Characterization of Korean-Made Prototypical Inconel Tube Materials for Steam Generators in Nuclear Power Plants

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ABSTRACT

Prototypical tubes of Alloy 600 and 690 (generally known as Inconel), Ni-base alloys, were fabricated by a company in Korea with a thorough process from vacuum melting to roll straight and belt polishing followed by final thermal treatment in a hydrogen atmospheric environment. The third and second prototypes of Alloy 600 and 690 materials tubes, respectively, had been manufactured and their mechanical and corrosion properties have been characterized. According to the results, the Korean-made prototypical tubes have shown to have mechanical and corrosion properties comparable to those of commercially available tubes having made by the known foreign companies.

I. INTRODUCTION

Steam Generator is one of the main facilities in nuclear power plants, whose tubes act as a pressure boundary between the primary and secondary cooling waters. Steam to rotate turbines to generate electricity is formed in the steam generators in pressurized water-cooled reactors.

Nuclear technologies in Korea have been developed very rapidly and thus Korea has developed its own nuclear power plant model design, so called, Korean Standard Nuclear Power Plant. Yongkwang units 5 and 6, and Uljin units 5 and 6 are being built on the basis of this model design. However, the main key materials including steam generator tubes are imported from foreign countries. In order for the Korean Standard Nuclear Power Plant Model to be her real technology, fabrication of the main key materials such as carbon steels for reactor vessels, Ni-base alloys for steam generator, stainless steels for reactor internals, etc. should be done by Korean technology.

For Alloy 600 and 690 tube materials, fabricating processes need three main technologies, such as, special melting (vacuum melting, and refining and remelting), working (hot forging, hot extrusion and cold rolling) and heat treatment. Korea Atomic
Energy Research Institute (KAERI) and a private steel manufacturing company in Korea have developed the whole processes for the fabrication of the tube materials in last several years. And, thus the prototypes of the Korean-made Alloy 600 and 690 tube materials have been manufactured and characterized to compare their mechanical and corrosion properties to those of the commercially available tube materials having made by the foreign companies. This paper is introducing a part of characteristics of the materials obtained so far. The characterization of the materials is still being carried out at KAERI.

II. MANUFACTURING PROCESSES

Process design for manufacturing U-bent Alloy 600 and 690 was performed by evaluating the whole sequences of the processes being used by the known foreign companies such as Sumitomo in Japan, Valinco in France or Sandvik in Sweeden. It was, however, difficult to get detailed information materials on the processes from these companies because they do not release them in public. The final processes, composed of 35 steps as shown in Fig. 1, were determined on the ground of the results obtained by the laboratory researches done at KAERI and the company.

Two different melting processes, i.e. vacuum induction melting (VIM) and electrode slag remelting (ESR), were adapted to decrease impurity residues in and to enhance hot workability of the ingot. After hot forging the ingot to a billet, it was hot extruded at 1170°C into seamless tubes having dimensions of a outer diameter of 60 mm and an inner diameter of 50 mm (a cross section reduction ratio of 94.2%), followed by primary cold pilgering (with 75 VMR) up to a reduction of 72.4% resulted in a tube having a outer diameter of 31.75 mm and 2.6 mm in thickness. After degreasing and water rinsing the cold pilgered tube, it subsequently was heat treated in a hydrogen environment at 1080°C for 9 min. Then, a secondary pilgering process was done with 25 VMR and reduced the size of the heat treated tube up to 19.10 mm and 1.08 mm in outer diameter and in thickness, respectively. The final heat treatment (in other words, mill annealing treatment) was applied to the tube at 1070°C for 8 min. in hydrogen environment. The final total length of the tube was 13 m. Fig. 2 shows U-tubes of Alloy 690 manufactured by the Korean company.

III. CHARACTERIZATION

1. CHEMICAL COMPOSITIONS

The fabricated final prototypical tubes of Alloy 600 and 690 were analyzed to figure out their chemical compositions, which were turned out to be as shown in Table 1. The table also shows the compositions specified by ASME on the nuclear grades of Alloy 600 and 690
tube materials. The notations used in this table represent as follow; S(sometimes used with C) stands for Korean made tubes and I means that the tube was fabricated by the Korean company with the ingot having been imported from INCO*. LC and HC stand for low carbon and high carbon, respectively. The last numbers in the tube notation represent the batch number (for example, 1 for first batch, 2 for second batch). According to this result, it can be seen that all the fabricated tubes by a Korean company satisfy the ASME spec. It should be noted here that the concentration of N in the tubes made in Korea from melting was analyzed to be very high, compared with the tubes made from the imported INCO Ingot.

2. MICROSTRUCTURES

Fig. 3 shows the typical microstructures of the mill annealed S690-2LC and S690-2HC tubes. Fig. 3(a) and (c) were obtained by etching them with a solution of H3PO4(40ml) + H2O(10ml) to reveal the precipitated carbides, while Fig. 3(b) and (d) show grain boundaries obtained after etching them in a Nital solution. These figures show some carbides precipitated along grain boundaries in S690-2LC, whereas intra-carbides are observed in S690-2HC due to the high content of carbon. These observations were confirmed from TEM micrographs shown in Fig. 4, as usually observed in commercial Alloy 690.

Grain sizes measured from and types of the carbides precipitated in Korea-made tubes are summarized in Table 2, which are all satisfied the ASME spec. However, the grain sizes formed in the Korean-made tubes look slightly smaller than those (about 40-50 um) usually observed in commercially available tubes fabricated by the foreign companies. This seems to be caused by low temperature or short time heat treatment. Due to this, the tensile properties of the Korean-made tubes were measured to be somewhat higher than those as usually obtained from the commercial Alloy 600 and 690 as shown in Table 3.

It has been known that heat treatment at temperature lower than the carbon solid solution temperature can induce precipitation of carbides along grain boundaries which acts as barriers to grain growth. In order to see the dependence of the grain growth on carbon contents in the alloys, two Korean-made Alloy 690 tube materials, S690-2LCMA and S690-2HCMA, were heat treated in the temperature range of 700 - 1100°C for 10 hrs. and then their microstructures were observed. According to this experiment, Cr-carbides having precipitated along grain boundaries were completely dissolved at the temperature ranges of 1020-1040°C for S690-2LCMA and 1040-1060°C for S690-2HCMA. And grain growth of these materials was observed to begin to occur steeply just above the temperature where the grain boundary carbides begin to dissolve, as shown in Fig. 5. This result represents that the grain boundary carbides are main barriers to grain growth in these alloys, too.
3. MECHANICAL PROPERTIES

ROOM TEMPERATURE TENSILE PROPERTIES

Tensile properties of the Korean-made tubes at room and high(800°C) temperatures were measured using Instron 4206 at an initial strain rate of 10-3/s under constant cross head speed. The room temperature tensile test results of the mill annealed(MA) tubes are presented in Table 3, which are all within the ASME spec. As mentioned before, the yield and ultimate tensile stresses seem to be higher than those of the commercial tubes. This result might be attributed to the small grain size of the tubes. High yield tensile strength may induce high residual stress in the tubes, which is known to result in high susceptibility to stress corrosion cracking. So, in order to increase resistance to stress corrosion cracking, the final annealing temperature should be slightly higher than that used in this case. From the tensile test results also show that there is no much difference in mechanical properties with carbon content.

HIGH TEMPERATURE TENSILE PROPERTIES

Fig. 6 represents the high temperature tensile test results of the Alloy 690 tubes tested at room temperature to 800°C. The tubes of Alloy 690 tested show very narrow scattering in the tensile properties, while as the test temperature increases, data scattering becomes slightly increased, and their yield and tensile stresses decrease. The stresses become nearly constant in a certain temperature range where the serration takes place during tensile test. For elongation, the specimens tested at around 600-700°C show low values possibly due to the weakening of their grain boundaries at these test temperatures.

EFFECT OF GRAIN SIZE ON MECHANICAL PROPERTIES

The effect of the microstructure, specially grain size, of the Korean-made tube materials was investigated in order to get proper mechanical properties(usually around 270-280 Mpa for yield stress). As mentioned previous section, the yield and tensile stresses of the Korean-made tube materials were measured to be slightly higher than those of the commercial tube ones. So, in order to get the proper values of the yield stress, the relationship between the grain size and the stresses of the tube materials was obtained as shown in Fig. 7. From this figure, it can be seen that the optimum grain size to get the needed mechanical properties would be 51 um for the Alloy 690 tube materials.

EFFECT OF THERMAL TREATMENT ON MECHANICAL PROPERTIES

Fig. 8 shows the dependence of the tensile properties of the Korean-made Alloy 690 tube materials on thermal treatment time. There is no much change in the yield and tensile
stresses of the materials with the thermal treatment time. Similar phenomenon also was observed with the materials in the variation of the tensile properties in the thermal temperature range from 700°C to 740°C, where thermal treatment has usually been done for the commercial tube materials.

**CREEP PROPERTY**

High temperature creep tests with the Korean-made tube materials were performed and the results of the Alloy 690 are represented in Fig. 9 with the Larson-Miller parameter. From this figure, it can be seen that the creep lives of the Korean-made Alloy 690 tube materials at low stress are longer than those in the INCO specifications.

**4. CORROSION PROPERTIES**

Stress corrosion cracking tests were carried out with the Korean-made tube materials in static autoclave tests or tensile test specimens for constant extension rate tests in two different environments such as simulated primary or secondary cooling waters of operating pressurized water reactor nuclear power plants. Fig. 10 shows the result of the primary water stress corrosion cracking tests with the materials under the simulated primary water conditions of operating pressurized water reactor (PWR) plants. This result represents that the PWSCC property of the Korean-made tube materials is comparable to that of the commercial tube materials. The measurement of PWSCC rates of the materials also confirmed that resistance to crack propagation of the Korean-made tube materials are similar to that of the commercial tube materials as shown in Fig. 11.

The intergranular stress corrosion cracking (IGSCC) properties of the materials in caustic environment are summarized in Table 4. This result also says that the Korean-made tube materials is on the same level with the commercial tube ones in IGSCC properties.

**IV. SUMMARY**

Alloy 600 and 690 (generally known as Inconel), Ni-base alloys, tube materials fabricated by a company in Korea with a through process from vacuum melting to roll straight and belt polishing followed by final thermal treatment in a hydrogen atmospheric environment were characterized. According to the results, the Korean-made prototypical tubes have shown to have mechanical and corrosion properties comparable to those of commercially available tubes having made by the known foreign companies.

**ACKNOWLEDGMENTS**
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REFERENCES


Table 1 Chemical compositions of the Korea-made Alloy 600 and 690 tubes (wt. %)

<table>
<thead>
<tr>
<th>Tube</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>S</th>
<th>C</th>
<th>Ti</th>
<th>P</th>
<th>O</th>
<th>N</th>
</tr>
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<tbody>
<tr>
<td>S600-1</td>
<td>15.55</td>
<td>6.98</td>
<td>0.16</td>
<td>0.04</td>
<td>0.23</td>
<td>0.002</td>
<td>0.020</td>
<td>0.28</td>
<td>0.003</td>
<td>20ppm</td>
<td>4ppm</td>
<td></td>
</tr>
<tr>
<td>S600-2</td>
<td>15.55</td>
<td>7.22</td>
<td>0.18</td>
<td>0.01</td>
<td>0.22</td>
<td>0.001</td>
<td>0.022</td>
<td>0.18</td>
<td>0.003</td>
<td>16ppm</td>
<td>9ppm</td>
<td></td>
</tr>
<tr>
<td>1600-1</td>
<td>14.99</td>
<td>8.63</td>
<td>0.17</td>
<td>0.03</td>
<td>0.23</td>
<td>0.001</td>
<td>0.024</td>
<td>0.35</td>
<td>0.003</td>
<td>12ppm</td>
<td>55ppm</td>
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<tr>
<td>1600-2</td>
<td>20.30</td>
<td>7.47</td>
<td>0.22</td>
<td>0.01</td>
<td>0.04</td>
<td>0.001</td>
<td>0.017</td>
<td>0.22</td>
<td>0.003</td>
<td>18ppm</td>
<td>257ppm</td>
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<td>1690-1</td>
<td>29.09</td>
<td>10.37</td>
<td>0.04</td>
<td>0.03</td>
<td>0.18</td>
<td>0.001</td>
<td>0.019</td>
<td>0.20</td>
<td>0.003</td>
<td>14ppm</td>
<td>91ppm</td>
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<tr>
<td>S690-2 LC</td>
<td>29.15</td>
<td>8.19</td>
<td>0.16</td>
<td>0.01</td>
<td>0.27</td>
<td>0.001</td>
<td>0.018</td>
<td>0.16</td>
<td>0.004</td>
<td>27ppm</td>
<td>271ppm</td>
<td></td>
</tr>
<tr>
<td>S690-2 HC</td>
<td>29.2</td>
<td>8.68</td>
<td>0.05</td>
<td>0.01</td>
<td>0.25</td>
<td>0.001</td>
<td>0.019</td>
<td>0.23</td>
<td>0.004</td>
<td>24ppm</td>
<td>144ppm</td>
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<tr>
<td>Sanicro 69TT</td>
<td>28.6</td>
<td>10.350</td>
<td>0.018</td>
<td>0.0890</td>
<td>0.255</td>
<td>0.0025</td>
<td>0.0023</td>
<td>0.27</td>
<td>0.008</td>
<td>0.0086</td>
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<td>UNS N66500 Min.</td>
<td>14.0</td>
<td>72.0</td>
<td>1.70</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.015</td>
<td>0.03</td>
<td>0.5</td>
<td>0.015</td>
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<td>UNS N6690 Min.</td>
<td>28.0</td>
<td>7.0</td>
<td>31.0</td>
<td>1.0</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
<td>0.01</td>
<td>0.5</td>
<td>0.5</td>
<td>0.015</td>
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Table 2 Grain sizes of and carbide types precipitated in the Korean-made Alloy 690

<table>
<thead>
<tr>
<th>Grain Size (μm)</th>
<th>Precipitates</th>
<th>Aver. ASTM #</th>
<th>Carbides</th>
<th>Nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>S690-1MA</td>
<td>34</td>
<td>6.9</td>
<td>Cr₂₃C₆ (G/B)</td>
<td>TiN</td>
</tr>
<tr>
<td>S690-2LCMA</td>
<td>35</td>
<td>6.8</td>
<td>Cr₂₃C₆ (G/B)</td>
<td>TiN</td>
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<tr>
<td>S690-2HCMA</td>
<td>36</td>
<td>6.7</td>
<td>Cr₂₃C₆ (G/B+I/B)</td>
<td>TiN</td>
</tr>
<tr>
<td>S690-1LC</td>
<td>34</td>
<td>6.9</td>
<td>Cr₂₃C₆ (G/B)</td>
<td>TiN</td>
</tr>
<tr>
<td>S690-2HCTT</td>
<td>32</td>
<td>7.0</td>
<td>Cr₂₃C₆ (G/B+I/B)</td>
<td>TiN</td>
</tr>
<tr>
<td>S690-1LT</td>
<td>36</td>
<td>6.7</td>
<td>Cr₂₃C₆ (G/B)</td>
<td>TiN</td>
</tr>
<tr>
<td>C.E. Spec. Over</td>
<td>32</td>
<td>Below 7</td>
<td>Cr₂₃C₆ (G/B)</td>
<td>TiN</td>
</tr>
<tr>
<td>Spec.</td>
<td></td>
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Table 3 Mechanical properties of the Korean-made Alloy 600 and 690 tubes.

<table>
<thead>
<tr>
<th>Spec.</th>
<th>Hardness (Hv:0.5Kg)</th>
<th>Y.S. (MPa)</th>
<th>U. T. S. (MPa)</th>
<th>Elong.</th>
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<tr>
<td>S600-1LTMA</td>
<td>178</td>
<td>330</td>
<td>677</td>
<td>34</td>
</tr>
<tr>
<td>S600-1HMTMA</td>
<td>158</td>
<td>282</td>
<td>654</td>
<td>38</td>
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<tr>
<td>S600-2MA</td>
<td>217</td>
<td>314</td>
<td>686</td>
<td>33</td>
</tr>
<tr>
<td>1600-1MA</td>
<td>211</td>
<td>300</td>
<td>718</td>
<td>33</td>
</tr>
<tr>
<td>S690-1MA</td>
<td>219</td>
<td>312</td>
<td>759</td>
<td>40</td>
</tr>
<tr>
<td>1690-1MA</td>
<td>227</td>
<td>328</td>
<td>766</td>
<td>38</td>
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<tr>
<td>S690-2LCMA</td>
<td>230</td>
<td>297</td>
<td>760</td>
<td>39</td>
</tr>
<tr>
<td>S690-2HCMA</td>
<td>229</td>
<td>300</td>
<td>761</td>
<td>40</td>
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</table>

Table 4 The comparison of IGSSC resistance of the Korean-made and commercial Alloy 600 and 690 tube materials, tested in 40% NaOH at 315°C using C-ring Specimens.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Results</th>
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<tbody>
<tr>
<td>Commercial Alloy 600 HTMA</td>
<td>Δ</td>
</tr>
<tr>
<td>Commercial Alloy 600 TT</td>
<td>X</td>
</tr>
<tr>
<td>Korean-made Alloy 600 MA</td>
<td>X</td>
</tr>
<tr>
<td>Korean-made Alloy 600 TT</td>
<td>O</td>
</tr>
<tr>
<td>Commercial Alloy 690 TT</td>
<td>O</td>
</tr>
<tr>
<td>Korean-made Alloy 690 TT</td>
<td>O</td>
</tr>
</tbody>
</table>

O : not visible, Δ : almost through wall cracking
X : through wall crack
Fig. 1  Flow diagram of the manufacturing processes of the Korean-made prototypical Alloy 690 tubes

- Vacuum Melting
- Electrode Grinding
- ElectroSlag Remelting
- Cutting Both End
- Soaking & Heating
- Press Forging
- Hammer Forging
- Stress Relieving Annealing
- Straightening
- Rough Turning
- Ultrasonic Test
- Cutting Billet
- Boring
- Radiusing
- Degreasing
- Billet Heating
- Hot Extrusion
- Roll Straightening
- Degassing/Pickling/Water Rinsing
- Cutting for Length Control
- Local Conditioning Of Outer Surface
- ID Grinding
- Beveling
- Cold Pilgering(75VMR)
- Degreasing & Cleaning
- Interstage Bright Annealing
- Cutting for Length Control
- Roll Straightening
- Beveling
- Cold Pilgering(25VMR)
- Degreasing & Cleaning
- Final Mill Annealing
- Cutting
- Roll Straightening
- Belt Polishing
- Stock

Fig. 2  Optical micrographs of the Korean-made Alloy 690 tubes. (a) Carbides and (b) grain boundaries in S690-2LC, (c) carbides and (d) grain boundaries in S690-2HC.

Fig. 3  TEM micrographs of the Korean-made Alloy 690 tubes. (a) S690-2LC and (b) S690-2HC
Fig. 4 The relationship of solid solution of intergranular carbides and grain growth after heat treatment of Alloy 690.

Fig. 5 (a) The yield and tensile strength, and (b) the elongation of the Korean-made Alloy 690 tubes with varying test temperatures.

Fig. 6 The variation of yield and tensile stresses with varying grain size of the Korean-made Alloy 690.

Fig. 7 The variations of mechanical properties with thermal treatment time.

Fig. 8 The comparison of the Larson-Miller parameters for the Korean-Made Alloy 690 and the INCO spec. for commercial Alloy 690 tubes.

Fig. 9 The comparison of resistance to PWSCC of the Korean-made and the Commercial Alloy 600 and 690.

Fig. 10 The comparison of average crack growth rates vs. the maximum stress intensity factors of the Korean-made and the commercial Alloy 600s.

Fig. 11 The Korean-made prototypical Alloy 690 U-bent tubes (R=76.2, 100.0, 150.0)

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