceptibility.

Therefore, in this study, in order to confirm or disprove the possibility of the creep driven mechanism of SCC in TT Alloy 690, the stress dependency of the formation of cavities at or near GB carbides and their behavior under prolonged heating in air and after exposure in simulated PWR primary water were studied. In addition, a laboratory melted CR MA Alloy 600 were tested as a reference material. The material characteristics of the test materials were determined before and after the SCCGR tests in simulated PWR primary water, and compared with SCCGRs for CR TT Alloy 690 after various levels of CR.

#### **Exprimental Procedures**

#### Test Materials and Test Specimens

In this study, two laboratory heats X and Y, two commercial heats N and S of TT Alloy 690 and one laboratory heat M of MA Alloy 600 were used. The laboratory heat X is a low carbon Alloy 690 with a relatively low density of eutectic  $M_{23}C_6$  primary GB carbides. The laboratory heat Y simulates the chemical composition of the 'Bettis' Alloy 690 Test Material 690B[12] and has a relatively high density of eutectic  $M_{23}C_6$  primary GB carbides due to the lightly forged or as cast condition. The commercial heats N and S were cut from the archive material of practical CRDM tube for Japanese PWRs. The laboratory heat M of MA Alloy 600 was applied to this study as the reference material for TT Alloy 690.

The two laboratory heats X, Y of TT Alloy 690 and laboratory heat M of MA Alloy 600 were melted in a 180 kg vacuum induction melting process and hot forged. The two heats of commercial TT Alloy 690 for a PWR CRDM tube were melted by an electric arc furnace and refined by vacuum oxygen decarburization process (60 ton capacity) and electro-slag re-melting process. The two commercial heats were fabricated into billets by hot forging process and into CRDM tubes by a hot extrusion process. Heats S and N were machined to slabs from the archive CRDM tubes. The slabs of about 25 mm thick x 40 mm width x more than 300 mm length were machined from CRDM tubes.

The TT Alloy 690 of the laboratory heats and commercial heats were FSA at 1,075 °C and TT at 700 °C for 15 hours after hot working processes. The laboratory melted heat M of MA Alloy 600 was MA at 990 °C after final hot working process. The chemical compositions, which were determined by ladle analyses are shown in Table 1. The hot working processes for the laboratory melted heats and commercial heats were shown in Table 2.

In the Table 2, Processes SA1 and SA2 are re-solution annealing at 1,075 °C and 1,100 °C after TT for the commercial heat S of TT Alloy 690, respectively.

CR was performed by one-directionally CR process for these test materials in the levels of 5 or 10 or 15 or 20 or 30 % reduction of thickness. After CR or as TT condition, 0.7T CT specimens with side grooves were machined with T-L orientation for the SCCGR tests, and small platelet test coupons of 1.3 mm or 1.6 mm thick were machined with perpendicular to the CR direction for three point bent beam SCC specimens.

Heat	Features	Chemical Compositions by Ladle Analysis (Wt%)								
No.		С	Si	Mn	Р	S	Ni	Cr	Ti	Fe
х	Lab. Melt Alloy 690	0.019	0.25	0.30	0.009	0.001	60.0	29.9	<0.001	9.60
Y	Lab. Melt (simulated Bettis') Alloy 690	0.031	0.04	0.06	0.003	0.001	60.60	29.60	0.34	9.00
Bettis' Test material in literature 12)		0.031	0.032	0.05	0.002	<0.001	60.61	29.63	0.34	8.89
S	Commercial Heat Alloy 690 for CRDM Pipe		0.25	0.29	0.008	0.002	59.39	29.80	0.21	9.88
Ν	Commercial Heat Alloy 690 for CRDM Pipe		0.39	0.31	0.008	0.002	59.66	29.57	0.20	9.43
м	Lab. Melt Alloy 600		0.30	0.30	0.007	0.001	75.61	15.39	0.20	7.95

Table 1 : Chemical compositions & tensile properties of test materials

12) : Metallurgical and Materials Transactions A, 33A, 2002, p.1725, Test Material : 690B

Table 2 : Hot working process a	d final heat treatment condition
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Alloy	Process	Hot Working Process	Final Heat Treatment			
690	Process A	As Cast	SA(1,075°C x 1hr) + TT (700°C x 15hrs)			
	Process B	Lightly Forged	SA(1,075°C x 1hr) + TT (700°C x 15hrs)			
	Process C	Lightly Forged + Heavily Forged	SA(1,075°C x 1hr) + TT (700°C x 15hrs)			
	Process P	Hot Extruded	SA(1,075°C x 1hr) + TT (700°C x 15hrs)			
	Process SA1	Lightly Forged + Heavily Forged or Hot Extruded	SA(1,075°C x 1hr)			
	Process SA2	Lightly Forged + Heavily Forged or Hot Extruded	SA(1,100°C x 1hr)			
600	Process C	Lightly Forged + Heavily Forged	MA(990°C x 2hr)			

SA : Solution Annealed, TT : Thermally Treated, MA : Mill Annealed

#### SCCGR Measurement Test and Observation on Micro-Cavities at or near GB Carbides

The 0.7 T CT specimens with side grooves for SCCGR measurement test were fatigue precracked in air. The SCCGR measurement tests using these 0.7 T CT specimens were conducted at 360 °C in the simulated PWR primary water. The SCCGR measurement tests were conducted in four stages. The first stage was a corrosion fatigue test with R=0.3 (R= minimum load / maximum load), and triangular wave loading at 0.01 Hz during 24 hours. The second stage was a corrosion fatigue test with R=0.5 and triangular wave loading at 0.01 Hz during 5 hours. The third stage consisted of periodic partial unloading with R=0.5 at a nominal frequency of 0.001 Hz for the rising part and 0.01 Hz for the falling part of the loading and a holding time of 9,000 sec., and was conducted during more than 100 hours. (But for the specimens of lower than 15% CR TT or SA Alloy 690, the periodic partial unloading was conducted during more than 1,500 hours.) The fourth stage was a constant load test at 13.89 kN giving an initial crack tip K value of 30 MPa $\sqrt{m}$ .

After the SCCGR measurement tests, the fracture surfaces were artificially opened and fractography was conducted on the fracture surface of CT specimens by stereoscope and SEM. The SCCGRs were evaluated using in-situ DCPD monitoring and post-test fractography data.

After fractography on the fractured surface, Vickers hardness at 5kg load was measured on the cross section near the pre-fatigue crack of the CT specimens.

In order to evaluate the effect of stress dependency on the formation of micro-cavities at or near GB carbides, three point bent beam SCC test specimens, which were made of heavily CR commercial TT Alloy 690, were exposed at 360°C in simulated PWR primary water, and the number of micro-cavities at or near GB carbides were observed in both stressed area and stress free area of the three point bent beam specimens after exposure in simulated PWR primary water.

The micro-cavities at or near GB carbides were observed on the specimens, which were polished by choroidal and iron-polisher (Hitachi IM-4000), by high resolution scanning electron microscope (Hitachi SU-70) and FEI Helios Nano Lab Dual Beam 600i.

The micro-cavities at or near GB carbides were observed under 10,000 times magnification in 30 observed fields. The numbers of the micro-cavities at or near GB carbides were counted on 10 times magnified photographs for every observed fields under 10,000 times magnification. So, the number of the micro-cavities at or near GB carbides was counted on 100,000 times magnified GBs. The average number of micro-cavities at or near GB carbides was taken from the average for the numbers in each observed field.

#### **Experimental Results and Discussions**

## Effect of CR Ratio (Vickers Hardness) on SCCGR for Laboratory Heats and Commercial Heats of TT or SA Alloy 690

In order to confirm the effect of CR ratio on SCCGR for CR TT or SA Alloy 690, the SCCGR tests were conducted for various degrees of CR in simulated PWR primary water at 360°C. After the SCC tests, the Vickers hardness was measured on a cross section near the fatigue precrack location for each CT specimen. A good correlation was observed between the Vickers hardness and CR ratio for TT Alloy 690, as shown in Figure 1. The laboratory heat Y and commercial heats S and N showed the same tendency for the correlation between the Vickers hardness and CR ratio. However, laboratory heat X showed slightly lower Vickers hardness compared to that of laboratory heat Y, presumably due to the low carbon content of TT Alloy 690 heat X.

The results of the SCCGR tests on all materials are summarized as a function of Vickers hardness in Figure 1.

Laboratory melted TT Alloy 690 Heat Y showed the very highest SCCGR regardless of Vickers hardness. The SCCGRs for laboratory melted TT Alloy 690 Heat X and commercial TT Alloy 690 Heats N and S (i.e. the archive material from a PWR CRDM tube) increased with increasing CR ratio. However, the SCCGR of Heat X was higher than those of the commercial heats N and S for each CR ratio.

In the case of SA Alloy 690, the SCCGR was very low regardless of laboratory heat Y, commercial heat, and Vickers hardness, when compared to CR TT Alloy 690. GB carbides were not detected, or only in very small numbers, in the SA Alloy 690 heats.

Microstructural analyses were conducted by SEM for all test materials. Figure 2 shows typical microstructures observed. In the CR, laboratory melted Heat Y, many cracks were detected in the eutectic  $M_{23}C_6$  primary GB carbides, and the number of cracks increased with increasing of CR ratio. The cracks in eutectic  $M_{23}C_6$  primary GB carbides were particularly marked in the CR, Heat Y Process A (as cast) TT Alloy 690. However, cracking of eutectic  $M_{23}C_6$  primary GB carbides was hardly observed at all in the commercial Heat S. Cracks in the eutectic  $M_{23}C_6$  primary GB carbides were significantly less numerous in laboratory melted Heat X compared to laboratory melted Heat Y.



Figure 1 Effect of GB carbides & Vickers hardness on SCCGR at 360 °C in the simulated PWR primary water for CR TT or SA Alloy 690.



Figure 2 Observed cracks in eutectic  $M_{23}C_6$  primary GB carbides in CR laboratory heats X and Y and commercial heat S.

### Effect of Stress on the Number of Micro-Cavities at or near GB Carbides for Heavily CR Commercial TT Alloy 690

K.Arioka et al. have reported that cavities were observed in intergranular locations at the crack tip peripheries of both IGSCC and creep cracks in CR TT Alloy 690. They indicated that there is a similarity in the temperature dependence of crack growth rate between IGSCC and creep cracking for heavily CR TT Alloy 690, leading them to hypothesize that the mechanism of IGSCC in heavily CR TT Alloy 690 can be caused by creep damage (Refs. 5, 6 and 7).

However, as described earlier, in order to confirm the creep damage hypothesis as the precursor mechanism for IGSCC, it is necessary to prove not only the necessary conditions but also sufficient conditions i.e. not only that the temperature dependency of crack growth rate and cavity formation are similar, but also that cavity formation and deformation are stress dependent.

Consequently, the effect of stress on cavity formation for the 30% CR commercial TT Alloy 690 was tested in this study using the three point bent beam SCC test specimens. High resolution SEM photographs were taken on the stressed area and stress free area in the SCC specimens after testing for 8,532hrs in simulated PWR primary water at 360°C. As shown in Figure 3, the micro-cavities at or near GB carbides were detected in not only stressed areas but also stress free areas. Moreover, these micro-cavities are quite similar to the "creep driven cavities" reported by K. Arioka et al [7].

Micro-cavities at or near GB carbides were observed and counted in 30 observed locations in the stressed area and stress-free area of the three point bent beam SCC test specimens after exposure in simulated PWR primary water at 360°C for 4,137hrs and 8,532hrs. Figure 4 shows the average number of detected micro-cavities at or near GB carbides versus exposure time.

Each point shows the average number of detected micro-cavities for each three point bent beam SCC specimen. Red marks show the average number of detected micro-cavities at or near GB carbides in the stressed area while the blue marks show the average number in the stress free area. From this figure, it is clear that there is no difference in the average number of microcavities at or near GB carbides observed between the stressed and stress-free areas.



Figure 3 Detected micro-cavities at or near GB carbides in not only stressed areas but also stress free areas of three point bent beam SCC test specimen for 30% CR commercial TT Alloy 690 after exposure at 360°C in simulated PWR primary water during 8,532hrs.



Figure 4 The effect of applied stress on the average number of observed micro-cavities at or near GB carbides in 30 observed zones in three point bent beam SCC specimens of 30% CR TT Alloy 690 after exposure in simulated PWR primary water at 360°C during 4,137, 6,312 and 8,532hrs.

Figure 5 shows the average number of micro-cavities detected at or near GB carbides in 30 observed zones versus CR reduction ratio for the laboratory melted and commercial TT Alloy 690. The average number of micro-cavities at or near GB carbides in 30 observed zones increases with increasing of CR reduction ratio. But, any micro-cavities at or near GBs were not detected in the laboratory melted and commercial MA Alloy 690, regardless CR reduction ratio.

Figure 6 shows the relationship between the SCCGR in simulated PWR primary water at 360°C and the average number of micro-cavities at or near GB carbides of the CR laboratory melted and commercial TT Alloy 690 and MA Alloy 690. The good correlation was detected between the SCCGR in simulated PWR primary water at 360°C and the average number of micro-cavities at or near GB carbides of the CR laboratory melted and commercial TT Alloy 690 and MA Alloy 690.

Therefore, the detected micro-cavities for 30% CR commercial TT Alloy 690 after exposure in the simulated PWR primary water at 360°C are clearly not related to creep damage. And also, it is considered that the SCCGR of CR TT Alloy 690 is closely related to the amount of micro-cavities at or near GB carbides due to the CR.



Figure 5 The average number of micro-cavities detected at or near GB carbides in 30 observed zones versus CR reduction ratio for the laboratory melted and commercial TT Alloy 690.



Figure 6 The relationship between the SCCGR in simulated PWR primary water at 360°C and the average number of micro-cavities at or near GB carbides of the CR laboratory melted and commercial TT Alloy 690 and MA Alloy 690.

# Effect of GB orientation relative to the CR direction on the number of cavities observed at or near GB carbides

In order to better understand the mechanism responsible for high SCCGRs observed in heavily CR TT Alloy 690 exposed to simulated PWR primary water, the relationship between the generation of cavities at or near GB carbides and the characteristics of SCCGR were examined.

Initially, in the process of counting the number of cavities at or near GB carbides by increasing the number of observation zones, it was found that the number of cavities at or near GB carbides was dependent on the orientation of GBs relative to the CR direction. Therefore, in order to clarify this defined as S-T, T-L and S-L planes in relation to the CR direction, as shown in Figure 7. The observed GB orientation was defined as "parallel to GB" or "orthogonal to GB" to within relationship, the observation surfaces were  $\pm$  30 degrees relative to the plate thickness direction, as shown in Figure 8. The number (N) of cavities at or near GB carbides was counted in planes parallel to GBs and orthogonal to GBs in each of the 30 observed zones. The length (L µm) of the each observed GB was measured to obtain N/L x 10 per GB length of 10 µm.

Figure 9 shows the results for the averaged number of cavities at or near GB carbides per GB length of 10  $\mu$ m as a function of the observation plane and GB orientation for the 30% CR commercial heat of TT Alloy 690, before heating in air or exposure to simulated PWR primary

water. Representative photographs of the data in Figure 9 are shown in Figure 10, and locations where cavities were recognized are indicated by blue arrows.

From these figures, the number of cavities at or near GB carbides observed in the TL and SL planes parallel to GBs is much larger than in orthogonal GBs. However, in the ST plane both parallel GBs and orthogonal GBs have almost the same number of cavities. This observation was invariant; i.e., in the TL and SL planes, parallel GBs are parallel to the rolling direction, but in the ST plane both parallel GBs and orthogonal GBs are perpendicular to the rolling direction. Thus, it can be seen that many cavities at or near GB carbides are always observed in GBs that are parallel to the rolling direction.

From these observations, it is considered that the crystal grains are compressed during CR and cavities form at or near GB carbides due to the shear strain generated between adjacent grains. Furthermore, it is considered that the shear strain is large in the parallel GBs but small in the orthogonal GBs. It therefore seems that the difference in the number of cavities at or near GB carbides depending on their orientation relative to the rolling direction is caused by differences in shear strain.



Figure 7 Defined observation surfaces as S-T, T-L and S-L planes relative to the CR direction.



T-L Plane Orthogonal GB Orthogonal GB Parallel GB S-T Plane

Figure 8 Observation of GB orientation parallel (± about 30 degrees) to the plate thickness direction is referred to as "parallel GBs" while GN orientation perpendicular (± about 30 degrees) to the thickness direction is defined as "orthogonal GBs".





Figure 10 Representative photograph of cavities at or near GBs in parallel GBs and orthogonal GBs observed in the S-T, T-L and S-L planes for the 30% CR commercial TT Alloy 690 before heating in air or exposure to simulated PWR primary water.

Effect of CR Ratio, Heating in Air and Hydrogen Content in Simulated PWR Primary Water on the Number of Micro-cavities at or near GB Carbides for CR Commercial TT or SA Alloy 690

In order to clarify the reason why the large SCCGRs are observed on heavily CR TT Alloy 690 despite very low SCCGRs in non-CR (as-received) TT Alloy 690 as well as CR SA Alloy 690, their micro-structures near GBs were comprehensively examined using high resolution SEM.

Figure 11 shows the average number of micro-cavities detected at or near GB carbides in 30 observed zones versus CR reduction ratio for the commercial TT or SA Alloy 690, before and after heating at 475°C in air for 2,010 hours or after exposure in simulated PWR primary water at 360°C with different Hydrogen concentrations. From this figure, the average number of detected micro-cavities at or near GB carbides in the 30 observed zones is negligibly small for  $\leq 10\%$  CR TT Alloy 690, but increases with increasing of CR ratio for >15% CR TT Alloy 690. The average numbers of detected micro-cavities at or near GB carbides after exposure to simulated PWR primary water.

Additionally, these average numbers of detected micro-cavities at or near GB carbides in the 30 observed zones increased with increasing of Hydrogen concentration in simulated PWR primary water.

In case of SA Alloy 690, however, the average number of detected micro-cavities at or near GB carbides in the 30 observed zones was always zero, regardless of CR ratio.

In case of MA Alloy 600, the average number of detected micro-cavities at or near GB carbides in the 30 observed zones was zero for less than 20 % CR ratio, very small number of micro-cavities at or near GB carbides (remaining un-solved GB carbides) in the 30 observed zones was detected for 30% CR ratio and the number of micro-cavities at or near GB carbides in the 30 observed zones increased with increasing of Hydrogen concentration in simulated PWR primary water, as shown in Figure 12.



Figure 11 The averaged number of detected micro-cavities at or near GB carbides in 30 observed locations vs. CR reduction ratio before and after heating at 475°C in air or exposure in simulated PWR primary water at 360°C under different Hydrogen content for CR commercial TT or SA Alloy 690.



Figure 12 The average number of detected micro-cavities at or near GB carbides in 30 observed locations vs. CR reduction ratio before and after exposure in simulated PWR primary water at 360°C under different Hydrogen content for laboratory melted MA Alloy 600 (remaining un-solved GB carbides).

Transmission electron microscopy was conducted on the commercial TT Alloy 690 at the relatively low level of 5% CR in order to study the underlying reason for the generation of micro-cavities at or near GB carbides. Many tangled dislocations surrounded the GB carbides in the 5% CR commercial TT Alloy 690, as shown in Figure 13.

From these photographs, it is deduced that micro-cavities can be generated by condensation of lattice defects surrounded the GB carbides.

Subsequently, the trapped Hydrogen contents in the test specimens were analyzed by vacuum heating extraction to examine the effect of Hydrogen concentration in the simulated PWR primary water on the formation of micro-cavities at or near GB carbides in CR TT Alloy 690. Figure 14 shows the results of these analyses.

It can be seen that the Hydrogen contents in the CR commercial TT Alloy 690 specimens (before heating in air or exposure in simulated PWR primary water) were about 2 to 5ppm, which is not considered unusual. After heating at 360°C in air for 6,312hours, the Hydrogen content in the alloy decreased to 0.3ppm after baking in air at 475°C. On the other hand, the Hydrogen content in the alloy after exposure in simulated PWR primary water at 360°C increased with increasing Hydrogen concentration in the aqueous environment. These trapped Hydrogen concentration analyses in each of the TT Alloy 690 samples are expected.

From the data above, it is deduced that the cavities at or near GB carbides are not formed by a creep mechanism. This is consistent with no stress dependency for the appearance of cavities.

Micro-cavities can also be generated by condensation of many lattice defects (vacancies) surrounding GB carbides due to the shear strain. Their number will increase by diffusion on heating to temperatures where lattice defects are sufficiently mobile and are also stabilized by Hydrogen absorbed from hydrogenated, simulated PWR primary water.



Figure 13 Dislocations near GB of 5% CR commercial TT Alloy 690 for CRDM tube after heating at 400°C in air.

Original Material for Three Point Beam SCC Test Specimen		Hydrogen Content (ppm)			
		No. 1	No. 2	No.3	Ave.
As 30% CR Commercial TT Alloy 690 for CRDM Tube	S69-30-1	5.1	4.4	4.2	4.6
As 30% CR Commercial TT Alloy 690 for CRDM Tube	S69-30-2	2.5	2.3	-	2.4
As 30% CR Commercial TT Alloy 690 for CRDM Tube	N69-30-1	4.3	4.4	-	4.4
After Heated in Air at 360°C for 6,312hrs	S69-30-A	0.4	0.2	0.4	0.3
After Exposure in Primary Water with 30cc Hydrogen at 360°C for 6,312hrs	S69-30-30	1.4	1.3	1.8	1.5
After Exposure in Primary Water with 5cc Hydrogen at 360 $^{\circ}$ for 925hrs	S69-30-5	0.4	1	0.8	0.7
After Exposure in Primary Water with 50cc Hydrogen at 360°C for 925hrs	S69-30-50	1.7	1.9	1.5	1.7



Figure 14 Effect of heating in air or exposure in simulated PWR primary water on trapped Hydrogen content in TT Alloy 690.

#### **Conclusions**

The objective of this work was to clarify the effect of CR on the SCCGR in CR TT or SA Alloy 690 in PWR primary water and to investigate the mechanism by which large SCCGRs are possible in heavily CR TT Alloy 690. The effects of CR ratio, heating in air at 475°C and exposure to simulated

PWR primary water at 360°C on the formation of micro-cavities at or near GB carbides in CR commercial and laboratory melted TT or SA Alloy 690 were studied.

From these studies, the following conclusions were deduced.

- The number of micro-cavities at or near GB carbides is strongly affected by the CR ratio. They are not detected in ≤10% CR commercial TT Alloy 690 nor in CR commercial SA Alloy 690 nor in CR laboratory melted MA Alloy 600 (without any visible GB carbides or small number of GB carbides). No stress dependency for their formation was observed. However, the number of micro-cavities increased with increasing of time at temperature in air at 475°C and with exposure time at 360°C in simulated PWR primary water.
- 2) The number of micro-cavities at or near GB carbides in heavily CR TT Alloy 690 increased with increasing of Hydrogen concentration in simulated PWR primary water.

- 3) The formation of micro-cavities in heavily CR TT Alloy 690 is therefore unrelated to creep damage.
- 4) Micro-cavities at or near GB carbides in the TT Alloy 690 are deduced to be generated by shear strain due to heavy CR. A high density of lattice defects is observed near GB carbides after CR and they agglomerate near GB carbides during heating at temperatures where lattice defects are sufficiently mobile. They may possibly also by stabilized by Hydrogen absorption from hydrogenated PWR primary water. New micro-cavities or coarse micro-cavities can be generated by prolonged heating and stabilized by Hydrogen absorbed from simulated PWR primary water. Nevertheless, in the case of  $\leq 10\%$  CR (the likely upper limit of effective CR in practical components), the generation of micro-cavities at GBs is negligible.

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