Research on Corrosion Resistance of Steam Generator Tube

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In order to improve the reliability of PWR steam generators, we have performed research to improve the tubing material and tube-support-plate configuration, based on our wide operating experience, and have developed and verified TT Alloy 690 as the optimum tubing material and the BEC type tube-support design. In the research, we have studied the metallurgical mechanism of the alloy to improve its corrosion resistance, evaluated corrosion susceptible region quantitatively, estimated the actual environment in a steam generator and confirmed the reliability by a model boiler test over a long period. It has been verified that the steam generator with the latest design has higher reliability with respect to the corrosion resistance of tubes.

1. Introduction

The steam generator under discussion is a heat exchanger for transferring the heat of water in an nuclear reactor system (hereinafter called a primary system) in pressurized water reactor plants (PWRs) to a turbine system (hereinafter called a secondary system), which incorporates approx. 3 400 tubes (approx. 70 km total). They are exposed to high-temperature and high-pressure water while in operation. In the early history of PWR operation over a span of more than 20 years, corrosion problems of tube were exposed and sincere effort to solve the steam generator problem has been continuously made. Ongoing research and development has been advanced, based on operational experience. Its reliability has been enhanced by successively taking in the results from this effort. Further, numerous important design modifications have been employed in the latest steam generator now under construction, thereby improving performance. This, together with the replacements of the early designed steam generators which are presently underway, is thought to be able to contribute to the enhancement of the reliability of PWRs as a whole.

This report describes the results of this study, focusing attention on TT Alloy 690 tubing material (specially thermally-treated Alloy NCF 690) and quatrefoil (BEC: Broached Egg Crate) type tube-support-plate configuration. These efforts have borne fruit on the basis of many continuing studies including five power company cooperative studies on PWRs. The results of verification tests that appear in Chapter 3 especially reflect the results of a national project "Steam Generator Tubing Reliability Test[(1)]."

2. Development of TT Alloy 690 tubing material

For the initial steam generator tubing material, Ni base Alloy 600 (JIS NCF 600: 74 Ni-16 Cr-9 Fe) had been utilized. This was hardly susceptible to stress corrosion cracking (SCC) attributable to Cl-, even if sea water was mixed into the secondary system.

However, to further improve its corrosion resistance, systematic studies have been pursued on SCC in primary water and tubing corrosion in an environment which is affected by alkalis or sea water mixed into the secondary water, and developed and marketed, as a superior material, specially thermally-treated (aging treatment at 700°C for 15 hr: commonly called TT) Alloy 690 (the alloys themselves are currently standardized by JIS. JIS NCF 690: 60 Ni-30 Cr-9 Fe).

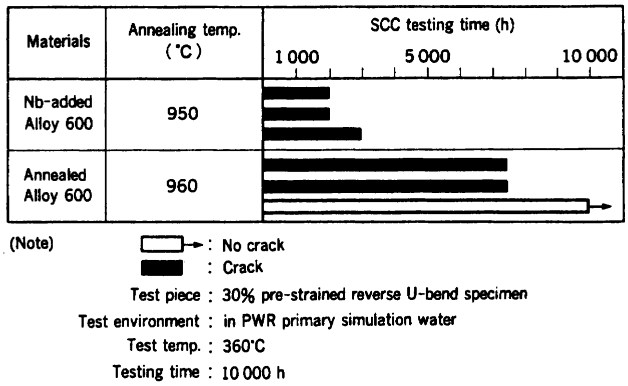

Fig. 1 Effect of Nb stabilizing on stress corrosion cracking resistance of Alloy 600 plate material
Addition of Nb did not enhance its corrosion resistance, suggesting that its susceptibility is irrelevant thereto.

2.1 Examination of SCC characteristic in high-temperature and high-pressure water

Generally, it is known that SCC resistance of austenitic stainless steel in high-temperature and high-pressure water is improved by inhibiting grain boundary precipitation of $M_{23}C_6$ (M refers to metal element) and preventing sensitization (formation of chromium-depleted zones near grain boundaries).

In order to make sure whether or not the SCC resistance is also improved by a similar mechanism with Alloy 600, effects of C, Nb, Cr and Ni etc., were examined. As a result, it turned out that reduction of C content from 0.04% to 0.015% gives no notable change in the SCC resistance, and that as shown in **Fig. 1**, Alloy 600 in which C is stabilized by addition of Nb shows, contrarily to expectation, reduced SCC resistance, as compared with the ordinary Alloy 600. Further, as shown in **Fig. 2**, fully solution-annealed Alloy 600 was found to be inferior in SCC resistance to annealed alloys.

From this evidence, the sensitivity of Alloys to SCC in high-temperature and high-pressure water is believed to be irrelevant to the formation of chromium depleted zone near grain boundaries.

On the other hand, the result of examination on the effect of Cr and Ni on the SCC resistance of Ni-Cr-Fe alloys in high-temperature and high-pressure water clarified that it does not depend on the Ni content, but that it increases with increasing Cr contents[(2)]. It was proven by metallurgical evaluation of various test materials that especially when Cr carbide which is

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coherent to the matrix is precipitated, their SCC resistance is further improved.

Among these alloys, those having semicontinuously precipitated $M_{23}C_6$ in grain boundaries, which alternately cohered to neighboring matrices as if to tie them by zippers (coherent type B)[3], had the highest SCC resistance. **(Fig. 3)** In TT Alloy 690 with Cr content as high as 27—31%, which was subjected to the aforementioned TT after full solution annealing, the $M_{23}C_6$ precipitated in grain boundaries showed the morphology of coherent type B. It is believed to have the highest SCC resistance.

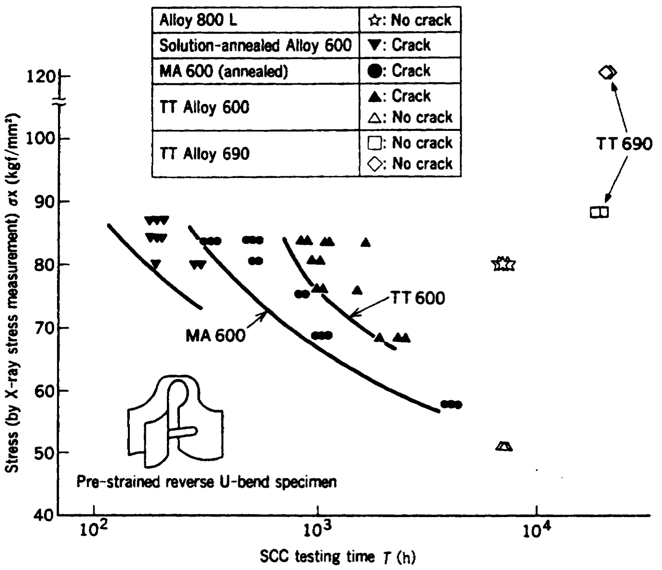


Fig. 2 Stress corrosion cracking resistance of tubing material at 360°C in temperature accelerated PWR primary water
The order of susceptibility to SCC is solution-annealed 600, MA 600 and TT 600. No susceptibility is observed in TT Alloy 690.

2.2 Characteristics of TT Alloy 690 as a steam generator material

The aforementioned TT Alloy 690 was investigated concerning its operation performance as a tubing material in comparison with conventional mill annealed Alloy 600 (MA 600), thermally-treated Alloy 600 (TT 600) and Alloy 800 (JIS NCF 800) in which C content was reduced (Alloy 800 L). The investigation was performed with emphasis placed on corrosion resistance, besides mechanical properties such as tensile property, flattening and flaring characteristics, hardness and fatigue characteristics etc. which are required for PWR steam generator tubing material, and such other general characteristics as expansion workability, weldability and applicability of nondestructive inspection etc. In regard to the corrosion resistance, investigation was pursued on general corrosion resistance in PWR primary system simulation water, SCC resistance in primary system simulation water at elevated temperatures for accelerated test, and long term SCC resis-

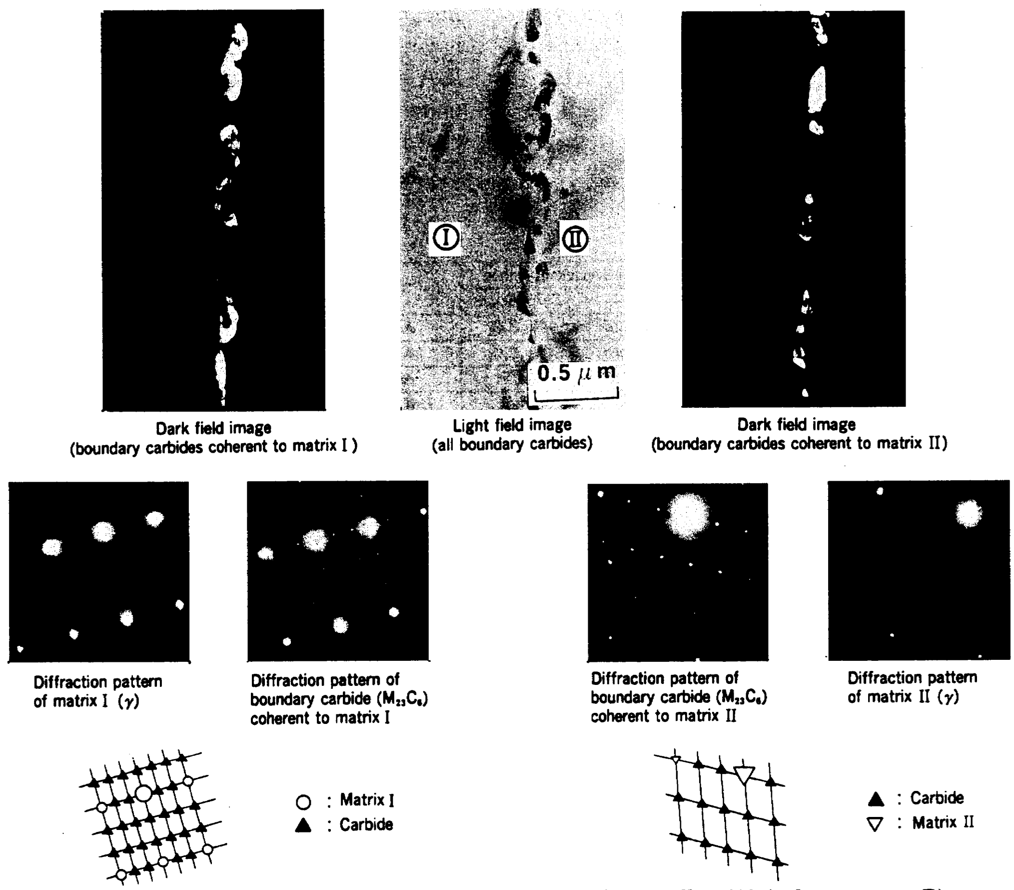


Fig. 3 Morphology and coherency of grain boundary carbides in Alloy 690 (coherent type B)
In Alloy 690 manufactured to a proper specification, carbides precipitated in grain boundaries semicontinuously are alternately coherent to respective neighboring matrices.

tance in secondary water with extremely accelerated test environment, where sea water, NaOH or the like impurities which were mixed into the secondary water were concentrated in the crevice region (clearance region between tube and tube sheet or tube support plate).

No outstanding differences were recognized in mechanical and other general properties between test sample materials. They were all found suitable as tubing materials.

However, whereas as shown in previous Fig. 2, in the primary system simulation water with the temperature raised by approx. 40°C to 360°C, an accelerated test environment, MA Alloy 600 and TT Alloy 600 show susceptibility to SCC, TT Alloy 690 in which Cr content was increased to approx. 30% was proven to have a very high SCC resistance, sustaining no SCC even in a test under extremely high stress.

From the results of the SCC test conducted in an accelerated test environment of 10% NaOH solution as the secondary water, TT Alloy 690, as compared with MA Alloy 600, TT Alloy 600 and Alloy 800 L, was proven to have higher SCC resistance and also showed high resistance to intergranular attack (IGA) that had raised problem with MA Alloy 600. A similar mechanism may be applicable to interpret the reason. Thus it was evident that materials subjected to the same TT treatment do not sustain SCC (IGA) in this environment in the region as defined by the combination of mill annealing temperature and C content, as shown in **Fig. 4**, where $M_{23}C_6$ form the coherent type B precipitation in grain boundaries.

Reflecting the above-described study result, use is made of a material having a maximal corrosion resistance obtainable through the appropriate selection of the mill annealing temperature and the C content in adapting TT Alloy 690 to the actual system.

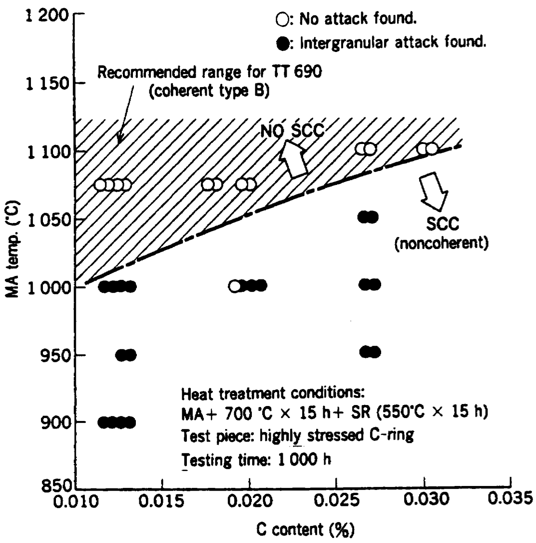
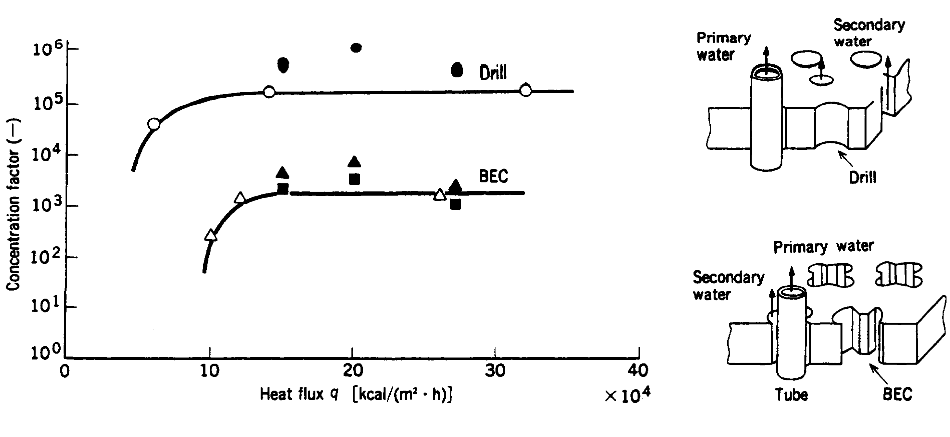


Fig. 4 Effect of mill annealing temperature, C content and grain boundary precipitates morphology on stress corrosion cracking resistance of Alloys TT 690 at 343°C in deaerated 10% NaOH solution
The region representing coherent type B and the region where the corrosion resistance in alkaline solution is high are closely in agreement.

3. Corrosion resistance of Broached Egg Crate (BEC) type tube support plate region[1]

The tube/tube support plate crevice region is a place where impurities tend to be concentrated and some steam generators having tube made of MA Alloy 600 were found susceptible to IGA etc. To deal with this problem, development of tubing materials having higher corrosion resistance and reduction of concentration factor through modification of tube support

Symbol	Tube support plate	Concentration factor evaluation method		Test press. (ata)
		Method	Bulk solution	
●	Drill	Film analysis method	$Na_2B_4O_7$	Actual press. 62.5
▲	BEC	Film analysis method	$Na_2B_4O_7$	Actual press. 62.5
■	BEC	Film analysis method	NaOH	Actual press. 62.5
○	Drill	Precip. observ. method	NaF	Atmospheric press. 1.03
△	BEC	Precip. observ. method	NaF	Atmospheric press. 1.03



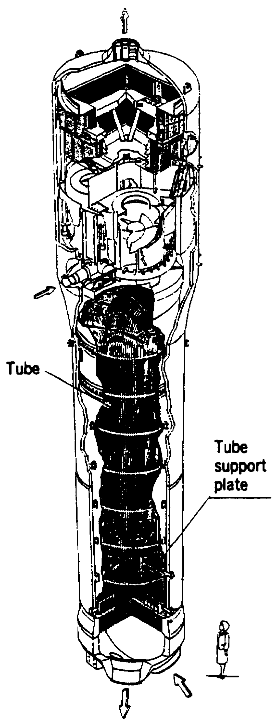


Fig. 5 Correlation between concentration factor in tube/tube support plate receive region and heat flux
Concentration factor in BEC type crevice is approx. 10^3 being lower by 1/100 than that in drill hole type, which is approx. 10^5.

plate hole configuration were sought. Then the reliability of the system is confirmed as follows:

3.1 Evaluation of concentration factor in tube support plate crevice region

In the heated surface crevice region, local concentration occurs due to the dry-and-wet phenomenon accompanying boiling, the concentration factor largely depending on the crevice configuration. In order to grasp the merit of the BEC type tube support plate which had been developed for the intended improvement, the concentration factor inside the crevice was evaluated and compared with that in the conventional drill hole type.

The concentration factor was evaluated by the two undermentioned methods:

- Precipitation observation method: Evaluate the concentration factor from NaF concentration in test water when NaF begins to undergo supersaturated precipitation inside crevice (visualized test under atmospheric pressure condition).
- Film analysis method: Determine the concentration factor by making use of the relationship between tubing surface film property and impurity concentration in test water (evaluated by film analysis after conducting the test under actual pressure condition 62.5 ata, 15 to 30×10^4 kcal/m^2 · h).

The relationship between the concentration factor in the tube-support-plate region and the heat flux is depicted in **Fig. 5**. Nearly identical results were obtained both under actual pressure and atmospheric pressure conditions. While in the drill hole type, the concentration factor runs to approx. 10^5 —10^6 under high heat flux condition, in the BEC type, it remains at about 10^3. Thus a concentration factor reduction effect of 100 times or higher was recognized.

3.2 Understanding IGA susceptible conditions in a secondary water environment

For the purpose of understanding the upgrading effect of the improved tubing material, and in addition clarifying the susceptible conditions to IGA, the following test was carried out.

Using MA Alloy 600 and TT Alloy 690 as test samples, the test was conducted in an autoclave, with the pH of the solution at 300°C and the electrode potential as parameters. The IGA susceptibility was evaluated by the existence of intergranular fracture on fracture surfaces, using the constant elongation rate test (CERT) as the test method.

The IGA susceptible conditions for MA Alloy 600 and TT Alloy 690 are depicted in **Fig. 6** with the potential and the $pH_{300^\circ C}$ as parameters. Under acidic condition, the MA Alloy 600 showed IGA susceptibility under potential condition of 200 mV or above, in contrast the susceptibility of the TT Alloy 690 was recognized only in a transpassive region of 800 mV or above. Under alkaline condition, both materials showed IGA susceptibility under the potential condition of near the active-desolution/passivation transition region, at $pH_{300^\circ C}$ 10 or higher in MA Alloy 600, and 11.3 or higher in TT Alloy 690. This results corroborates the merit of TT Alloy 690 in the improvement of IGA resistance both under acidic and alkaline conditions.

3.3 Long term test under actual system simulation conditions

In order to make integral evaluation of the reliability improvement effected by the use of improved tubing material and BEC type tube-support-plate design, long term tests were performed in a model boiler. As a test sample, use was made of combinations of tube (MA 600 and TT 690)/tube support plate

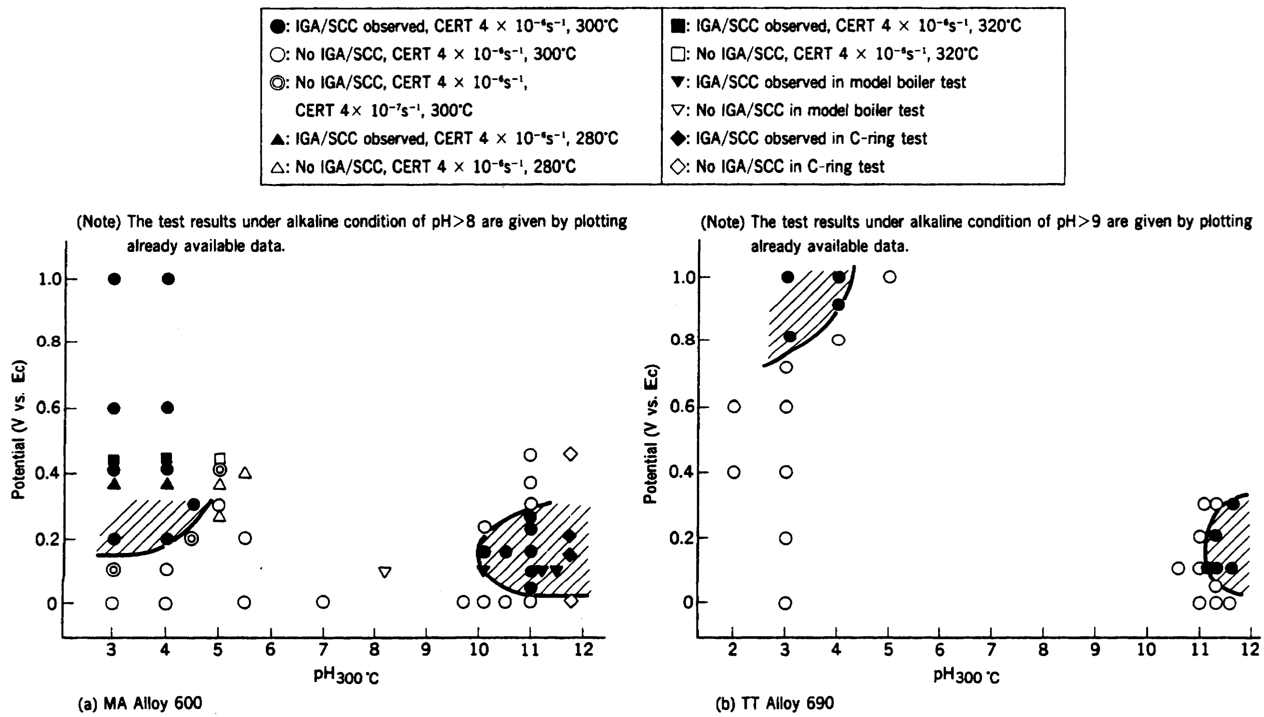


Fig. 6 IGA susceptible region of tubing materials in high temperature solutions
As the IGA susceptible regions are compared between the TT Alloy 690 and the MA Alloy 600, the regions in the former are much smaller than in the latter both on the alkaline and the acidic sides.

Table 1 Summary of model boiler test results

Tube	Tube support plate	Testing time	Destructive examination
MA 600	SB 42 drill	15 181 h	Approx. 100 μm max IGA was found.
TT 690	SB 42 drill	15 181 h	No corrosion
TT 690	SUS 405 BEC	15 181 h	No corrosion
TT 690	SUS 405 BEC	26 781 h	No corrosion
TT 690	SUS 405 BEC	33 913 h	No corrosion

(carbon steel/drill hole and SUS 405/BEC). For the test apparatus, use was made of a steam generator simulation loop which permits the actual system's operation conditions to be reproduced. In this test, for the intention of producing a corrosion accelerating atmosphere, not only the temperature was elevated, but a very small amount of alkali (to 10 ppb NaOH) was continuously added to the secondary system feed water (AVT treatment by use of NH_3 and N_2H_4) for water chemistry.

After the test, the test sample was broken, to make detailed examination. The results are presented in **Table 1**. Whereas MA Alloy 600 combined with drill hole tube support plate evidenced IGA of approx. 100μm max. depth, TT Alloy 690 combined with the same tube support plate and this alloy combined with BEC type tube support plate gave no evidence of abnormality in the tube. Comparison of the corrosive environment in the crevice region, as surmised from the NaOH concentration and the concentration factor in the bulk water inside a model boiler, with IGA susceptible condition (NaOH concentration) for each tubing material showed good agreement according to the results of this model boiler test (**Fig. 7**), attesting at the same time to the reasonableness of each element test result. It should be further noted that in the actual steam generator the Na ion concentration in the secondary side is controlled less than 1 ppb and as shown in Fig. 7, the probability of IGA initiation is very low even with MA 600/drill hole design, suggesting further margin in case of improved design.

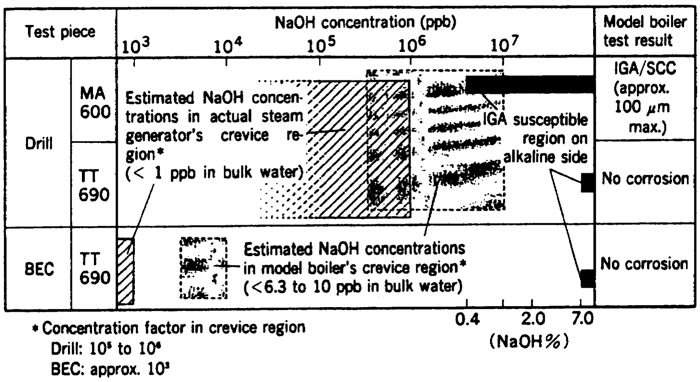


Fig. 7 Comparison between results of model boiler test and fundamental experiments
Good agreement is observed between the IGA susceptible regions estimated from combined fundamental experiment results and model boiler test results.

4. Conclusion

As described in the foregoing, the latest steam generator is provided with adequate reliability in regard to corrosion resistance of tube due to adoption of improved tubing material and improved tube-support-plate configuration and furthermore employs many improved design modifications in other respects. And further developments of steam generators for use with APWR are at present being advanced. In view of the social and economic importance of problems concerning steam generators, the accumulation of good operation experiences of steam generators is most important for recovering the confidence. Accordingly, it is believed essential to exert endeavors with major emphasis placed on continuous reliability enhancement.

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