Effect of Cold Working and Long-Term Heating in Air on the Stress Corrosion Cracking Growth Rate in Commercial TT Alloy 690 Exposed to Simulated PWR Primary Water

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The authors have previously reported that the number of cavities at or near grain boundary (GB) carbides in commercial thermally treated (TT) Alloy 690 increases with increasing cold work reduction ratio and with heating temperature in air. In the present work after very long-term heating in air, the number of cavities at or near GB carbides in cold worked commercial TT Alloy 690 was observed to saturate, and the shape and size of the cavities changed. The shape and size of cavities and cracks were categorized, and a GB defect index number was defined as a function of their number, shape, and size. Stress corrosion cracking growth rates in a commercial TT Alloy 690 with various levels of cold work exposed to simulated PWR primary water at 633 K (360 °C) have been measured and correlated with the defined GB defect index number. Cavities and cracks in the same materials before and after long-term heating in air have also been correlated with the defined GB defect index number. For the heavily cold worked (≥ 15 pct) commercial TT Alloy 690, a good correlation has been observed between the PWSCCGR and the GB defect index number. By contrast, for lightly cold worked (≤ 10 pct) commercial TT Alloy 690, the SCCGR in the simulated PWR primary water was very low and the GB defect index number was usually zero, regardless of cold working reduction ratio ≤ 10 pct. It is concluded that the mechanism of SCCGR for lightly cold worked TT Alloy 690 in PWR primary water is likely to be different from that for heavily cold worked TT Alloy 690.

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I. INTRODUCTION

ALLOY 690 was developed about 50 years ago by the International Nickel Company as a corrosion resistant Nickel based 30Cr–9Fe alloy for many demanding high temperature environments.[1] For application as a steam generator (SG) tube material in Pressurized Water Reactors (PWRs) as an alternative to mill annealed (MA) Alloy 600 (Ni based 15Cr–9Fe alloy), a high-temperature, fully solution heat treated (SHT) and thermally treated (TT) Alloy 690 was originally developed about 37 years ago by the first author of this paper together with his then colleagues from Mitsubishi Heavy Industries, Ltd. and Sumitomo Metal Industries, Ltd. (now Nippon Steel Corporation).[2,3] This development of TT Alloy 690 depends on controlling combinations between the fully SHT and TT conditions as a function of carbon content that are selected to generate an optimized microstructure, as revealed by transmission electron microscopy (TEM).[4,5] This TT Alloy 690 has excellent stress corrosion cracking (SCC) resistance in not only concentrated secondary water SG crevice environments but also in PWR primary water environments. It has been widely used as the alternative material to MA Alloy 600 not only for PWR SG tubes, but also for various PWR primary circuit pressure boundary components exposed to the primary water environment. TT Alloy 690 has now been used for more than 30 years in PWR primary water environments without any known SCC indications anywhere in the world.[6]

On the other hand, from the viewpoint of why the SCC can occur in the MA Alloy 600, the mechanism of the SCC for Ni-based alloys in the simulated PWR primary water has been discussed during more than 40 years.
That is, aspects of the mechanism have been described from the viewpoints of microstructure, electrochemistry, hydrogen embrittlement, slip dissolution mechanism, the internal oxidation mechanism etc.\textsuperscript{[17–26]}

Moreover, cracks or cavities at or near grain boundaries (GBs) were observed at or near secondary GB carbides in the laboratory melted and cold worked commercial TT Alloy 690.\textsuperscript{[28]}

However, from the present authors’ previous study,\textsuperscript{[29]} it was concluded that PWSCCGRs in heavily (≥ 15 pct) cold worked, laboratory melted heats of TT Alloy 690 depended on the particular heat and fabrication process examined. Moreover, cracks or cavities at or near eutectic M\textsubscript{23}C\textsubscript{6} primary GB carbides were already observed immediately after cold working. By contrast, in the cold worked commercial TT Alloy 690, eutectic M\textsubscript{23}C\textsubscript{6} primary GB carbides were hardly ever observed and the GB carbides were mostly secondary GB carbides precipitated during TT. After cold working, cavities at or near secondary GB carbides were detected even in the commercial TT Alloy 690. However, the number of such cavities at or near secondary GB carbides for the commercial TT Alloy 690 was very much smaller than the number of the cavities at or near eutectic M\textsubscript{23}C\textsubscript{6} primary GB carbides and also secondary GB carbides in the laboratory melted and cold worked TT Alloy 690.

The authors deduced that the GB carbides in the TT Alloy 690 used by Arioka \textit{et al}., and by Paraventi \textit{et al}., were mainly retained eutectic primary M\textsubscript{23}C\textsubscript{6} carbides resulting from industrially unrepresentative casting and hot working procedures, and that the high PWSCCGRs of their heats of TT Alloy 690 therefore depended on the presence of cracks and cavities at or near these eutectic primary M\textsubscript{23}C\textsubscript{6} carbides. Thus, the PWSCCGRs for their cold worked heats of TT Alloy 690 were much larger than those for the authors’ commercial heats of TT Alloy 690.\textsuperscript{[29]}

In addition, Arioka \textit{et al}.
reported that voids and cavities were observed at or near grain boundaries (GBs) in zones in front of the PWSCC tip after long-term exposure in simulated PWR primary water at 633 K.\textsuperscript{[30,31]} The authors of these papers\textsuperscript{[30,31]} proposed that the crack embryos originating from the coalescence of vacancies induced by cold work absorbed hydrogen and played an important role in the process of crack growth, both of PWSCC and of creep crack growth in cold worked TT Alloy 690 and cold worked MA Alloy 600 and even in cold worked carbon steel in high temperature water. Bruemmer \textit{et al}.
have also reported that cavities were observed in uniaxial tensile type SCC specimens of heavily cold forged commercial TT Alloy 690 after long-term exposure in simulated PWR primary water. On the basis of these data, Bruemmer \textit{et al}.
supported the creep damage hypothesis proposed by Arioka \textit{et al}.,\textsuperscript{[32–34]}

If PWSCCGR in heavily cold worked TT Alloy 690 can be caused by creep damage, then it is expected that the residual stress in heavily cold worked TT Alloy 690 must reduce due to creep relaxation. Since residual stress is the driving force of most in-service PWSCC (and SCC of industrial components in general), then creep relaxation would be expected to progressively reduce PWSCC susceptibility by eliminating the stress driving force. From this perspective, we conclude that the hypothesis that PWSCC growth in heavily cold worked TT Alloy 690 is caused by the creep damage is not a sustainable hypothesis.

Moreover, to verify the involvement of “the creep damage hypothesis” as the mechanism of PWSCC, it is essential to show that it is not only a necessary condition but also a sufficient condition. Thus, not only must cavities be detected after a PWSCC test, but they should also exhibit the same stress dependency. The hypothesis of Arioka \textit{et al}., is based on the observation of cavities in the specimens only after PWSCC tests and not on observations of the specimens before the PWSCC tests. It is also noted that in the paper by Bruemmer \textit{et al}., no observations of cavities in the cold worked specimens are reported before the SCC tests.

In the present study, in order to examine the possibility of the creep driven mechanism of PWSCC in heavily cold worked commercial TT Alloy 690, the stress dependency of the number, shape and size of cavities at or near GB carbides was evaluated using three point bent beam SCC specimens and reverse U-bend SCC specimens before and after long-term exposure at 633 K to simulated PWR primary water. Additionally, to try to clarify the mechanism of PWSCCGR in cold worked commercial TT Alloy 690 with various levels of cold work, the PWSCCGR in simulated PWR primary water and the number, shape and size of the cavities at or near GB carbides were measured. The number, shape and size of the cavities at or near GB carbides in specimens of the cold worked commercial TT Alloy 690 were also observed before and after long-term heating in air as well as before and after long-term exposure in simulated PWR primary water at 633 K.

II. EXPERIMENTAL PROCEDURES

A. Materials

One heat of commercial TT Alloy 690 pipe originally procured for industrial use as a PWR control rod drive mechanism (CRDM) nozzle and a re-solution heat treated (Re-SHT) Alloy 690 of the same heat were used in this study. The chemical composition by ladle analysis of the test material is shown in Table I. This commercial TT Alloy 690 was fabricated by a 60 ton vacuum oxygen decarburization, electro slag re-melting and hot extrusion processes and was finally thermally treated (TT) at 973 K for 54 ks (15 hours) after SHT at 1,348 K for 3.6
Table I. Chemical Composition and Heat Treatment for the Test Materials

| Features | Chemical Compositions by Ladle Analyses (Wt Pct) | Heat Treatment |
|----------|-----------------------------------------------|----------------|
| Commercial Heat TT Alloy 690 | C 0.020, Si 0.25, Mn 0.29, P 0.008, S 0.002, Ni 59.39, Cr 29.80, Ti 0.21, Fe 9.88 | SHT(1)+TT |
| Re-Solution Heat Treated for Commercial Heat TT Alloy 690 | | SHT(1)+TT+SHT(2) |

SHT: Solution Heat Treatment, TT: Thermal Treatment.
SFT(1): 1,348 K x 3.6 ks, SFT(2): 1,373 K x 3.6 ks, TT: 973 K x 54 ks.

ks (1 hour). The Re-SHT Alloy 690 heat was finally SHT in the laboratory at 1,373 K for 3.6 ks (1 hour).

The test materials were prepared by one-directional cold rolling to 5 or 10 pct or 15 or 20 pct or 30 pct reduction of 25 mm thick slabs machined from the commercial TT Alloy 690 CRDM nozzle material. The Re-SHT was carried out on 25 mm thick slabs machined from the commercial TT Alloy 690 CRDM nozzle. One of the Re-SHT 25 mm thick slabs was subsequently subjected to one-directional cold rolling to 15 pct reduction.

One directional cold rolling was conducted by multiple passes of ~50 or 100 times, due to the relatively low load capacity of the 500 ton press available.

B. Long-Term Heating in Air

To evaluate the effect of heating time in PWR primary water up to the end of the estimated PWR plant lifetime and its effect on PWSCCGR and other metallurgical properties, long-term heating in air was conducted on the 0 to 30 pct cold rolled TT Alloy 690. Many test coupons in the form of 25 mm thick, 40 mm wide, 50 mm long were machined for this purpose from the 0 to 30 pct cold rolled TT Alloy 690 slabs. These test coupons were heated in air at 633, or 673, or 693 K for about 21.6 or 36 or 57.6 or 72 Ms (about 6,000 or 10,000 or 16,000 or 20,000 hours) or at 748 K for about 7.2 or 21.6 Ms (about 2,000 or 6,000 hours) and then water cooled. From these test coupons, CT test specimens for PWSCCGR test, Vickers hardness measurement test specimen, etc., were machined. SEM test specimens were cut from the above test specimens. The electric furnace for long-term heating in air controlled the temperature to within ±1 K. The heating time of 72 Ms (20,000 hours) at 693 K in air is equivalent to about 2,600 Ms (about 80 years) at a PWR hot-leg operating temperature of 598 K for an activation energy estimated to be 130 kJ/mol. Considering the typical annual operating availability of PWRs, it is equivalent to more than 100 calendar years.

C. PWSCC Test and Crack Growth Rate Measurement Test

0.7T compact tension-type (CT) specimens with side grooves in the T-L orientation to the cold rolling (RD) were selected for the PWSCCGR measurement tests; the susceptibility of T-L orientation is directly related to the likely PWSCC propagation direction in practical components. These CT specimens were machined from the 15 or 20 or 30 pct one directionally cold rolled plates of the TT Alloy 690 or the 15 pct one directionally cold rolled plates of the Re-SHT Alloy 690.

The CT specimens were fatigue pre-cracked in air using sine wave loading at 30 Hz and a $K_{\text{max}}$ value of 15 MPa$\sqrt{m}$ with a load ratio ($K_{\text{min}}/K_{\text{max}}$) $R \geq 0.3$.

After fatigue pre-cracking in air, the CT specimens were subjected to further in-situ triangular wave fatigue pre-cracking at 633 K in simulated PWR primary water of composition 1,200 ppm B as H3BO3, 3.0 ppm Li as LiOH, dissolved oxygen ≤ 5 ppb, dissolved hydrogen = 30 cc(STP)/kgH2O. An autoclave with a single axis loading rod incorporating 6 test specimens in series was used for the PWSCCGR measurements. The triangular wave loading for the in-situ fatigue pre-cracking was conducted in a series of steps: (1) $f = 0.01$ Hz, $K_{\text{max}}$ 30 MPa$\sqrt{m}$, $R = 0.3$, during 180 ks (50 hours), (2) $f = 0.01$ Hz, $K_{\text{max}}$ 30 MPa$\sqrt{m}$, $R = 0.5$, during 180 ks (50 hours). After fatigue pre-cracking, a trapezoidal wave loading mode was applied as step (3) $f = 0.0001$ Hz (with stress increasing), 0.01 Hz (with stress decreasing), $K_{\text{max}}$ 30 MPa$\sqrt{m}$, $R = 0.5$, holding time at $K_{\text{max}}$ 30 MPa$\sqrt{m}$ during 9 ks (2.5 hours) to initiate inter-granular PWSCC (IGSCC). Step 3 was conducted during more than 7.2 Ms (2,000 hours). Subsequently, each specimen was held at a constant load at 13.89 kN giving an initial crack tip $K$ value of 30 MPa$\sqrt{m}$ during more than 7.2 Ms (2,000 hours).

The crack length in each specimen was continuously monitored by an in-situ direct potential drop technique linked to a data-logging system. All crack lengths were calibrated against the actual values measured on the fracture surfaces at the end of the test when the scheduled test time was completed.

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

D. Observations of Cracks and Cavities for Each Test Material by High-resolution SEM

To evaluate the stress dependency of cavity formation, the number, shape and size of cavities at or near GB carbides were observed in 30 different zones of both stressed and stress-free areas of the three-point bent beam SCC test specimens made from 30 pct cold rolled
commercial TT Alloy 690. In these cases, the applied tensile stress was 750 MPa (as measured by X-ray diffraction) while exposed at 633 K in simulated PWR primary water for various exposure times 14.9, 22.7 and 30.7 Ms (4,137, 6,312 and 8,532 hours). In addition, the number, shape and size of cavities at or near GB carbides were observed in 30 different zones at GBs both parallel to and orthogonal to the cold rolling direction (RD). These observations were made at the maximum stressed area of the reverse U-bend specimens made from 30 pct cold rolled commercial TT Alloy 690 both before and after exposure at 633 K in simulated PWR primary water for 36.4 Ms (10,108 hours).

To evaluate the effect of cold working, long-term heating in air, and exposure time in simulated PWR primary water on cavity formation, a total 160 specimens were tested. These specimens were heated in air at 633 or 673 or 693 or 748 K during about 7.2 or 21.6 or 36 or 72 Ms (2,000 or 6,000 or 10,000 or 20,000 hours) or exposed at 633 K in simulated PWR primary water with different hydrogen concentrations during 3.33 Ms (925 hours). Cavity observations were made on every specimen before and after heating in air or exposure in simulated PWR primary water after the specimens had been polished by colloidal alumina followed by ion milling (Hitachi IM-4000). The number, shape and size of cavities at or near GB carbides in 30 different zones on each specimen without any applied stress was observed using high resolution scanning electron microscopy (SEM) : Hitachi SU-70 and FEI Helios Nano Lab Dual Beam 600i instruments) with a 15 kV acceleration voltage, a column condition with a small probe-current mode and a high probe-current range, in order to obtain the required resolution of 1.0 nm. In order to detect the tiny cavities and the relationship between the cavities and stripped pattern due to cold working, the SEM photos were intentionally taken using the electron channeling contrast.

The total number of observed zones by high resolution SEM was 4,800 (i.e. 30 observed zones × 160 specimens). The dimensions of each zone for the high-resolution SEM observations was about 12 × 9 microns. Cavities at or near GB carbides were observed at 10,000 times magnification in each zone examined. The number, shape and size of cavities at or near GB carbides were counted on 4 times magnified photographs (taken at 10,000 times magnification) in each observed zone. The number, shape and size of cavities at or near GB carbides were therefore counted in a total of 4,800 zones at 40,000 times magnification.

Using the above various level of cold rolled commercial TT Alloy 690 after long-term heated in air, the effects of long-term heating in air on the Vickers hardness and PWSCCGR will be reported in the near future, as the next step of this study.

By the way, even in the Alloy 690, the amount of Cr carbide precipitation is depended on the amount of solute C content in the matrix. Since the TT Alloy 690 is subjected to Thermal Treatment (ageing) at 700 °C (973K) for 15 hours (in this study), the remained solute C content in the matrix and the possible amount of Cr GB carbide precipitation at 360 °C (533 K) to 420 °C are higher than those at 475 °C (748K). But, the diffusion rate and reaction rate at 360 °C to 420 °C are much lower than those at 475 °C. Therefore, in case of the heating at 360 °C to 420 °C even for long-term, the precipitation of the grain boundary carbides is not remarkable, and only agglomerate of the lattice defects and voids are detected. On the other hand, in case of heating at 475 °C for a long-term, not only the agglomeration of lattice defects and voids but also the precipitation of the grain boundary Cr carbides is remarkable.

So, regarding the effect of heating in air on the microstructure for TT Alloy 690, this study focuses on the cavities near GB carbides and cracks of the GB carbides.

III. TEST RESULTS AND DISCUSSION

A. Cavity Distributions At or Near GB Carbides vs GB Orientation Relative to the RD

In order to better understand the mechanism of cavity formation for heavily cold rolled TT Alloy 690, the relationship between the number of cavities at or near GBs and carbides as a function of GB orientation to the RD had to be determined for each specimen. Initially, during the process of counting the number of cavities at or near GB carbides, it was found that as the number of observed zones increased, the number of cavities at or near GB carbides was dependent on the orientation of GBs relative to the RD. Therefore, in order to clarify the orientation of GBs relative to the RD, the observed surfaces were defined as S–T or S–L planes in relation to the cold rolling T–L plane, as shown in Figure 1. The observed GB orientations parallel to the plate thickness or RD were defined, as shown in Figure 2(a), as “GBs parallel to or orthogonal to the plate thickness or RD”. GBs designated parallel to or orthogonal to the plate thickness or RD were within about ± 15 degrees relative to the exact parallel or orthogonal orientations.
GBs parallel to or orthogonal to the plate thickness or RD were observed on the T–L, S–T and S–L planes before heating in air or before exposure to simulated PWR primary water. The average numbers of cavities at or near GB carbides according to these categories are shown in Figure 2(b). Representative micrographs of the data given in Figure 2(b) are shown in Figure 3. Locations where cavities were detected are indicated by blue arrows. From these figures, it is clear that the average number of cavities at or near GB carbides in each of the batches of 30 observed zones along GBs parallel to the RD in the T–L and S–L planes is much larger compared to GBs orthogonal to the RD.

However, in the S–T plane, both GBs parallel to and orthogonal to the plate thickness were observed to have almost the same number of cavities. In the T–L and S–L planes, GBs parallel to the RD have the same parallel orientation relative to the RD but in the S–T plane GBs parallel and orthogonal to the plate thickness are both perpendicular to the RD. Thus, it can be seen that many cavities at or near GB carbides are always observed in GBs that are parallel to the RD.

From these observations, it is considered that as grains are compressed during cold rolling, the cavities are generated at or near GB carbides by the shear strain between adjacent grains. Furthermore, it is considered...
that the shear strain is large in parallel GBs but small in orthogonal GBs. Therefore, it seems that the difference in the number of cavities at or near GB carbides, depending on their orientation relative to the RD, is caused by differences in shear strain.

B. Definition of the GB Defect Index Number

The authors have reported in a previous paper the effect of cold rolling reduction ratio, heating at 673 and 748 K in air for about 7.2 Ms (2,000 hours) and exposure for 3.33 MS (925 hours) in simulated PWR primary water with two different Hydrogen concentrations on the average number of detected cavities at or near GB carbides in cold rolled commercial TT Alloy 690. They also reported the effect of cold rolling reduction ratio, heating at 748 K in air for about 7.2 Ms (2,000 hours) on the average number of detected cavities at or near GB carbides for the Re-SHT Alloy 690. These data are shown in Figure 4, from which the authors estimated that the number of cavities at or near GB carbides for cold rolled commercial TT Alloy 690 increases with increasing cold rolling reduction ratio and temperature of heating in air. However, in case of the Re-SHT Alloy 690, cavities at or near GB carbides were not detected regardless of cold working or heating in air.

From the extensive additional observations reported here, and after further heating at 633 or 693 K for about 72 Ms (20,000 hours) or at 748 K during 22.82 Ms (6,340 hours) in air, it can no longer be claimed that the number of cavities at or near GB carbides in cold rolled commercial TT Alloy 690 increases with increasing heating temperature in air. However, in case of the Re-SHT Alloy 690, cavities at or near GB carbides were not detected regardless of cold working or heating in air.

Consequently, in this study, the shape of cavities formed in cold worked commercial TT Alloy 690 were categorized according to cavity type and crack type. The sizes of each cavity and crack type were categorized as A to D and x to γ, respectively, according to their diameter or width, as shown in Figure 7. By definition, the size categories of cavity types A, B, C and D are, respectively, ≤ 20 nm, 50 nm, 100 nm and 200 nm in diameter, and the crack width categories x, β and γ are, respectively, ≤ 20 nm, 50 nm and 100 nm wide. According to this categorization scheme, the typical distributions of the numbers of cavities or cracks in each size type for 30 pct cold rolled TT Alloy 690 after different heating temperatures and times are shown in Figure 8. It is clear that the numbers of large cavities or crack types increase with increasing heating temperature in air.

Based on the defined categories A, B, C and D for cavity size types, the authors assigned coefficients 1, 3, 5 and 7, respectively. Similarly, for the crack type categories x, β and γ, coefficients 2, 4 and 6, respectively, were assigned. Subsequently, the numbers of cavities in categories A, B, C and D were multiplied by the coefficients 1, 3, 5 and 7, respectively, and summed and designated \( \sum \). Similarly, the number of cracks in categories x, β and γ were multiplied by the coefficients 2, 4 and 6, respectively, and the sum designated \( \sum \). The sum of \( \sum \) and \( \sum \) was then defined as the GB defect index number, as shown in Figure 7 and by the following equation:

\[
\text{GB defect index number} = \sum (\text{total number of } A \times 1 + \text{total number of } B \times 3 + \text{total number of } C \times 5 + \text{total number of } D \times 7) + \sum (\text{total number of } x \times 2 + \text{total number of } \beta \times 4 + \text{total number of } \gamma \times 6)
\]  

This GB defect index number was calculated for each observed zone, and calculated the average number and standard deviation of GB defect index in the 30 observed zone.

![Fig. 4—The effect of cold rolling reduction ratio, heating at 748 K in air for about 7.2 Ms (2,000 h) or exposure at 633 K for 3.33 Ms (925 h) in simulated PWR primary water with different Hydrogen concentrations on the average number of detected cavities at or near GB carbides in 30 observed zones for the cold rolled commercial TT Alloy 690 and Re-SHT Alloy 690. All data in this figure were measured for stress free specimens.](image)
C. Stress Dependency of the GB Defect Index Number

Arioka et al. have reported that a high density of cavities was observed at grain boundaries ahead of PWSCC tips after long-term exposure at 633 K in simulated PWR primary water. They also reported that the cavities appeared to nucleate at or near intergranular carbides by condensation of vacancies at the crack tips of both PWSCC and creep cracks in cold rolled TT Alloy 690. They indicated that there is a similarity in the temperature dependence of crack growth rate between PWSCC and creep cracking for heavily cold rolled TT Alloy 690, leading them to hypothesize that the mechanism of PWSCC in heavily cold rolled TT Alloy 690 can be creep damage. [28,30,31]

However, as previously stated, to confirm the creep damage hypothesis as the precursor mechanism for IGSCC, it is necessary to prove that not only is creep a necessary condition but also a sufficient condition. In other words, it is necessary to show not only that the temperature dependency of crack growth rate and creep cavity formation are similar, but also that cavity formation and deformation have the same stress dependencies.

As reported previously, the effect of stress on cavity formation for the 30 pct cold rolled commercial TT Alloy 690 was tested using the three-point bent beam SCC test specimens. [35] High resolution SEM photographs were taken of the stressed area and of a stress-free area for each of the three-point bent beam SCC specimens after exposure at 633 K in simulated PWR primary water during 14.9, 22.7 and 30.7 Ms (4,137, 6,312 and 8,532 hours).

As shown in Figure 9, cavities at or near GB carbides were detected in not only the maximum tensile stressed...
areas but also in the stress-free areas of three point bent beam SCC specimens. The observed cavities are quite similar in appearance to the "creep driven cavities" reported by Arioka et al.

The cavity observations previously reported for the 30 different zones of the maximum tensile stressed areas and stress-free areas of the 3-point bent beam specimens after three exposure times (14.9, 22.7 and 30.7 Ms) (4,137, 6,312 and 8,532 hours) in simulated PWR primary water were re-analyzed as a function of the GB defect index numbers, as shown in Figure 10. From this figure, it is clear that there is no difference in the GB defect index number between the maximum tensile stressed areas and the stress-free areas for the three-point bent beam SCC test specimens after the three exposure times.

But, the three point bent beam specimens are not so easy to reproduce the PWSCC in the laboratory test due to relatively low residual stress. So, in addition, in this study, reverse U-bend specimens were additionally manufactured from the 30 pct cold rolled commercial TT Alloy 690 according to ISO/TC 156 N 1172[36] and were exposed at 633 K in simulated PWR primary water during 36.4 Ms (10,108 hours). (A summary of the manufacturing procedure for the reverse U-bend specimens is illustrated in Figure 11.) High-resolution SEM BSE photos were taken of GBs parallel and orthogonal to the RD at the highest stressed peak of each reverse U-bend specimens before and after exposure and the GB defect index numbers were calculated and compared in Figure 11 (SEM BSE photos in Figure 11 were taken stressed specimen after exposure in simulated PWR primary water). It is well known that the applied tensile stress level at the top of U bend area is substantially the same along the longitudinal and orthogonal axes of the specimens. (In Figure 11, the longitudinal axis is "parallel to the RD" and the orthogonal axis is "orthogonal to the RD".) However, the applied total strain in the

| Cavity Type | Crack Type |
|-------------|------------|
| OD (nm)     | OD (nm)    | Width (nm) | Width (nm) |
| Typical Photo | Typical Photo | Typical Photo | Typical Photo |
| A ≤ 25nm, B ≤ 50nm, C ≤ 100nm, D ≤ 200nm | A ≤ 25nm, B ≤ 50nm, C ≤ 100nm, D ≤ 200nm |
| Defect Index = A x 1 + B x 3 + C x 5 + D x 7 + α x 2 + β x 4 + γ x 6 | Defect Index = A x 1 + B x 3 + C x 5 + D x 7 + α x 2 + β x 4 + γ x 6 |

Fig. 7—Categorization of the shape and size of cavities at or near GB carbides for cold rolled commercial TT Alloy 690 where categories A to D are based on the diameter of cavities and categories α to γ are based on the width of cracks that are usually transverse to the longest dimension of the carbides. The GB defect index number is defined as $A \times 1 + B \times 3 + C \times 5 + D \times 7 + \alpha \times 2 + \beta \times 4 + \gamma \times 6$.

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Fig. 8—Effect of heating temperature at 633 to 693 K for 72 Ms (20,000 h) or at 748 K for 22.82 Ms (6,340 h) on the cavity and crack types in 30 observed zones with error bar of standard deviation from the viewpoint of their diameter and width, respectively.
orthogonal axis is slightly higher than that in the longitudinal axis.

As shown in Figure 11, the GB defect index number for GBs orthogonal to the RD is slightly larger than that for GBs parallel to the RD before and after exposure at 633 K in simulated PWR primary water for 36.4 Ms (10,108 hours). The difference between the GB defect index numbers for GBs parallel and orthogonal to the RD is thought to be due to the differences in total applied strain for these GB orientations relative to the RD.

From Figures 10 and 11, it is clear that there is no stress dependency for cavity formation for both the three-point bent beam SCC test specimens and reverse U-bend SCC test specimens. It is concluded, therefore, that the detected cavities for heavily cold rolled com-

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**Fig. 9**—Observed cavities at or near GB carbides in the stress-free area (a) and maximum tensile stressed area (b). The cavities reported by Arioka et al are shown in (c).

**Fig. 10**—Comparison of the average number of GB defect index in 30 observed zones with error bar of standard deviation between the maximum tensile stressed area and a stress-free area for three point bent beam SCC specimens after various exposure times (14.9, 22.7 and 30.7 Ms) (4,137, 6,312 and 8,532 h) at 633 K in simulated PWR primary water.
commercial TT Alloy 690 after exposure in the simulated PWR primary water at 633 K are clearly not related to creep damage.

**D. Effect of Long-Term Heating Temperature and Time in Air and of Exposure in the Simulated PWR Primary Water with Different Hydrogen Concentrations on the GB Defect Index Number**

According to the definition of the GB defect index number described earlier, Figure 12 shows the change in the GB defect index number as a function of the heating temperature in air and cold rolling reduction ratio. Figure 13 shows the change in the GB defect index number with respect to the cold rolling reduction ratio, as a function of heating temperature in air and exposure to simulated PWR primary water with different hydrogen concentrations. Figure 14 shows the change in the GB defect index number as a function of the heating time at 673 K (400 °C) in air and cold rolling ratio.

From Figures 12 and 13, it is clear that the GB defect index number for cold rolled commercial TT Alloy 690...
increases with increasing cold rolling reduction ratio, heating temperature in air and hydrogen concentration in the simulated PWR primary water. From Figure 14, the effect of heating time at 673 K in air on the GB defect index number is not significant for cold rolled commercial TT Alloy 690 of ≤ 20 pct. However, for 30 pct cold rolled commercial TT Alloy 690, the GB defect index number definitely increases with increasing heating time at 673 K in air. It is deduced that in case of the heavily cold worked (e.g. 30 pct cold rolled) commercial TT Alloy 690, too many voids and vacancies are generated near the GB carbides so that the sizes of cavities and cracks are enlarged by longer times heating in air. (in this paper, it was defined that the cavities were agglomerated voids, voids were agglomerated vacancies or lattice defects).

E. Correlation Between Vickers Hardness or GB DEFECT Index Number and Average SCCGR in Simulated PWR Primary Water for Cold Rolled Commercial TT Alloy 690 and the Possible Cracking Mechanism

In the authors’ previous paper, it was deduced from TEM observations (as shown in Figure 15) that cavities at or near GB carbides in cold worked TT Alloy 690 are generated by shear strain due to heavy cold rolling. A high density of lattice defects is also observed.
at or near GB carbides after cold rolling, which agglomeration of lattice defects or voids near GB carbides during heating at high temperatures where lattice defects are sufficiently mobile. So, the size of cavities increases and the width of cracks enlarge due to the agglomeration of lattice defects or voids. And then, the GB defect index number for cold rolled TT Alloy 690 without stress will be increased after heating in Air.

While, it was also deduced from the analysis of Hydrogen content in the test specimens as shown in Figure 16. The hydrogen contents in the test specimens as cold rolled condition were measured as 2 to 5 ppm (as normal number of Ni base alloy), but mostly zero after heating in air (may be mostly baked out by heating in air), but the hydrogen content in the exposed specimens increased with increasing hydrogen content in the
simulated PWR primary water based on the solute hydrogen level in the simulated primary water. That is, the cavities could be stabilized by Hydrogen absorption from hydrogenated PWR primary water.

From Figures 15 and 16, the new cavities or coarse cavities can be generated by prolonged heating and also stabilized by absorbed Hydrogen.

Figure 17 shows a correlation between the Vickers hardness of cold rolled commercial TT Alloy 690 and the average PWSCCGR observed at 633 K in simulated PWR primary water. Figure 18 shows a correlation between the GB defect index number and the average PWSCCGR at 633 K in simulated PWR primary water for cold rolled commercial TT Alloy 690.

From these figures, it is clear that the average PWSCCGRs at 633 K in simulated PWR primary water for the higher than 15 pct cold rolled commercial TT Alloy 690 increase with increasing of Vickers hardness or the GB defect index number.

While the average PWSCCGR for the ≤ 10 pct cold rolled commercial TT Alloy 690 does not increase despite increasing Vickers hardness or GB defect index number, it is considered that the generation of cavities at or near GB carbides is negligible for ≤ 10 pct cold rolling (the likely upper limit of cold working level in practical components).

From these observations, it is concluded that the mechanism of SCCGR for the ≥ 15 pct cold rolled commercial TT Alloy 690 could be different from that for ≤ 10 pct cold rolled commercial TT Alloy 690.

As described in the beginning of this paper, although the TT Alloy 690 has been used as actual PWR component materials for more than 30 years in the PWR primary water environment without any SCC indications in the world, some researchers reported that the PWSCCGRs of the TT Alloy 690 are relatively large in their testing.

But, based on the above, it is considered that the reason why their PWSCC data are very large is to using the heavily cold worked TT Alloy 690 in their tests, but the TT Alloy 690 in the actual PWR components is using relatively low or non-cold worked materials.

IV. CONCLUSIONS

The objective of this study was to examine the possibility of a creep driven mechanism for PWSCC in heavily cold worked commercial TT Alloy 690. The stress dependency of the number, shape and size of cavities observed at or near GB carbides was evaluated using three point bent beam SCC specimens and reverse U-bend SCC specimens before and after long-term exposure at 633 K in simulated PWR primary water. In addition, the PWSCCGR in simulated PWR primary water and the number, shape and size of cavities observed at or near GB carbides close to and remote from growing crack tips in cold rolled commercial TT Alloy 690 were evaluated. The number, shape and size of cavities at or near GB carbides in specimens of the
been deduced. 

1. In case of heating at 633 to 748 K for about 7.2 Ms (2,000 hours), the number of the cavities at or near GB carbidies in cold rolled commercial TT Alloy 690 increased with increasing cold rolling reduction ratio and heating temperature in air. However, after heating at 633 to 693 K during about 7.2 Ms (2,000 hours) or at 748 K for 22.82 Ms (6,340 hours) in air, it can no longer be claimed that only the number of the cavities at or near GB carbidies in cold rolled commercial TT Alloy 690 increase with increasing heating temperature since not only the number of cavities, but also the shape and size of the cavities changed as a function of increasing temperature and time.

2. The shape of cavities observed in cold worked commercial TT Alloy 690 were categorized according to cavity and crack type, size, and numbers and a GB defect index has been defined on this basis.

3. No stress dependency was observed for the GB defect index number either for three-point bent beam SCC test specimens or reverse U-bend SCC test specimens. Therefore, the detected cavities at and near grain boundary carbidies in heavily cold rolled commercial TT Alloy 690 after exposure in the simulated PWR primary water at 633 K are clearly not related to creep damage.

4. The GB defect index number for cold rolled commercial TT Alloy 690 increased with increasing cold rolling reduction ratio, heating temperature in air and hydrogen concentration in the simulated PWR primary water.

5. The average PWSCCGR for ≥ 15 pct cold rolled commercial TT Alloy 690 increased with increasing Vickers hardness and GB defect index number. However, the average PWSCCGR for ≤ 10 pct cold rolled commercial TT Alloy 690 did not increase in spite of increasing Vickers hardness or GB defect index number.

6. It is likely that the generation of cavities at or near GB carbidies is negligible for ≤ 10 pct cold rolling (the likely upper limit of cold work in practical components).

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