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# R E P O R T S U M M A R Y

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SUBJECTS	Steam generator reliability / Nuclear plant life extension / Nuclear plant operations and maintenance	
TOPICS	Steam generators Nickel alloys Tubes	Stress corrosion cracking Mechanical properties Physical properties
AUDIENCE	Engineering and technical managers	

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## **Alloy 690 for Steam Generator Tubing Applications**

NiCrFe alloy 690 is currently the material of choice for steam generator heat transfer tubing applications because of its corrosion resistance in a variety of environments. This report describes the mechanical and corrosion properties of the commercially produced alloy, which has been the subject of two international EPRI workshops.

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BACKGROUND	NiCrFe alloy 690 was developed in the late 1960s to offer improved corrosion and stress corrosion cracking resistance over other commercially available alloys. Related information has been collected and published in two EPRI workshop proceedings, reports NP-4665S-SR and NP-6750-SD. After the development activity, considerable preproduction and production testing helped prepare alloy 690 tubing for steam generator service.
OBJECTIVE	To provide a background report documenting research performed since EPRI's 1985 workshop on alloy 690.
APPROACH	The project team compiled published and unpublished data available within Westinghouse to develop a comprehensive and interpretive review of the present status of alloy 690 steam generator tubing.
RESULTS	<p>The background report covers</p> <ul style="list-style-type: none"><li>• Physical metallurgy of alloy 690</li><li>• Tube manufacturing</li><li>• Properties of produced tubing</li><li>• Steam generator manufacturing</li><li>• Corrosion behavior</li><li>• Performance of alloy 690 implants in Farley unit 1 and Diablo Canyon unit 1 steam generators</li><li>• Status of the ASME code and <i>NRC Regulatory Guide</i></li><li>• Comparative ranking of alloy 690 with alloys 600 and 800</li></ul>

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The material is presented in two reports: report NP-6997-M provides a summary of the alloy's present status, and report NP-6997-SD contains a detailed description of alloy 690 tubing.

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**EPRI PERSPECTIVE** NiCrFe alloy 690 underwent approximately 15 years of evaluation before it was selected for use in steam generator sleeves, plugs, and tubing. No other tubing material has ever received such an extensive evaluation before service. The comprehensive documentation provided in this report and the previously published EPRI workshop proceedings provide utilities with excellent background on material selection for new or replacement steam generators.

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**PROJECT** RPS408-6  
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# Alloy 690 for Steam Generator Tubing Applications

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NP-6997-M  
Research Project S408-6

Final Report, October 1990

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## ABSTRACT

This report has been prepared to provide background information for Ni-Cr-Fe Alloy 690 which is currently the material of choice for steam generator heat transfer tubing applications. Activities directed toward the qualification of Alloy 690 for these applications are summarized; this includes efforts which focused on optimization of materials procurement specifications. Emphasis is placed on research accomplished primarily in the four year period from June 1985, the time of the first EPRI Workshop on Alloy 690, through April 1989, when the second EPRI Workshop on Alloy 690 was held. The topic is treated in a broad sense, and includes review of the physical metallurgy of the alloy, tube manufacturing processes, the properties of commercial production tubing, and the corrosion behavior of Alloy 690 in environments appropriate to steam generator service.



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## Section 1

### INTRODUCTION

Alloy 690 was developed and patented by INCO Alloys International in the late 1960s and was offered as an alloy with additional corrosion resistance in a variety of environments of industrial interest. A few years later, steam generator manufacturers began consideration of Alloy 690 as a candidate tubing material. There followed a decade or more of extensive laboratory investigations, mostly corrosion studies, the results of which led many organizations to conclude that Alloy 690 was the material of choice for steam generator tubing applications. Attention then focused on the broader aspects of physical metallurgy, mechanical properties, tube manufacturing practices and controls, specification requirements, etc. - all of those aspects which required complete qualification prior to implementing Alloy 690 into production steam generator units. This led EPRI to sponsor an Alloy 690 workshop in 1985 which gathered together the available data and information from organizations around the world. Since then Westinghouse, Framatome, MHI, KWU and B&W have each manufactured steam generators using Alloy 690 tubing. It was timely, therefore, that EPRI sponsored a second international workshop on Alloy 690 tubing in April 1989. The information gathered at this latter workshop makes clear that significant progress has been made in resolving the issues and concerns raised at the earlier workshop.

Recognizing, then, that Alloy 690 is now the preferred tubing material of most steam generator manufacturers and utility customers alike and that substantial knowledge and understanding now exists with respect to most aspects of Alloy 690 tubing, it seemed appropriate to attempt a comprehensive, interpretive review of the present status of Alloy 690 for steam generator tubing applications.

To this end, extensive use is made of data and information available within Westinghouse, much of which has not been previously published. In doing this, no conscious effort is made to place Westinghouse in more favorable light than other steam generator manufacturers. Rather, the aim is to provide this previously unpublished information to EPRI and EPRI customers and to use it to provide support of the conclusions reached. Information available from other sources are also included in order to make the review as comprehensive as possible. As for the

interpretive aspect of the review, concise positions are expressed to reflect the perceived consensus opinion regarding issues and concerns which have been raised. At the 1989 EPRI workshop there was remarkably good agreement on the most important matters. Where differences of opinion persist, the issue may relate more to implementation of a goal than to the goal itself. For example, it is generally agreed that a certain microstructure is desired (the goal) but opinions differ, and reasonably so, as to how often tests should be made during production to verify that the desired microstructure is achieved (implementation of the goal). Both the perceived consensus position and alternative positions are presented where possible.

## Section 2

### COMPOSITION

Alloy 690 is nominally a nickel-chromium-iron substitutional solid solution alloy composed of about 60% Ni, 30% Cr and 10% Fe. However there are other elements present as indicated by the chemistry requirements listed in Table 2-1 for Huntington Alloys (1), SB-163 (2), Code Case N-20-3 (3) and EPRI (4) specifications.

The elements in Alloy 690 fall into several categories depending on their purpose and origin:

- Ni, Cr and Fe form the basic matrix composition and are present in controlled amounts according to the alloy design.
- Carbon, in essence, is now a minor alloy addition (minor in amount but major in importance). Thus the goal is not to reduce carbon to as low a level as possible. Not only is there a maximum limit but also a minimum limit for carbon in the EPRI specification. This carbon range (0.015-0.025%) is based on the solubility of carbon in Alloy 690, practical heat treatment considerations, the amount of carbon needed to form the desired grain boundary carbide microstructure, and corrosion studies - all discussed later.
- Mn, Si, Al and Ti are present in the alloy as a result of their use in the melting and refining practices - deoxidation, decarburization, desulfurization, etc. These elements, in combination with the melting and refining practices, effect control on tramp elements and also affect processes of deformation, recovery, recrystallization and grain growth in ways generally favorable with respect to microstructure, mechanical properties and other technological properties. Specification limits for these elements are based on the levels that actually result from generally accepted commercial melting practices.

Table 2-1

## SPECIFICATIONS FOR ALLOY 690 CHEMICAL COMPOSITIONS

<u>Element Name</u>	<u>Symbol</u>	<u>Huntington Alloys*</u>	<u>SB-163**</u>	<u>Code Case N-20-3**</u>	<u>EPRI***</u>
Nickel	Ni	58.0 min.	58.0 min.	58.0 min.	58.0 min.
Chromium	Cr	28-31	27.0-31.0	27-31	28.0-31.0
Iron	Fe	7-11	7.0-11.0	7-11	7.0-11.0
Carbon	C	0.04 max	0.15 max	0.05 max	0.015-0.025
Manganese	Mn	0.50 max	1.0 max	0.50 max	0.50 max
Silicon	Si	0.50 max	0.5 max	0.50 max	0.50 max
Aluminum	Al	-			0.50 max
Titanium	Ti	-			0.50 max
Boron	B	-			0.007 max
Nitrogen	N	-			0.05 max
Sulfur	S	0.015 max	0.015 max	0.015 max	0.010 max
Phosphorus	P	-			0.015 max
Copper	Cu	0.50 max	0.5 max	0.50 max	0.50 max
Niobium	Nb	-			0.1 max
Molybdenum	Mo	-			0.2 max
Cobalt	Co	0.10 max		0.10 max	0.015 Average with no heat to exceed 0.020

\* Nuclear Grade

\*\* Heat Analysis

\*\*\* Heat and Product Analyses



- Boron has historically been used as an additive, albeit in small amounts, to nickel base alloys to enhance hot workability. Some tubing manufacturers still adhere to this practice. Nagano, et al. (5) observed an effect of boron on the kinetics of carbide precipitation and suggested keeping the boron level as low as possible. By way of perspective, boron levels above about 0.001% are probably indicative of intentional additions. Otherwise boron is a residual tramp element.
- N, S, P, Cu, Nb, Mo and Co are tramp elements in that they serve no known useful purpose with respect to melting or manufacturing practices and the goal is to keep their levels as low as possible. Nitrogen and sulfur can be controlled by the melting practice. P, Cu, Nb, Mo and Co are controlled primarily by control of the raw materials (charge or melting stock), i.e., what goes in, stays in. Nitrogen is present primarily as TiN inclusions, and hence affects microcleanliness. Sulfur and phosphorus may segregate to grain boundaries and could be detrimental if present in excessive amounts. SB-163 places limits on Cu, apparently in anticipation that high Cu-bearing scrap might be used as melting stock. This Cu limit of SB-163 is carried over to other specifications in order to maintain compliance with ASME Code requirements. However, the actual Cu level in steam generator tubing is expected to be much less than 0.5%. Nagano, et al. (5) observed that Nb and Mo alloying additions up to several percent degraded the corrosion resistance of Alloy 690. Therefore the EPRI specification places limits on Nb and Mo so that these elements will not be present in more than residual carry-through amounts. Cobalt, of course, is of special concern because of radioactivity considerations.

## REFERENCES - SECTION 2

1. Huntington Alloys Inconel Alloy 690 Brochure, 1980.
2. Boiler and Pressure Vessel Code, Materials Specifications, Section II, Part B, Nonferrous Materials. New York: The American Society of Mechanical Engineers, July 1, 1989.
3. Boiler and Pressure Vessel Code, 1989 Code Cases, Nuclear Components. New York: The American Society of Mechanical Engineers, July 1, 1989.
4. Specification for Alloy 690 (UNS06690) Steam Generator Tubing, Electric Power Research Institute, Project S407-7.
5. H. Nagano, K. Yamanaka, T. Minami, M. Inoue, T. Yonezawa, K. Onimura, N. Sasaguri and T. Kusakabe, "Effect of Alloying Elements and Heat Treatment on the Corrosion Resistance of Alloy 690," Paper 10 in Reference 1.

### Section 3

#### TUBE MANUFACTURING

In this section are reviewed the various manufacturing steps associated with the production of thermally treated Alloy 690 tubing for steam generator applications. Individual subsections follow the manufacturing plan from initial melting through packing and shipment of the final product tubing. The descriptions presented reflect recent Westinghouse experience associated with the procurement of pilgered Alloy 690 tubing. The specific data presented are appropriate to tubing manufactured as described. Some variations are to be reasonably expected for tubing manufactured by other mills; this might be particularly true for variations in such processing steps as cold reduction, straightening, grinding and final thermal treatment.

#### MELTING

Melting practices currently being used in the manufacturing of Alloy 690 steam generator tubing include:

- AIM: Air Induction Melting
- AAM + AOD: Air Electric-Arc Melting + Argon-Oxygen-Decarburization
- VIM + ESR: Vacuum Induction Melting + Electroslag Remelting

Other combinations of primary and secondary melting might also be used; for example, AAM + ESR. The choice of melting practice involves both economic and technical considerations. Economic and technical considerations include prior experience, equipment availability, choice of starting materials (charge or melting stock), purchaser specification requirements on chemical composition and inclusions. Purchaser specifications may require that the tube mill identify the melting practice, but generally do not specify a specific melting practice. There have been no published reports claiming a superiority of one melting practice over another with respect to service performance of steam generator tubing. It should be left up to the tube mill to select a melting practice that is consistent with the purchaser's specification requirements for finished tubing.

Melt sizes are typically less than 10 tons and may be cast into several ingots. The sample for heat analysis is usually taken from the pouring stream. In the case of electroslag remelting, each ESR ingot is treated as a separate heat and the sample for heat analysis is obtained from drillings from the ingot.

#### HOT WORKING

Primary ingot breakdown is done by hot rolling in a blooming mill followed by hot rolling to round bars. Samples for inclusion tests are generally taken from this bar stock. The bars are surface conditioned, cut to appropriate length and drilled or trepanned to produce hollow billets for extrusion. Hot extrusion generally uses glass lubricant which is later removed by pickling. These extrusion hollows provide the starting material for processing to final size.

#### COLD WORKING

The extrusion hollows (sometimes called a TREX for tube reduced extrusion) are reduced to final tube size by a sequence of cold working and intermediate annealing operations. Cold working involves two or more passes (reduction steps) by pilgering or drawing (these are the main processes in current use) or a combination of pilgering and drawing. Cold drawing and pilgering operations are depicted schematically in Figure 3-1. (If both pilgering and drawing are used in sequence, the final pass would be by drawing.) The amount of reduction per pass is typically rather high for pilgering, and relatively low for drawing. The choice between pilgering and drawing involves both economic and technical considerations. One technical consideration of considerable importance to the utility customer in connection with in-service inspectability is the eddy current noise level of the tubing. As discussed later in the Non-Destructive Examination part of this section, drawn tubing typically shows lower noise level than pilgered tubing. However, there are many factors to consider in addition to noise level. Any given tubing manufacturer will no doubt have the potential capability to produce either drawn or pilgered tubing but each manufacturer typically optimizes and standardizes a given practice for a given alloy based on industry specification requirements.

#### INTERMEDIATE ANNEALING

As just discussed, two or more cold working steps are used in reducing the hot extruded tube hollows to final tube size. The material is annealed in between these steps to soften it so as to permit additional cold working. This intermediate annealing is done in a continuous belt furnace (i.e., the tubes move slowly but continuously through the furnace as opposed to a stationary batch

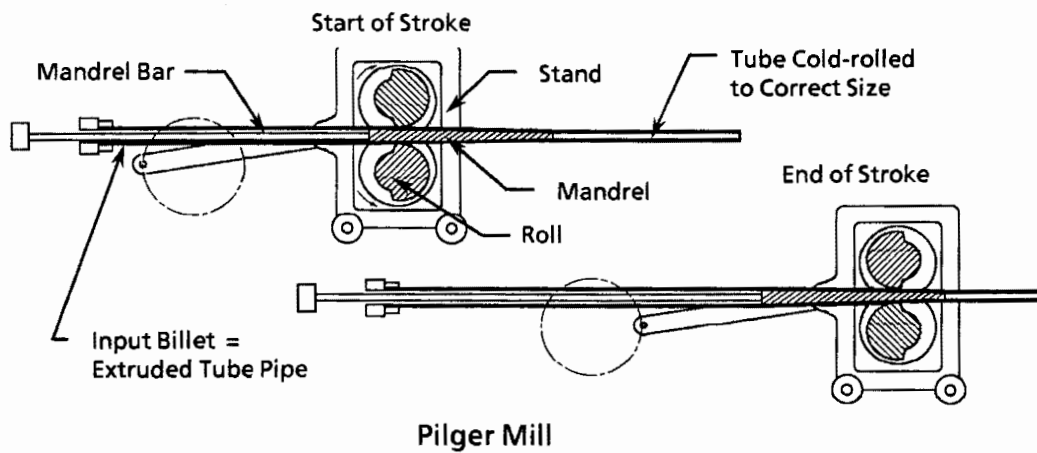
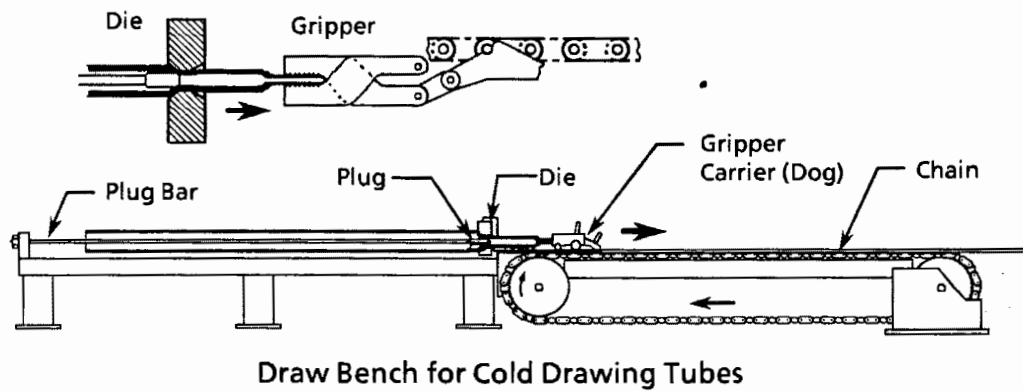


Figure 3-1. Schematic illustrations of equipment for cold drawing (top) and pilgering (bottom) steam generator tubing.

operation) at a temperature of typically 1100°C in either an air or hydrogen atmosphere. Following intermediate annealing the tubing is pickled, cleaned and surface conditioned as necessary prior to the next cold working pass.

#### FINAL MILL ANNEALING

Final mill annealing is an extremely important manufacturing operation as it very significantly affects the microstructure and properties of the finished tubing. It is this stage and subsequent stages of the tube manufacturing process where most specification requirements apply. Mill annealing is done as a continuous process as opposed to a batch process. A number of tubes - which may be anywhere from 4 to 20 or more depending on the manufacturer - lying side by side on a conveyer pass through the furnace at a constant speed, typically a few feet per minute. The most important process parameters are temperature, time at temperature, heating and cooling rates and furnace atmosphere.

#### Temperature

The mill annealing temperature is selected so as to take most of the carbon initially present as carbides in the final cold worked tubing into solid solution. This temperature is dependent on the carbon content as shown by the carbon solubility curve discussed in Section 2. Over the years, the mill annealing temperature has been gradually pushed higher and higher to ensure proper response to subsequent thermal treatment (microstructural control) with the associated enhanced corrosion resistance. For the relatively narrow range of carbon required by the EPRI specification a single peak mill annealing temperature is adequate. Today there is general agreement within the industry that this temperature should be above 1040°C and preferably above about 1060°C (1940°F), with the maximum temperature being limited only by other requirements such as grain size and mechanical properties of the finished tubing. It is further desired to control the range of the mill annealing temperature in order to promote uniformity of product with a narrow dispersion in properties. There are two different but related aspects to this temperature range control. Recognizing that there will exist a radial as well as the designed axial temperature gradient in the furnace, a limit is placed on the maximum difference in temperature between the hottest and coldest tube passing through the furnace. This limit is 20°C (36°F) in the EPRI specification. This limit can be met with existing mill annealing furnaces but tube manufacturers tend to interpret the requirement as applying to any given furnace load but not to all tubes over a long production run. For example, suppose the coldest and hottest tubes for a given run, or for all runs in a given week,

were 1060°C and 1075°C, respectively. Months later suppose the temperatures were 1075°C and 1090°C. For both local periods of time the temperature difference was only 15°C but over the long run it was 30°C. The reason for this is that the furnace is periodically shut down, e.g., over a weekend, and stabilizes at different temperatures after re-startup. Once stabilized, even small adjustments in temperature are time consuming. Hence tube manufacturers prefer a temperature range limit of  $\pm 20^\circ\text{C}$  over the long run. This would still lead to a very high percentage of all tubes being annealed at a mean temperature plus or minus 10°C. This is not unreasonable since only a minimum, not a maximum, mill annealing temperature is specified and there are stringent requirements on the finished tubing with respect to mechanical properties and microstructure.

### Time

Closely related phenomenologically with temperature is time at temperature. Figure 3-2 shows an example of a temperature-time plot provided by Sandvik Steel for an Alloy 690 mill annealing production run made for Westinghouse. This example is for a particular loading of tubes on the conveyer, conveyer speed and furnace temperature profile. During production the furnace temperature was monitored continuously whereas the tube metal temperature was measured periodically - in this case, one tube per lot - by thermocoupling a tube. The EPRI specification requires a minimum holding time of 2 minutes above the minimum metal temperature of 1060°C. For the example in Figure 3-2, the peak metal temperature was 1085°C and the times above selected temperatures were approximately 1 minute above 1080°C, 2 minutes above 1075°C, 3 minutes above 1060°C and 3 2/3 minutes above 1040°C. Though the specification requirements were met in this example, it must be recognized that narrow limits on peak temperature and minimum holding time present a difficult combination for any tube manufacturer to guarantee over a long production run. For the production run represented in Figure 3-2, the contract specification called for 1 minute holding time above a minimum metal temperature of 1040°C but with the tube manufacturer to determine and propose for approval the actual parameters to be used in production based on all specification requirements. The parameters selected were: 1090  $\pm$  20°C furnace temperature, 1080  $\pm$  20°C metal temperature, 1 minute holding time. These parameters, though still not easy to meet, gave the tube manufacturer the necessary flexibility for production and yielded excellent results. For example, peak metal temperatures based on over 200 thermocoupled tube tests varied by only 16°C over one 4 month long production run.

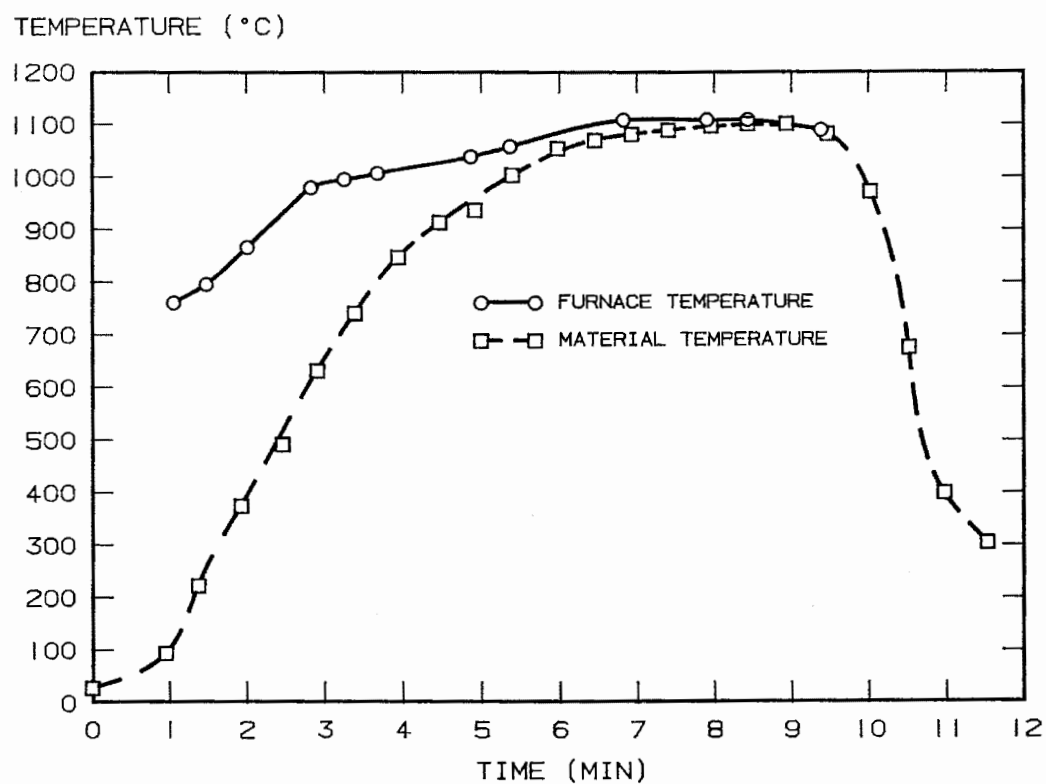


Figure 3-2. Temperature vs. time history for a typical mill annealing operation for production Alloy 690 tubing.



### Heating and Cooling Rates

The heating and cooling rates shown by the example in Figure 3-2 are reasonably typical of industrial practice but the specific rates shown are unique to the particular furnace design, including furnace temperature profile and cooling features, and the tube loading and conveyer speed actually used. There appears to be general agreement within the industry that there is no need for specification control limits on heating rate. This rate is known approximately prior to production. It is acceptable and cannot vary by much during production. Concern about the cooling rate has a more rational physical basis in that, for tubing that will be subsequently thermally treated, it is desired that the cooling rate be sufficiently fast to minimize carbide precipitation during cooling from the mill anneal temperature. For the example shown in Figure 3-2, it was required that the tube cool from the minimum required mill annealing temperature (1060°C) to below 500°C in less than 3 minutes. As shown, the actual time was about 1 minute. The EPRI specification does not specify limits for either heating or cooling. This is a reasonable position in view of the relatively slow kinetics of carbide precipitation in Alloy 690, as discussed in Section 2, and the microstructural controls on finished tubing. If a cooling rate limit is desired in the purchase specification, it should not be so tight as to unduly restrict the tube manufacturer. For cooling between the annealing temperature and 500°C, a time limit of 3 or even 5 minutes is adequate to ensure process control.

### Atmosphere

All steam generator tubing manufacturers perform final mill annealing in a flowing dry hydrogen gas atmosphere. This atmosphere protects the tubing from harmful environmental interactions. Figure 3-3 (1) shows a plot of dew point versus hydrogen gas temperature for the chromium-chromium oxide equilibria. The dew point, in effect, is a measure of the oxygen concentration in the hydrogen which could cause oxidation or reduction. When the dew point-temperature combination is above or below the line, oxidation or reduction, respectively, occur. As illustrated by the curve, the dew point required to maintain reducing conditions decreases with a decrease in temperature. During the mill anneal operation, the dew point must be low enough to be reducing at the mill anneal temperature and to minimize oxidation during fast cooling of the tubes. Through the years, tube manufacturers have found that a hydrogen dew point of -40°C is adequate for bright annealing; the tubes go in bright and come out bright. If the dew point is not low enough the tubes will come out discolored. Thus, a reasonable position with respect to specification requirements would be to simply specify bright annealing

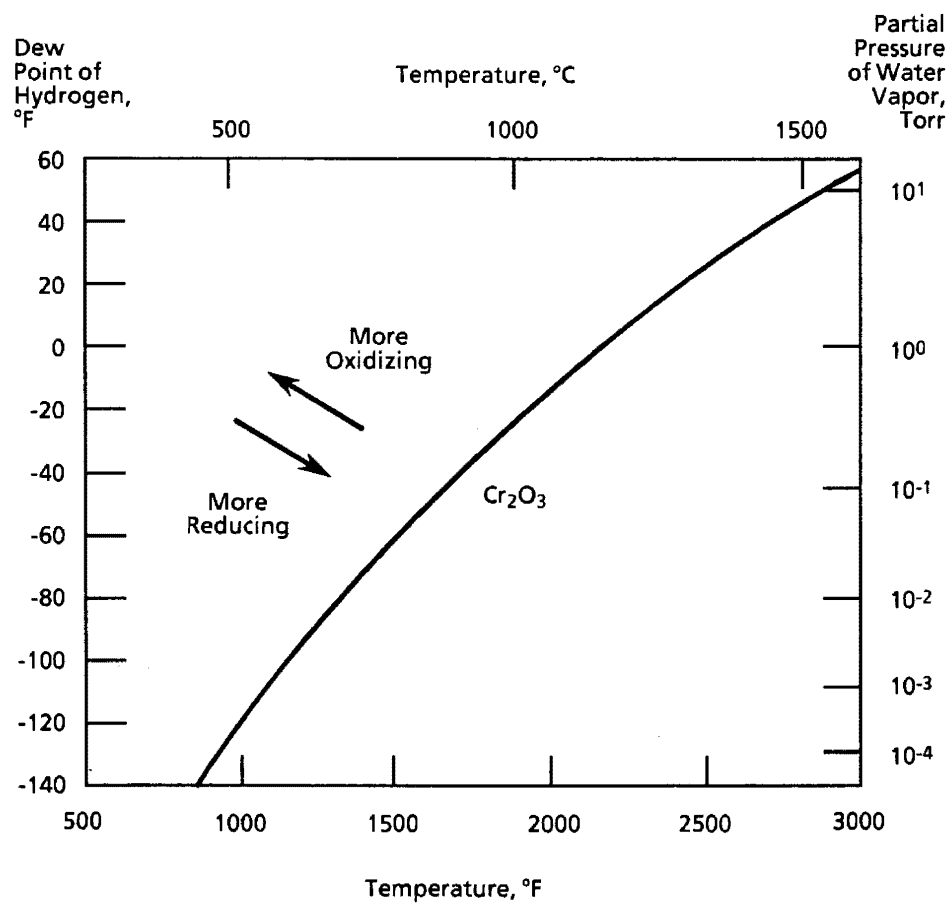


Figure 3-3. Chromium-chromium oxide equilibria in a pure hydrogen atmosphere.

in a dry hydrogen atmosphere and require that the annealed tubing meet visual discoloration acceptance standards. This leaves it up to the tube manufacturer to use hydrogen with an adequately low dew point.

#### Mill Annealed Properties

The final mill annealing operation determines the grain size of the finished thermally treated tubing and has a significant influence on the mechanical properties of the finished tubing. Section 5 presents the properties, including grain size and tensile properties, of finished production tubing made to specification requirements essentially the same as in the EPRI specification. Here the mechanical properties of that same production tubing are presented but for the as-mill annealed (nominally 1080°C) condition. Figure 3-4 (a, b and c) shows histograms for room temperature yield strength, ultimate strength and elongation for the production tubing. As discussed in Section 8, the minimum yield strength requirement for ASME Code authorized Alloy 690 tubing is 40 ksi (275 MPa). Notice in Figure 3-4a that there is virtually no margin between the observed yield strength and the 40 ksi minimum. Thus, a tubing manufacturer would be reluctant to guarantee the minimum yield strength requirement - unless compensated for the risk - for as-mill annealed tubing if the tubing had to be manufactured to the controls placed on this tubing (or those in the EPRI specification). However, as discussed later, the finished thermally treated tubing is considerably stronger. The as-mill annealed ultimate tensile strength and elongation exceed the ASME Code requirements (80-85 ksi ultimate strength and 30% elongation) by a considerable margin.

#### STRAIGHTENING

The tubing coming out of the mill annealing furnace is usually crooked or warped and must be straightened. Various straightening machines are in use. Figure 3-5 depicts schematically a six and a nine roll rotary straightener. The tubing necessarily must be plastically deformed (cold worked) to some extent in order to straighten it and this cold work increases strength and induces residual stresses. There has always been concern about the increase in yield strength due to straightening. Supplementary Requirement S7 of SB-163, for example, states: "No additional cold working over and above that normally required for these alloys shall be used in order to meet the higher yield strength". As previously discussed (Figure 3-4a), for a high mill annealing temperature the margin between the as-mill annealed yield strength and the required 40 ksi minimum yield strength is unacceptably low from a tube manufacturer's point of view if that was the final

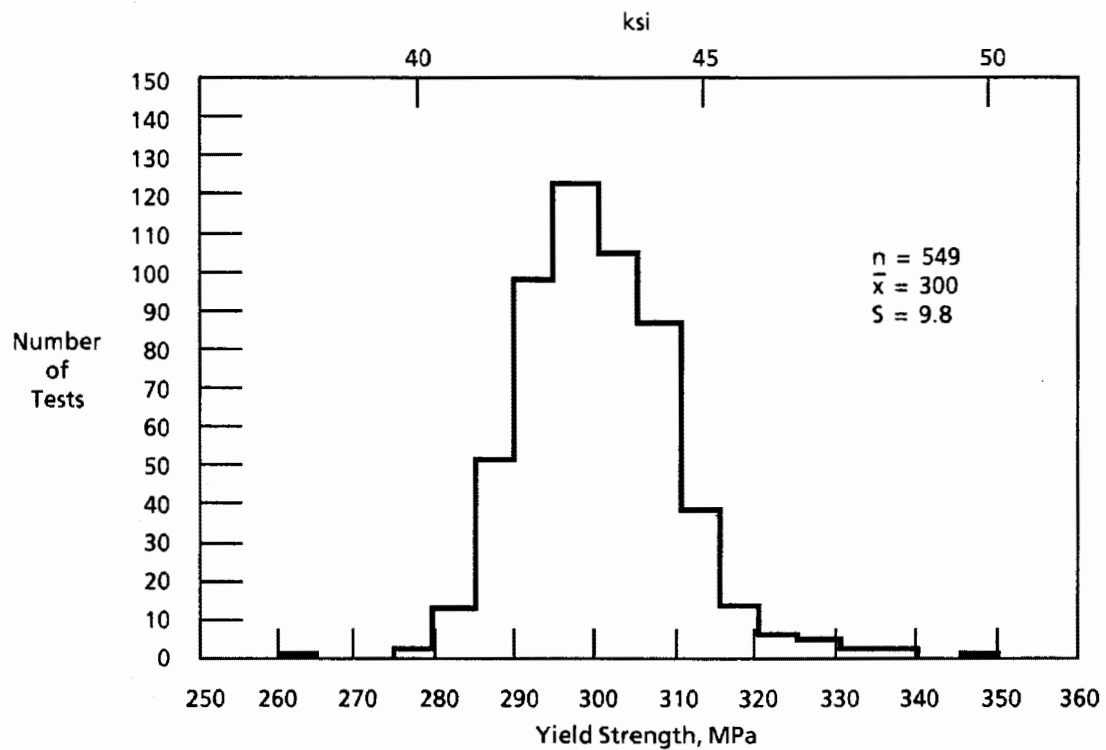


Figure 3-4a. Tensile yield strength data for as-mill annealed Alloy 690 production tubing.

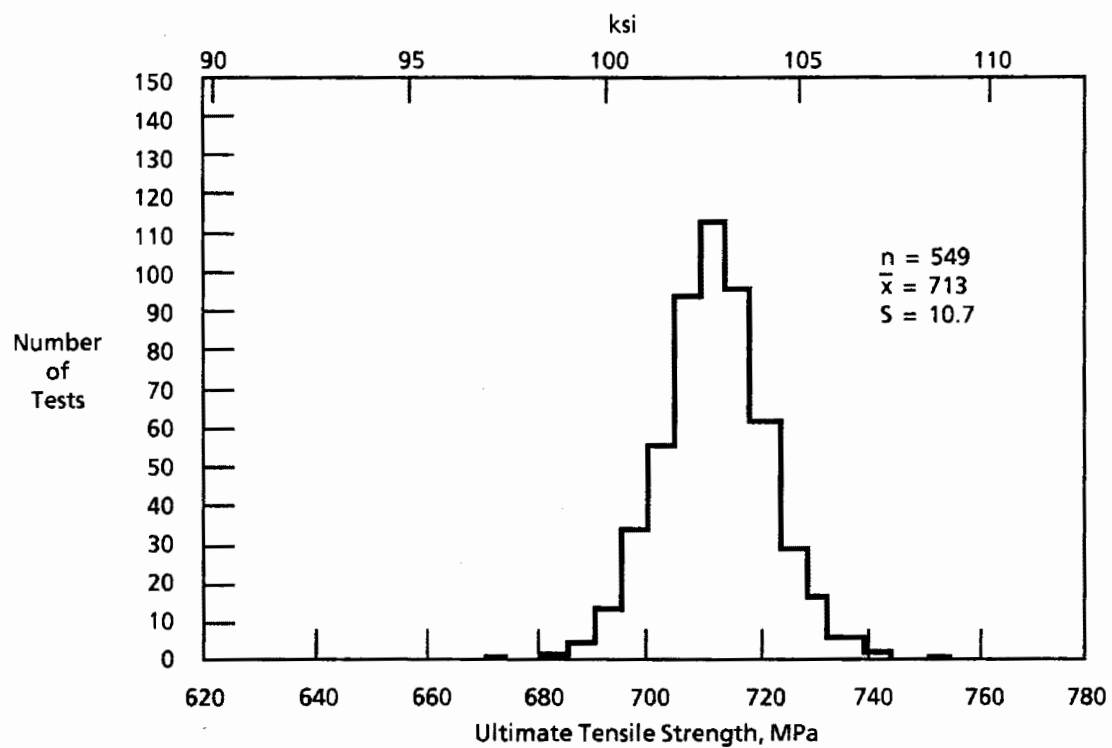


Figure 3-4b. Ultimate tensile strength data for as-mill annealed Alloy 690 production tubing.

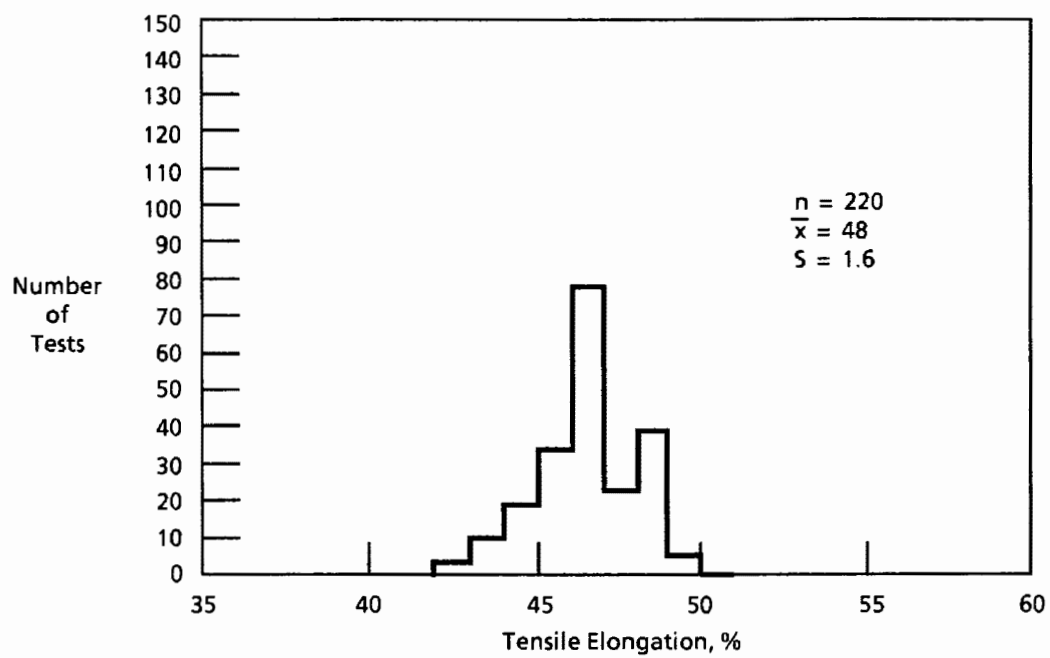


Figure 3-4c. Tensile elongation data for as-mill annealed Alloy 690 production tubing.

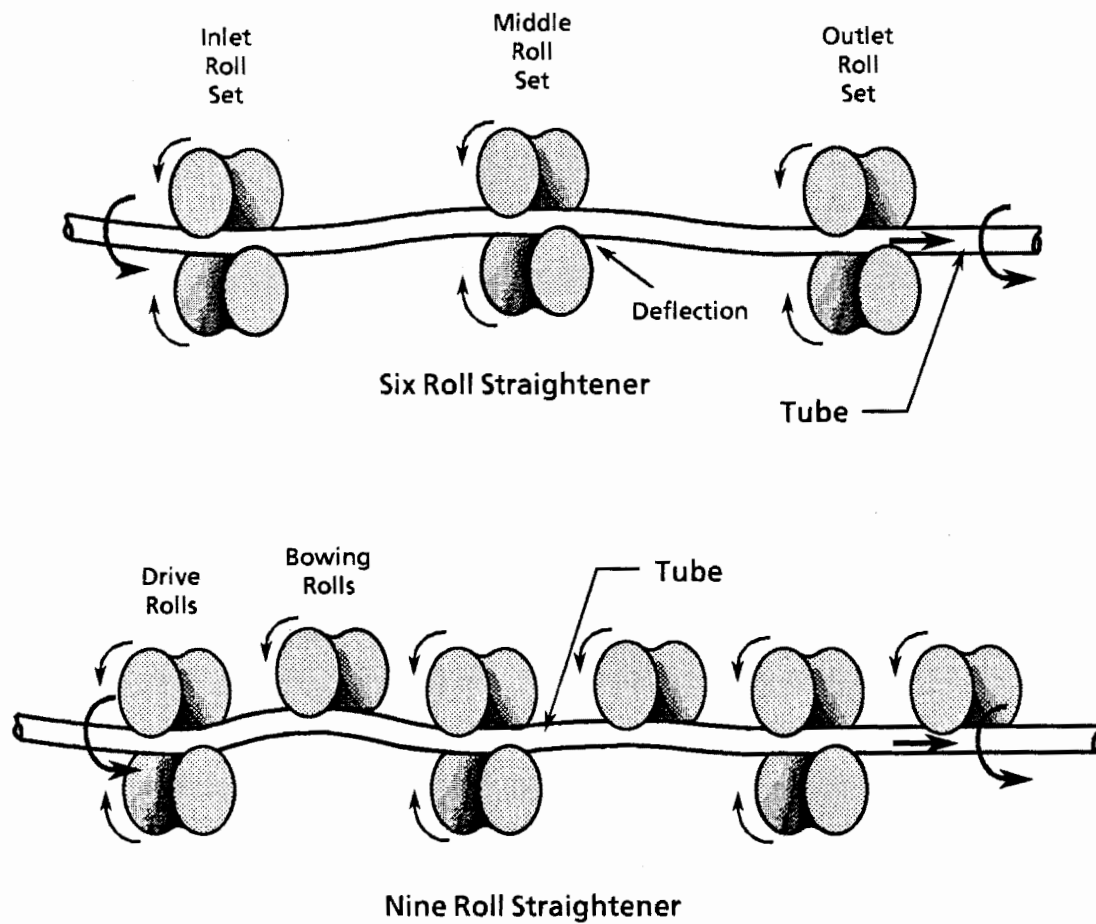


Figure 3-5. Schematic illustration of six and nine roll rotary straighteners.

strength of the finished tubing. However, the tube manufacturer knows that the strength will be increased by straightening, and counts on it, but does not, and need not, intentionally boost the strength by straightening any more than the minimum necessary to straighten the tube.

#### SURFACE GRINDING

Following straightening, the tubing is surface ground on the OD by passing the tubes through a series of graded (coarse to fine) abrasive belts or wheels. This operation is variously called: belt grinding, though not always done on belts; centerless grinding, though not done with hard disk wheels as usually used in a machine shop; or polishing, though not done for the purpose of smoothing or brightening the surface. Whether paper or cloth belts or impregnated hard rubber wheels, the abrasive particles are usually aluminum oxide or silicon carbide. In the very early days of steam generator tubing manufacturing, surface grinding the OD was considered necessary to ensure freedom from adverse surface conditions due possibly to pickling, oxidation, carburization, decarburization, etc. Some tubing manufacturers reasoned that if OD grinding was necessary then some such operation should be used on the ID also and therefore instituted the practice of cleaning up the ID by routinely grit blasting the ID after mill annealing. With present day manufacturing controls, particularly bright annealing, the need for OD surface grinding has been questioned. However, the practice is not likely to be discontinued. Steam generator manufacturers typically require removal of a minimum of either 1/2 or 1 mil per surface, which incidentally generates up to 1 ton of grindings per steam generator tube bundle.

#### THERMAL TREATMENT

Thermal treatment enhances the overall corrosion resistance of Alloy 690 relative to the mill annealed condition by developing the desired microstructural condition described in Section 2 and by reducing the residual stresses from straightening and surface grinding. The temperature range for thermal treatment of Alloy 690 is basically a carryover from prior experience with thermal treatment of Alloy 600. Different specifications specify slightly different time-temperature parameters; some examples are:



<u>Specification</u>	<u>Temperature Range</u>				<u>Minimum Holding Time</u>
	<u>°C</u>	<u>ΔC°</u>	<u>°F</u>	<u>ΔF°</u>	
EPRI	704-726	22	1300-1340	40	5 hrs
Framatome	705-725	20	1301-1337	36	5 hrs
Westinghouse	715-732	17	1319-1350	31	10 hrs

The temperature range in a given specification may be based more on the temperature control capability of a given tube manufacturer's thermal treatment furnace, or sheer precedent - this is the way it has always been done - rather than on any precise knowledge of the upper and lower bounds required to give the desired result. Any temperature within the total range of all of the above specifications is generally considered adequate to develop the desired microstructure, with no significant effect on mechanical or other properties.

The holding time required at the thermal treatment temperature for Alloy 690 is shorter than the 10 to 15 hours typically used for Alloy 600. The issue with respect to holding time is partly an economic concern; tube manufacturers obviously prefer a shorter holding time, primarily to coordinate the heat treatment cycle with day-to-night manpower shift changes. As discussed in Section 2, five hours is generally considered adequate, with ten hours merely being conservative. Most specifications, as with the EPRI specification, require that, once thermally treated, any tubing which must be re-straightened or re-surface ground must be re-thermally treated.

The EPRI specification limits the combined cumulative holding time for thermal treatment plus U-bend stress relief to 35 hours. This too is a carryover from experience with Alloy 600. The basis of 35 hours as the limit is somewhat arbitrary. It guards against excessive holding time which could possibly cause carbide growth and agglomeration while allowing the tube manufacturer to re-thermal treat and recover tubes that have to be reworked. Re-thermal treatment is seldom necessary. For a 10 hour holding time, as in the Westinghouse specification, the 35 hour limit would allow two (2) re-thermal treatment cycles (3 cycles total). The need for more than three (3) cycles would imply that something is wrong and would be prohibited simply as a matter of general principle. Framatome requires a minimum holding time of 5 hours, and therefore limits the cumulative time to 25 hours (2).

It might seem advisable to standardize the thermal treatment parameters within the industry but this would seem to be unwarranted. These details should be left up to the discretion of the steam generator manufacturer.

Concerning the effect of re-thermal treatment on mechanical properties, Table 3-5 summarizes the results of special tests run by Sandvik for Westinghouse using tubes from ten (10) different production lots of Alloy 690 tubing. Note that the production tubing itself was not re-thermally treated; only the test specimens. (None of the production tubing discussed in Section 5 was re-thermal treated.) The results show that re-thermal treatment has no significant effect on mechanical properties. The same tubes were also evaluated with respect to grain size, corrosion rate per ASTM A-262 Practice B (Streicher Test), surface roughness and microstructure. For all tubes, the grain size was ASTM No. 7 to 7.5; the corrosion rate was 0.026 to 0.030 mm/year; the surface roughness was 16 to 18 microinch Ra on average for the OD and 6 to 7 microinch Ra on average for the ID; and all microstructures were the same and in perfect agreement with the Westinghouse standard.

The current major steam generator tubing manufacturers perform thermal treatment and stress relief of U-bends in specially designed and constructed vacuum furnaces. These vacuum furnaces were first introduced into production simultaneously with the introduction of thermal treatment of Alloy 600 in the mid-1970s, and to many people the terms thermal treatment and vacuum thermal treatment are synonymous. The EPRI specification does not mandate a vacuum furnace, only that the thermal treatment be done in a protective atmosphere. This opens the way for tubing manufacturers who do not have a vacuum furnace (a multimillion dollar investment) to compete in the steam generator tubing market. Similarly, some tubing manufacturers have initiated efforts to develop quality alternatives to conventional thermal treatment. One option is to control the cooling rate from the mill annealing temperature so as to develop the desired microstructure (carbide precipitation), thereby eliminating special thermal treatment altogether. Another option is to mill anneal and then give a short time, high temperature thermal treatment, e.g. 10 minutes at 1600°F, in a hydrogen atmosphere (3).

The EPRI specification does not specify heating and cooling rates for thermal treatment since heating and cooling rates are not generally considered to be important with respect to the resulting microstructure. The tubing manufacturer obviously wants to minimize the cycle time but must control the heating and cooling

Table 3-1

EFFECT OF RE-THERMAL TREATMENT ON MECHANICAL PROPERTIES  
OF ALLOY 690 TUBING

Thermal Treatment <u>Cycle, Hours</u>	Yield Strength			Ultimate Strength		
	MPa			MPa		
	<u>Min</u>	<u>Max</u>	<u>Avg</u>	<u>Min</u>	<u>Max</u>	<u>Avg</u>
10	333	350	343	720	741	731
10 + 10	333	350	343	722	739	731
10 + 10 + 2	333	351	341	722	738	729

rates so as to prevent dimensional distortion and to maintain a uniform temperature distribution throughout the furnace. Heating and cooling are done under vacuum, or cooling may be accelerated by back-filling with an inert gas, so as to prevent oxidation, which is readily detectable by discoloration of the tubing.

### REFERENCES - SECTION 3

1. N. Bredzs and C. C. Tennenhouse, "Metal-Metal Oxide-Hydrogen Atmosphere Chart for Brazing or Bright Metal Processing," Welding Journal Supplement, May 1970.
2. G. Perrat, M. Martinovitch and D. Lafourcade, "Procurement Specifications," presented at the Alloy 690 Workshop, New Orleans, LA, April 12-14, 1989, to be published by EPRI.
3. J. R. Crum, K. A. Heck, T. M. Angeliu and M. A. Cordovi, "A New Thermal Treatment for Alloy 690", presented at the Alloy 690 Workshop, New Orleans, LA, April 12-14, 1989, to be published by EPRI.



## Section 4

### TUBING MANUFACTURERS

There are many manufacturers of seamless tubing around the world, but only three are presently active in the production of heat transfer tubing for commercial nuclear steam generators: AB Sandvik Steel in Sandviken, Sweden; Valinox, of the French Vallourec Group, in Montbard, France; and Sumitomo Metals Industries, Ltd. in Amagasaki, Japan. Each of these companies has extensive background experience, accrued over many years, in the manufacture of Alloy 600 tubing, and have recently acquired significant experience in the manufacture of Alloy 690 tubing. Table 4-1 summarizes the Alloy 690 production experience.

#### PRE-PRODUCTION QUALIFICATION PROGRAMS

With the closing of the steam generator tubing section of the Westinghouse Specialty Metals Division plant in Blairsville, PA in 1984, Westinghouse initiated a pre-production qualification program to establish new suppliers of tubing for Westinghouse steam generators. This program served not only to establish acceptable suppliers but also to develop detailed materials procurement specification requirements, manufacturing practices and controls.

Initially, potential tubing suppliers from around the world were invited to attend an orientation and program review meeting, and were asked to respond with an expression of interest. Most suppliers withdrew, either immediately or eventually, from further participation for various reasons; typically, lack of equipment capability, lack of experience with the stringent requirements on steam generator tubing, or scheduler restraints. Only Sandvik and Valinox completed the full qualification program, and at this time both Sandvik and Valinox have been formally approved as suppliers of heat transfer tubing for Westinghouse steam generators.

In view of the production experience which now exists (Table 4-1) and the information presented throughout this report, presentation here of the full details of the pre-production qualification program is not warranted. Hence, a brief description is presented below of the nature and scope of the program with some mention of what are judged to represent significant accomplishments of that effort.

Table 4-1

## TUBING MANUFACTURERS' EXPERIENCE WITH ALLOY 690

<u>Manufacturer</u>	<u>Tube Size OD, Inches</u>	<u>Number of Tube Bundles</u>	<u>Dates of Manufacturing</u>
Valinox	3/4	25	1985-Present
	7/8	5	
Sandvik	7/8	8	1987-1988
	3/4	3	
	1 1/16	4	
Sumitomo	7/8	16	1988-Present



The program was conducted with active participation of the Central Electricity Generating Board (CEGB) of Great Britain in preparation for the purchase of tubing for the steam generators for the Sizewell B nuclear power station. Quality assurance audits were conducted of the suppliers quality assurance programs and software documentation practices. The materials specifications were prepared and issued, and procedures were prepared covering all stages of manufacturing, inspection and testing, from melting through packing for shipment. Pilot size production runs consisting of approximately 50 tubes each of Alloys 600 and 690 were made by both Sandvik and Valinox. The tubing was nominally 11/16 inch OD by 0.040 inch wall thickness; full-length U-bends for Rows 1, 3 and 11 of Westinghouse Model F steam generators were included in this pilot production.

Frequent source inspections were conducted by Westinghouse and the CEGB, including inspections by a third party inspection agency (Lloyds of London). Thus the tubing was manufactured, inspected and tested in full compliance with all specification requirements in the same manner as if it were production tubing. In addition there were various special inspections and tests not normally included in materials specifications. For example, hardness and residual stress tests and extra dimensional inspections of the tube hollows (for eccentricity) and the straight tubes before and after mill annealing, after straightening, and after surface grinding, were also performed. The success of the program led to unequivocal qualification of Sandvik and Valinox as acceptable suppliers of tubing for Westinghouse steam generators.

The results from the program also led to refinements of the materials procurement specifications with respect to such features as final mill annealing practice, controls on pilgering and straightening, in-service-inspection eddy current noise level testing and acceptance criteria, and finalization of microstructural acceptance criteria. Thus the program led to a final Alloy 690 material specification essentially identical with the current EPRI specification and provided assurance that the specification requirements could be met.

The EPRI specification identifies a supplementary requirement option for a pre-production trial tubing qualification program; this is intended to provide assurance that the manufacturing parameters selected for production will in fact yield a uniform product in compliance with all aspects of the specification. The program outlined is not trivial, being both expensive and time consuming. No issue can be raised with either the spirit or intent of the program, but the actual need for such a program depends on the circumstances. If the steam generator

manufacturer (who actually places the order with the tubing supplier) has already qualified the vendor and the tubing produced by the vendor, repeating the pre-production trial tubing qualification program over and over for successive contracts is judged unnecessary.

## Section 5

### STEAM GENERATOR MANUFACTURING

#### PRODUCTION UNITS WORLD-WIDE

The steam generators which have been built and those now planned to be built using Alloy 690 tubing are identified in Table 6-1. The table includes information about the tubing manufacturer, the steam generator manufacturer, the utility customer, plant name and site, and the start-up date, actual or planned. Thus, 64 Alloy 690 tubed steam generators have been built to date or are planned and 11 of these at three sites are now in service with others soon to go on-line.

#### MANUFACTURING OPERATIONS

Steam generator manufacturers are necessarily concerned about any change in tubing material and must assess the possible consequences of such a change on the tubing related manufacturing operations. Since the mechanical and physical properties and tubing dimensions are similar for Alloy 600 and Alloy 690 it was not expected that a change from Alloy 600 to Alloy 690 tubing would require any change in the manufacturing operations and generally this has been the case. The details of the various manufacturing operations vary from one steam generator manufacturer to another but the common general features suffice for purposes of the present discussion.

#### TUBE INSERTION

The ease with which tubes can be inserted through the support plates and tubesheet depends only on the OD dimension of the tubing and the diameter of the holes in the support plates and tubesheet and their alignment. The Westinghouse experience is that there is no difference between Alloy 600 and Alloy 690 with respect to propensity for scratching of the tubing during handling and tube insertion. Thus, with respect to scratching, the OD surface of Alloy 690 appears to be neither harder nor softer on average than the surface of Alloy 600. Vickers 1000 gram hardness tests made on the OD surface gave a hardness of 160.4 for Alloy 690 and 159.9 for Alloy 600 finished thermally treated production tubes made by Sandvik

Table 5-1

## STATUS OF STEAM GENERATORS WITH ALLOY 690 TUBE BUNDLES

<u>Steam Generator Manufacturer</u>	<u>Tubing Manufacturer</u>	<u>Number of SGs</u>	<u>Tube OD</u>	<u>Utility</u>	<u>Plant</u>	<u>Commercial Operation</u>
Westinghouse	Sandvik	4	7/8	AEP	D. C. Cook	3/89
Westinghouse	Sandvik	4	7/8	NYP&A	Indian Pt. 3	6/89
Westinghouse	Sandvik	4*	11/16	CEGB	Sizewell B	(1992)
Kraftwerk Union	Sandvik	3	3/4	SSPB	Ringhals 2	8/89
Framatome	Valinox	4	3/4	EdF	Chooz B1	5/91
Framatome	Valinox	3	7/8	--	--	--
Framatome	Valinox	4	3/4	EdF	Penly	6/91
Framatome	Valinox	4	3/4	EdF	Golfec	5/92
Framatome	Valinox	3	3/4		Guangdong 1	11/92
Framatome	Valinox	3	3/4		Guangdong 2	12/93
Framatome	Valinox	1	3/4		--	--
Framatome	Valinox	4	3/4	EdF	Chooz B2	5/93
Framatome	Valinox	2*	7/8	NOK	Beznau 1	--
Babcock & Wilcox	Valinox	2*	3/4	NEU	Millstone 2	--
Mitsubishi	Sumitomo	4	7/8	Kansai	Ohi 3	--
Mitsubishi	Sumitomo	4	7/8	Kansai	Ohi 4	--
Mitsubishi	Sumitomo	4*	7/8	Kyushu	Genkai 3	--
Mitsubishi	Sumitomo	4*	7/8	Kyushu	Genkai 4	--
Mitsubishi	Sumitomo	3**	7/8	Shikoku	Ikata 3	--

\* Being Manufactured

\*\*Planned

using similar manufacturing practices except for appropriate differences in mill annealing temperature.

#### Tack Expansion

The tube ends are tack expanded against the tubesheet for a depth of 1/2 to 1 inch to facilitate welding of the tubes to the tubesheet cladding. Since the mechanical properties of Alloy 690 and Alloy 600 are similar, no changes to the tack expansion operations are necessary because of a change in tubing material from Alloy 600 to Alloy 690.

#### Tube-to-Tubesheet Welding

The tube-to-tubesheet welding process (typically autogenous gas tungsten arc welding, GTAW, with repairs, as necessary, by manual GTAW using electrodes such as SFA-5.14 Class ERNiCr-3) is qualified by a weld procedure qualification test which, in turn, qualifies the weld procedure specification (WPS) used in production. Alloy 600 and Alloy 690 tubing can be welded to the cladding using exactly the same WPS with equally good results. Any actual differences in the welding parameters would merely reflect further optimization and not necessarily a basic difference in welding behavior between the two alloys.

#### Full Depth Expansion

As with tack expansion, since the mechanical properties of Alloy 600 and Alloy 690 are similar, the manufacturing operations for full depth expansion are the same for both alloys, at least for hydraulic expansion and presumably for mechanical rolling and explosive expansion. Thus, the as-expanded crevice depth, residual stresses and joint tightness are similar for both alloys. However, as reported at the 1985 EPRI workshop on Alloy 690 (1), the difference in thermal expansion characteristics between Alloy 600 and Alloy 690 does lead to a difference in joint tightness relaxation behavior upon exposure to elevated temperatures. This happens, for example, during post weld heat treatment (PWHT) of the tubesheet-to-channelhead weld seam. During this post weld heat treatment cycle some of the peripheral tubes are exposed to elevated temperatures which can induce relaxation of the expanded tube-to-tubesheet joint.

For a given degree of relaxation, relaxation occurs at a somewhat lower temperature for Alloy 690 than for Alloy 600. This effect can be controlled by minimizing the temperature to which the tubes are exposed during post weld heat treatment and, in the case of hydraulic expansion, by increasing the expansion pressure. For a

complete assessment, the effects of mechanical and thermal loadings during service operation must also be considered. In general, adequate joint tightness can be achieved with either alloy.

#### Wear Considerations

The wear characteristics of the tubing are important in connection with the design of support plate holes and the design and installation of antivibration bars (AVBs), and the selection of support plate and AVB materials. These design and installation practices aim to minimize wear of the tubing material as well as wear of the support plate and AVB materials, but these practices are the same whether the tubing material is Alloy 600 or Alloy 690. Very little information has been published in the open literature on the wear characteristics of Alloy 690 coupled with support plate and AVB materials (2) but a larger data base does exist. However, this unpublished data is protected by proprietary agreements and cannot be summarized here but it can be stated that in general the wear characteristics of Alloy 600 and Alloy 690 are quite similar.

## REFERENCES - SECTION 5

1. M. Perrat and M. Gimond, "Some Steam Generator Fabrication Aspects for Alloy 690 Tubing," Proceedings: Workshop on Thermally Treated Alloy 690 Tubes for Nuclear Steam Generators, EPRI NP-4665M-SR, Electric Power Research Institute, July 1986.
2. R. Y. Schonenberg and P. L. Ko, "Fretting/Wear of Alloy 600 and Alloy 690 Steam Generator Tubing in Simulated PWR Secondary Environment," Proceedings: Workshop on Thermally Treated Alloy 690 Tubes for Nuclear Steam Generators, EPRI NP-4665M-SR, Electric Power Research Institute, July 1986.





## Section 6

### STATUS OF ALLOY 690 WITH REGARD TO THE ASME CODE AND NRC REGULATORY GUIDE

#### ASME CODE

Materials used in the construction of ASME code components must be selected from materials authorized by the Code. The Code authorizes materials for Code Section III Division 1 Class 1 (Subsection NB) components (which includes steam generator tubing) in one of two ways: (1) by listing acceptable materials in Table I-1.0 of Appendix I of Division 1 (specifically Table I-1.2 for Ni-Cr-Fe alloys), or (2) by issuing a Code Case. Table I-1.0, in turn lists ASME Code Section II Material Specifications and associated allowable design stress intensity values  $S_m$ .

Alloy 600 in various Section II specification product forms (tubing, plate, bar, etc.) has long been authorized via Table I-1.2. Alloy 690 has now been included in most of the Section II product form specifications as indicated in Table 6-1. However, it is important to recognize that Section II specifications do not in themselves provide authorization for use of the material in ASME Code Section III components. Again, for this, the material must be listed in Table I-1.0 or authorized by a Code Case. As shown in Table 6-2, Alloy 690 has now been listed in Table I-1.2 but only for tubing per SB-163. (A code case (N-474), expected to be issued early in 1990, will authorize the Alloy 690 product forms listed in Table 8-1 for Section III Class 1 components.)

With respect to the Code Case, in the late 1960's and very early 1970's it was recognized that Alloy 600 production tubing consistently showed yield strengths considerably higher than the 35 ksi minimum required by SB-163, and in most cases was higher than 40 ksi. Hence Code Case 1484 was issued in late 1971 to authorize a "High Yield Strength" version of Alloy 600 tubing, i.e., 40 ksi minimum yield strength and associated higher design stress intensity values  $S_m$ . It was expected that the tubing manufacturers could meet the higher strength requirement without making any changes in manufacturing practices and the higher  $S_m$  values would benefit structural analyses. Since then this Code Case has been revised and reaffirmed many times, including a change in number from 1484 to N-20, up to the present revision N-20-3, which is scheduled to expire 11-30-91. As shown in Table 6-3, Alloy 690 (40 ksi yield strength) was added to the 2nd revision (1484-2) of

**Table 6-1**  
**STATUS OF ALLOY 690 IN ASME CODE SECTION II**

<u>Material Specification</u>	<u>Product Form</u>	<u>Date Included In Code</u>
SB-564	Forgings	Not yet
SB-168	Plate, Sheet, Strip	Summer 1985 Addendum
SB-167	Smls. Pipe & Tube	Summer 1985 Addendum
SB-166	Rod & Bar	Summer 1985 Addendum
SB-166	Rod, Bar & Wire	1986 Addendum
SB-163	Smls. Condenser & Heat Exchanger Tubing	1986 Addendum

**Table 6-2**  
**STATUS OF ALLOY 690 IN APPENDIX I OF SECTION III**

<u>Where</u>	<u>When</u>
SB-163	1986 Addendum
Table I-1.2 (Sm)*	1987 Addendum
Table I-2.2 (Sy)*	1987 Addendum
Table I-3.2 (Su)	Not Yet
Table I-4.0 (Thermal Conductivity/Diffusivity)	Not Yet
Table I-5.0 (Thermal Expansion)	Not Yet
Table I-6.0 (Young's Modulus)	Not Yet
Table I-9.2.2 (Fatigue)	1987 Addendum
Table I-14.2 (External Pressure)	1987 Addendum

\*Requires Supplementary Requirements S5 through S10 of SB-163.

Table 6-3  
STATUS OF ALLOY 690 IN ASME CODE CASE

<u>Code Case</u>	<u>Date Approved/Reaffirmed</u>
1484	8-04-71
(Started with Alloy 600)	
1484-1	4-29-74
1484-2	11-04-74
(Added Alloy 690)	
1484-3	8-13-76
(Added Alloy 800)	
N-20	8-13-76
(Changed Number)	
N-20	8-30-79
N-20	7-16-82
N-20-1	9-05-85
N-20-2	12-07-87
(Added CW Alloy 800)	
N-20-3	11-30-88

the Code Case in late 1974. The Code Case requires that the tubing be manufactured in compliance with SB-163. Since Alloy 690 was not initially identified in SB-163, the Code Case specifies chemistry and mechanical property requirements. Though the Code Case has been revised many times, the requirements for Alloy 690 have not changed.

Following is a brief discussion of important points about the Code requirements and differences between the various specifications.

- The text of SB-163 identifies low yield strength (35 ksi) Alloy 600 and low yield strength (35 ksi) Alloy 690. SB-163 also contains two groups of Supplementary Requirements. The first group (S2-S4) is applicable to U-Bend tubes (as opposed to the purchase of straight tubes) and the second group (S5-S10) is applicable to higher yield strength (40 ksi) tubing. These supplementary requirements apply only if specified by the purchaser.
- Table I-1.2 of Section III Appendix I authorizes both low strength and high strength Alloy 600 but only authorizes high strength Alloy 690 (S5-S10 are required). Code Case N-20-3 authorizes only high strength Alloy 600 and Alloy 690.
- Items 1 through 5 of Table 6-4 show the mechanical property requirements in the various specifications. The standard mechanical property requirements (low strength) in SB-163 are the same for Alloy 600 and Alloy 690 except for ultimate tensile strength (U.T.S.). The requirements in Code Case N-20-3 are the same for Alloy 600 and Alloy 690 and are the same as in SB-163 + S6 for Alloy 600 and Alloy 690 except for the ultimate tensile strength of Alloy 690.
- Items 6, 7, and 8 of Table 6-4 show the stress intensity limits  $S_m$  given in the various specifications. These limits are the same in Table I-1.2 and Code Case N-20-3 and in both specifications the limits are the same for Alloy 600 and Alloy 690. The limits are higher for the high strength material than for the low strength material (Alloy 600).
- Items 9, 10 and 11 show the design allowable yield strength  $S_y$  given in the various specifications. As expected, the limits are higher for the higher strength material but no explanation can be offered for the difference between Table I-2.2 and Code Case N-20-3.

Table 6-4

MECHANICAL PROPERTY REQUIREMENTS FOR ALLOY 600 AND ALLOY 690  
AS GIVEN IN VARIOUS ASME CODE SPECIFICATIONS

<u>Spec</u>	<u>Alloy</u>	<u>YS, ksi</u>	<u>Min UTS, ksi</u>	<u>Min Elong %</u>
1. SB-163	600	35 min	80	30
2. SB-163	690	35 min	85	30
3. SB-163+S6	600	40-65	80	30
4. SB-163+S6	690	40-65	85	30
5. CCN-20-3	600&690	40-65	80	30

		Min YS Min UTS				Stress Intensity Sm, ksi, at T°F								
		ksi	ksi	100	200	300	400	500	600	650	700	750	800	
6.	Table I-1.2	SB-163 600	35	80	23.3	23.3	23.3	23.3	23.3	23.3	23.3	23.3	23.3	
7.	Table I-1.2	SB-163+S6 600 & 690	40	80	26.6	26.6	26.6	26.6	26.6	26.6	26.6	26.6	26.6	
8.	CCN-20-3	SB-163 600 & 690	40	80	26.6	26.6	26.6	26.6	26.6	26.6	26.6	26.6	26.6	

						<u>Yield Strength Sy, ksi, at T°F</u>								
9.	Table I-2.2	SB-163 600	35	-	35.0	32.7	31.0	29.8	28.8	27.9	27.4	27.0	26.5	26.1
10.	Table I-2.2	SB-163+S6 600 & 690	40	-	40.0	36.8	34.6	33.0	31.8	31.1	30.9	30.6	30.3	30.0
11.	CCN-20-3	SB-163 600 & 690	40	-	40.0	38.2	37.3	36.3	35.7	35.3	35.2	35.0	34.9	34.8

- The chemistry requirements for Alloy 690 in SB-163 differ from those in Code Case N-20-3 (see Table 2-1 of this report) in that the Code Case specifies a lower maximum limit for carbon and also includes a limit on cobalt.
- As discussed in Section 2: Physical Properties (this report) and indicated in Table 6-2, some of the design data for Alloy 690 has not yet been provided in the ASME Code, either in Appendix I or the Code Case.
- ASME Code Section III, NB-4000 requires weld procedure qualification tests per Section IX of the Code generally, as well as special requirements for tube-to-tubesheet welds. Section IX has not yet provided a P-Number for Alloy 690 but it is expected that Alloy 690 will eventually be assigned P-No. 43, the same as for Alloy 600. Code Case N-20-3 requires a separate weld procedure qualification test for Alloy 690.

Thus the ASME Code presently offers the utility customer and steam generator manufacturer two options for Alloy 690 tubing: Code Case N-20-3 or Table I-1.2. There are some important differences between these two options but these differences are of no consequence to the EPRI tubing specification which complies with both options.

#### REGULATORY GUIDE

The Nuclear Regulatory Commission via 10 CFR Part 50, Section 50.55a, Codes and Standards, sanctions ASME Section III Code approved materials generally and authorizes Code Cases for materials on a case-by-case basis via Regulatory Guide 1.85. According to the latest available issue of RG 1.85, Revision 24 dated June 1986, the latest revision of the Code Case to be approved by the NRC is N-20 (reaffirmed by the ASME Code on 5-19-85). It is expected that the NRC will approve the latest revision of the Code Case (N-20-3) when subsequent revisions of the Regulatory Guide are issued.





## Section 7

### DISCUSSION AND RECOMMENDATIONS

#### DISCUSSION

The purpose of this section is to provide a brief summary of the current status of Alloy 690 for steam generator heat transfer tubing applications. This will be approached by first reviewing the data and/or experience needs that were identified in the 1985 Workshop on Alloy 690 sponsored by EPRI (1), followed by a summary of what has been learned in the intervening four-and-one-half years. Areas where specific data needs or experience remain to be acquired are identified.

#### Data or Informational Needs Defined at the 1985 Workshop

In the summary of the 1985 Workshop, two types of additional data or informational needs were identified. These reflected areas where: a) there appeared to be lack of agreement as to the most accurate data or most appropriate processing procedure for Alloy 690; or b) data or experience were essentially nonexistent. In the former category were:

- disagreement over the temperature dependence of the carbon solubility in Alloy 690;
- disagreement over the time required to achieve the desired carbide precipitation and chromium rediffusion during the ca. 700°C thermal treatment;
- identification of an appropriate test for detecting grain boundary chromium depletion ('sensitization').

Recommendations for additional work on Alloy 690 - the latter category referred to above - were made in the following areas:

- complete studies to optimize the thermal processing of Alloy 690 for steam generator tubing applications;
- continue efforts to establish the correlation between carbide morphology and distribution and corrosion resistance;
- complete the development of the corrosion data base for thermally treated Alloy 690;
- establish suitable NDE and quality control tests as required for the manufacture of steam generator tubing.

In addition, as a general consequence of the findings and discussions at the Workshop, EPRI hosted a 'Round Robin' evaluation by various laboratories. The goals of this program were to establish reliable methods for determining the carbon concentration in Alloy 690, and to establish the range of expected accuracy of such determinations, and to examine various methods for etching metallographically prepared sections so as to clearly delineate the location and relative density of carbides in the thermally treated alloy. [This Round Robin evaluation was performed under the aegis of EPRI Project S408-1; Optimization of Thermal Treatment of Alloy 690.]

Finally, it was noted that Alloy 690 with cobalt concentrations below 0.02% was available at the option of the purchaser.

#### Summary of Accomplishments: 1985 - 1989

Referring back to the specific issues identified at the 1985 Workshop, it is clear that significant progress has been made toward resolution of areas where disagreement prevailed or where data was lacking.

The temperature dependence of the carbon solubility in Alloy 690 has been determined with sufficient accuracy to support the selection of thermal-mechanical processing parameters - in particular, the final mill annealing temperature.

Corrosion studies have been performed and complemented by studies of chromium diffusion to the grain boundaries during thermal treatment, that suggest five (5) or ten (10) hours at the thermal treatment temperature are each able to produce a material possessing 'optimized' corrosion resistance. The specific choice should

be left to the purchaser and vendor unless specific data which contradict this observation are developed in the future.

The issue of a test for grain boundary chromium depletion has led to much discussion but no unanimous position. Arguments have been offered that a test for grain boundary chromium depletion in Alloy 690 is not necessary; an alloy with 30% Cr cannot be 'sensitized' to any technologically significant extent using current production practices. Indeed, using even the most sophisticated techniques available, the chromium level does not drop lower than 18% under any relevant thermal treatment condition, and even this level extends for a distance measured in fractions of a micrometer away from the grain boundary and is 'healed' after thermal treatment times of a few hours duration. If the decision is made by the purchaser and a test for grain boundary chromium depletion is to be performed during production, any of the standard tests can be used.

Current Alloy 690 purchasing specifications are requiring a maximum average cobalt content of 0.015%. This limit has been met by both Sandvik and Valinox in their runs of production tubing.

The Round Robin efforts showed mixed results. Evaluations by nine laboratories gave a greater spread in carbon analyses than anticipated. Much of the spread was concluded to have resulted from inadequate cleanliness in specimen preparation; the overall accuracy of carbon determinations was projected to be  $\pm 0.001\%$  carbon (2). Evaluation of various etching techniques for metallographic characterizations of mill annealed and thermally treated microstructures led to the general conclusion that the bromine-methanol etchant followed by scanning electron microscopic examination is the most effective and reproducible method. For laboratories or manufacturers reluctant to use an SEM for routine quality control, a combined glyceric-nital etchant or a glyceric-hot oxalic acid etchant suitable for optical microscopic characterizations showed considerable promise (2).

In the viewpoint of the tube manufacturers, and at least several vendors, the thermal processing of Alloy 690 - i.e., selection of the temperature-time conditions for final mill annealing and thermal treatment, and the underlying basis for these selections - has been completed. That these selections are consistent with the production on a commercial scale of Alloy 690 TT tubing having very reproducible mechanical properties and microstructural features is demonstrated.

The corrosion data continue to support the correlation between the presence of a high density of intergranular carbides and enhanced caustic corrosion resistance for Alloy 690 TT tubing. To a significant degree, the corrosion data base for Alloy 690 in primary side and faulted secondary side environments of interest for steam generator applications has been expanded since the time of the 1985 Workshop. Particularly important is the fact that the newer data have been generated for material produced according to the current specifications.

As essential elements in the manufacture of reproducibly high quality tubing, shop NDE methods and quality control tests have been defined and implemented by both Sandvik and Valinox that are consistent with all aspects of the purchaser's requirements.

A further important advance worth noting is that a considerable volume of manufacturing experience has been accrued in the last few years. Whereas the 1985 Workshop noted that the four Chooz B1 steam generators were to be built using Alloy 690 tubing and were to be in operation ca. 1991, in point of fact, by August of 1989 eleven replacement steam generators have been placed into service at three nuclear power plants. The ability of the tube manufacturers to meet this accelerated schedule, at the same time submitting themselves to comprehensive qualification programs, is an excellent example of mutual manufacturer-vendor cooperation and commitment.

#### RECOMMENDATIONS FOR ADDITIONAL DATA DEVELOPMENT

Despite the significant progress that has been made in the recent years, there remain a few areas where additional test data or experience have to be acquired.

In the area of corrosion resistance, the most important data needs are those associated with performance of Alloy 690 under heat transfer conditions simulating those which obtain in the secondary side of steam generators; the first significant data for current production grade Alloy 690 TT tubing is being developed as the major task of EPRI Project S408-6 (as part of which this report has been assembled).

The recent observation of the cracking of Alloy 690 in very high pH caustic-plus-lead environments suggests consideration be given to performing more carefully controlled corrosion tests in order to assess the potential significance of this form of degradation. Even recognizing these few data points, it is worth recalling that Alloy 690 clearly outperformed Alloy 600 in every environment evaluated.

An extremely important issue that has not yet been fully resolved is associated with the eddy current inspectability of pilgered tubing. The tube manufacturers have taken extreme measures in an effort to reduce the noise level in pilgered tubing. They have demonstrated a remarkable improvement in enhancing the signal-to-noise ratio; nevertheless, the noise level is approximately twice that observed in drawn tubing. The remaining concern is not associated with "in-production" inspection - this seems to be acceptably resolved consistent with good quality control NDE practice - but rather is related to concerns that the higher noise level will mask the earliest indications of degradation during in-service inspections.

The final issue that merits attention has surfaced recently with the onset of power production at the plants that have replaced steam generators originally tubed with Alloy 600 with new Alloy 690 TT bundles. Though the full rated power production has been achieved, each of the three plants now in operation reported that the steam pressure measured immediately after startup was somewhat lower than expected. This may be a transient effect - such effects are plausible - since at least one of the plants has reported that the steam pressure is steadily increasing. Further review, currently in progress, of the thermal conductivity data for Alloy 690 TT, including tests on archived samples from the recent production tubing and an additional set of data just recently acquired suggests that the thermal conductivity values previously used by Westinghouse for design basis calculations are substantially correct. Heat transfer parameters other than thermal conductivity are now being reviewed for Alloys 690 and 600 in order to assess basic differences that might contribute to the behavior observed; the lower thermal conductivity of Alloy 690 had already been recognized in the design process. In the meantime, the operating plants are being closely monitored for steam pressure performance.

## REFERENCES - SECTION 7

1. Proceedings: Workshop on Thermally Treated Alloy 690 Tubes for Nuclear Steam Generators, EPRI NP-4665M-SR, Electric Power Research Institute, July 1986.
2. J. Gorman, "Microstructural Etching and Carbon Analysis Techniques for Alloy 690", presented at the Alloy 690 Workshop, New Orleans, LA, April 12-14, 1989, to be published by EPRI.

NP-6997-M represents the results of Research Project S408-6. Additional explanatory information and supporting data are contained in a separate supplementary volume, NP-6997-SD.

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