Microstructural Characterization of Alloy 709 Plate Materials with Additional Heat Treatment Protocol

Applied Materials Division

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Prepared by

X. Zhang

Nuclear Science and Engineering Division
Argonne National Laboratory

T.-L. Sham

Applied Materials Division
Argonne National Laboratory

G. A. Young

School of Mechanical, Industrial, and Manufacturing Engineering
Oregon State University

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ABSTRACT

This report provides the results on microstructural characterization of the first commercial heat of Alloy 709 plate material which has undergone additional heat treatment protocol. The report is a Level 4 deliverable in FY19 (M4AT-19AN020502012), under the Work Package AT-19AN0205201, “A709 Development – ANL.”

The study involves thermodynamic-kinetic modeling, heat treating of materials, micro-hardness testing, x-ray diffraction (XRD) study, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) study. Through thermodynamic-kinetic modeling, it is determined that after an 1100°C solutionizing treatment, heat treating of Alloy 709 at 775°C for 10 hours or at 900°C for 10 hours are candidate recipes for promoting desired microstructural features. Both heat treatments were executed on small samples of the AOD-1100°C condition of the commercial heat of Alloy 709. Micro-hardness tests showed that both treatments increases the hardness of the material. XRD showed that both treatments brings out M23C6 and MX phases, though the 775°C/10h-treatment has more profound effect. The TEM study revealed that similar for both conditions, M23C6 precipitated on grain boundaries and within grain interior. In contrast, after the 775°C/10h treatment, the dislocations are decorated with MX nano particles, while after the 900°C/10h treatment, most of the dislocations are free of MX particles. It is thus determined that the 775°C/10h treatment has a better potential to provide enhanced creep properties by pinning the dislocations with nano particles. Following this study, the 775°C/10h treatment was carried out on a large ESR-1100°C plate at Idaho National Laboratory. Hardness testing and microstructural characterization were performed and compared between the two materials being heated treated under the same protocol. The implication on mechanical properties was briefly discussed.

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1 Introduction

Advanced materials are a key element in the development of advanced nuclear energy systems. High-performance structural materials allow for a more compact design of the reactor structure, and have the potential to reduce the construction and operational costs for the next-generation advanced nuclear reactors. Due to the significant enhancement in time-dependent mechanical properties of the austenitic Alloy 709 relative to 316H stainless steel, a reference construction material for Sodium Fast Reactors (SFRs), code qualification of Alloy 709 was recommended (Sham et al., 2015). A comprehensive plan for the development of a 500,000-hour, 760°C ASME Code Case and the resolution of licensing issues for Alloy 709 was developed in FY15. A Phase I implementation of this plan that includes a 100,000-hour, 760°C ASME code case and the initiation of very long-term creep tests, thermal aging, and sodium exposure of Alloy 709 was established.

Alloy 709 is derived from NF709 (Fe-20Cr-25Ni-1.5Mo-Nb,B,N), which was a commercial heat- and corrosion-resistant austenitic stainless steel developed by Nippon Steel Corporation in Japan for boiler tubing applications. The high strength of NF709 is achieved by controlling the carbon content to 0.07–0.10% and precipitation strengthening by Nb(C,N) (MX phase) and CrNbN (Z phase). NF709 also shows good fabricability properties and weldability. It was regarded as one of the best austenitic steels for elevated temperature applications among commercially-available austenitic alloy classes. The NF709 alloy provides time dependent strength nearly double that for conventional 304 and 316 stainless steels at sodium-cooled fast reactor relevant temperatures (Busby et al., 2008). Alloy 709 has the same chemical composition as NF709 but is intended for SFR applications that include reactor vessel, core supports, primary and secondary piping, and possibly intermediate heat exchanger and compact heat exchanger. There is also interest in using Alloy 709 for a nth-of-a-kind new material insertion for Fluoride-salt-cooled High Temperature Reactor (FHR) applications. Hence development of processing conditions and fabrication scale up for different product forms such as plates, pipes, bars, forgings and sheets, in addition to seamless tubing, are required to support these applications.

The Alloy 709 fabrication scale-up effort was completed in FY17 where one commercial heat, totaling about 45,000 lb., was procured. The heat was melted by a commercial vendor using three commercial mill practices: Argon-Oxygen-Decarburization (AOD), Electroslag Remelting (ESR), and ESR with subsequent Homogenization (ESR-homo). Three ingots from that heat were hot-rolled into plates. Test pieces were cut from the as-rolled plates for future confirmatory testing. Each of the remaining plates was solution annealed at 1050, 1100, and 1150°C. The plates were delivered to the Argonne National Laboratory (ANL) and Oak Ridge National Laboratory (ORNL.) The as-rolled and solution annealed plate materials were analyzed for their microstructures, hardness values, grain sizes, and tensile properties. The results showed that the scaled-up heat of Alloy 709 fabricated using commercial mill practice exhibited tensile properties that exceeded the minimum values specified in the ASME Code Case for commercial heats of NF709 (Natesan et al., 2017.)

The FY18 activities focused on performing scoping tests to down-select from the nine processing conditions. This task involves creep rupture, fatigue, and creep-fatigue testing of Alloy 709 using standard sized ASTM specimens from the first Alloy 709 commercial heat. Creep testing equipment was stood up at ANL through upgrade and refurbishment of existing equipment and procurement of new equipment to support the generation of creep rupture data for the Alloy 709

scoping tests and the code case. In FY18, 600°C/330 MPa tests were carried out on all nine processing conditions (Natesan et al., 2018). The results, in combination with the results from fatigue and creep-fatigue tests conducted at ORNL and the Idaho National Laboratory (INL), showed that the ESR-1100°C condition gave balanced mechanical properties.

The significant enhancement in the time-dependent mechanical properties, such as the creep property and the creep-fatigue property, of Alloy 709 over the reference 316H stainless steel is due to the precipitation of nano-sized MX (M=Nb, Ti, X=N, C) or Z-phase (CrNbN) particles on dislocations when the material is in service. However, under low temperature (below 500°C) and low stress conditions, there are concerns that 1) those precipitates are not going to form in a reasonable amount of time due to the slow kinetics, and 2) different types of precipitates, such as the intermetallic laves phase which is believed to be detrimental to creep properties, will be formed preferably over MX or Z-phase. As a result, development of an age-hardening heat treatment procedure was initiated in FY19, aiming at bringing out the desired nano-sized precipitates, such as MX or Z-phase, on dislocations, for improved mechanical performance in low stress, low temperature conditions.

2 Material Specifications

The product chemistry of the first commercial heat conforms to the ranges or maximum values specified in wt.% in Table 2-1. The chemistry targets and the actual melt compositions are also shown in the table.

Table 2-1. Chemical composition of melt of Alloy 709 heat # 58776 (in wt.%)

Alloy 709	C	Cr	Ni	Mn	Mo	N	Si	P	Ti	Nb	B	Fe
Specification range	0.04-0.10	19.5-23	23-26	1.5	1.0-2.0	0.14-0.16	1.0	<0.025	0.2	0.1-0.4	0.002-0.01	Bal
Target	0.07	20	25	0.9	1.5	0.15	0.40	*	0.05	0.25	0.002-0.005	Bal
Actual	0.066	19.93	24.98	0.91	1.51	0.148	0.44	0.014	0.04	0.26	0.0045	Bal

*The P shall not exceed 0.025 wt.%.

3 Thermodynamic and kinetics modeling

Continuous cooling transformation and time-temperature-transformation (TTT) simulations were performed for the commercial heat of Alloy 709. The TTT simulation was performed using the JMatPro software. The result for 1% transformation of minor phases after a solution treatment of 1100°C is shown in Figure 3-1. Based on this figure, two heat-treatment schedules of 775°C/10h and 900°C/10h were selected, mainly to avoid the formation of the intermetallic laves phase and to promote the formation of M₂₃C₆ type carbides. The figure also predicted the formation of the M₂N phase following those two recipes, instead of MX or Z-phase. M₂N phase is predicted to be Cr- and Nb- rich, and in this extent it is similar to the Z-phase. According to the literature, M₂X phase is hexagonal while Z-phase is tetragonal, but they both appear as faceted particles. It is unclear why the simulation does not predict the formation of the Z-phase or the MX phase, which are believed to be commonly observable in Alloy 709.

Figure 3-1. TTT diagram of the 1100°C solutionized Alloy 709 for 1% transformation.

4 Heat treatment of small samples of Alloy 709 commercial heat AOD-1100°C condition

Half-inch-sized small samples from the commercial heat of Alloy 709 AOD-1100°C condition were annealed in air using box furnaces at ANL. Samples were treated at 775°C/10h and 900°C/10h conditions. The samples were then sliced and polished for hardness, XRD, SEM and TEM studies.

Figure 4-1. Photos showing the inside of the box furnaces: (left) heat treating at 775°C/10h; (right) heat treating at 900°C/10h.

4.1 Micro-hardness measurement

The micro-hardness of the as-received and the two aged samples was measured using a Buehler Micromet 5104 indenter. Figure 4-2 shows the result. Each data point is the average over 30-50 single indents. It is obvious that the heat treatment increased the hardness, due to the formation of precipitates. Higher aging temperature may results in higher hardness, but the increment is subtle and is within the error bar range.

Figure 4-2. Micro-hardness data of the as-received and the heat-treated Alloy 709 AOD-1100°C samples.

4.2 X-ray diffraction study

The heat-treated samples were first fine polished down to $\sim 150\ \mu\text{m}$ and then brought to the Advanced Photon Source at ANL, beamline 1-ID, for wide-angle x-ray diffraction (XRD) study using a GE-RT41 area detector. The beam energy was 71.676 keV and the beam size was $0.2\ \text{mm} \times 0.2\ \text{mm}$. Due to the small volume fraction and the small sizes of the secondary phases, their scattering intensities were very weak compared to the austenitic matrix, and therefore, static exposure alone was hard to reveal the minor peaks without significantly supersaturating the main peaks. To bring up the intensity of the minor peaks, during the exposure of the 160 frames, totaling 3.2 seconds, the sample was rotated 40 degrees and simultaneously moved slowly in the vertical direction, instead of staying static. As a result, more areas were sampled and more reflections from one scattering domain were excited to bring up the statistics. The thin thickness of the samples also helped in revealing the minor phases.

During data reduction, instead of taking the sum or the average of the 160 frames from the area detector, the “max-over-all” algorithm was used, meaning that for each pixel on the detector, the maximum value it experienced over the 160 frames was taken. This algorithm greatly enhanced the signal from minor phases, but it had significant drawbacks: 1) the noise level was increased artificially; 2) the physical information contained in the peaks was lost because the shape of the peaks was completely artificial. Still, for the purpose of this study, the gain from using this method in terms of revealing the minor phases overcame the loss.

Figure 4-3 shows the peaks of the as-received, the 775°C/10h, and the 900°C/10h samples using the “max-over-all” method. The as-received sample was measured in a different beamline with different setup and exposed for 50 frames while the sample was moving vertically. Therefore, although the same “max-over-all” algorithm was used, the profile of the as-received sample appears noisier than the heat treated samples and the minor peaks were not as well defined. Nevertheless, it is observed that in the as-received sample, there were weak peaks from the MX phase which are the residual particles from fabrication (TEM Figure 4-6), while after both heat treatment, there were distinct peaks from the M23C6 and the MX phases. Compared to the 900°C/10h sample, the 775°C/10h sample had stronger peaks, indicating the volume fractions of those minor phases were higher. No peaks from the Z-phase were observed.

Figure 4-3. XRD "max-over-all" profiles of the as-received, the 775°C/10h, and the 900°C/10h heat-treated samples.

4.3 Scanning electron microscopy study

SEM study was performed on the two heat-treated AOD-1100°C samples. The samples were first fine polished to mirror finish and then etched to reveal the grain boundaries. Figure 4-4 shows the results for the 775°C/10h heat-treated AOD-1100°C sample. The etching revealed equiaxed grains with an average size of 30-40 μm , similar to that of the as-received material as reported in (Natesan et al., 2017). Micro-meter sized MX (M=Ti, Nb) particles were observed, with Ti often being the core and Nb being the shell, as shown by the energy-dispersive spectrometry (EDS) maps. Those particles are the residuals from materials fabrication. SEM is not particularly suitable for studying nano-sized secondary phases, so the results related to those phases will be presented in the TEM section. The observations for the 900°C/10h heat-treated sample are similar to the 775°C/10h heat-treated sample, as shown in Figure 4-5.

Figure 4-4. SEM images of the 775°C/10h heat-treated AOD-1100°C sample. To the left are the EDS maps showing the large particles are the residual MX particles from materials fabrication.

Figure 4-5. SEM images of the 900°C/10h heat-treated AOD-1100°C sample. To the left are the EDS maps showing the large particles are the residual MX particles from materials fabrication.

4.4 Transmission electron microscopy study

TEM studies were performed on the as-received and the two heat-treated samples to reveal the characteristics of the nano to sub-micro meter-sized secondary phases. The samples were first polished down to $\sim 100\text{ }\mu\text{m}$, and were punched into 3mm disks. The disks were then electro jet polished to electron transparent. The FEI Talos TEM/STEM at the Center for Nanoscale Materials at ANL was used to do the study.

Figure 4-6 is the bright-field (BF) scanning TEM (STEM) micrograph showing the microstructure of the as-received AOD-1100°C sample. Dislocations were observed as well as the residual MX particles. The grain boundaries and twin boundaries were free of precipitation or segregation (not shown in the image).

Figure 4-6. Bright-field (BF) scanning TEM (STEM) image showing the microstructure of the as-received AOD-1100°C sample. The dark particles are the residual MX particles from materials fabrication.

Figure 4-7 and Figure 4-8 show the BF-STEM images and the EDS element maps of the 775°C/10h heat-treated and the 900°C/10h heat-treated samples, respectively. The features in the micrographs are labeled. In both samples, the grain boundaries are decorated with 100-200 μm -sized M23C6 particles, and the residual MX particles are often coated with M23C6 forming 200-500 μm -sized core/shell particles. Often times, those particles attract more Cr to form M23C6 (or possibly other Cr-rich phase with less C) particles to form into chains, eventually evolving into needles. On the other hand, there are drastic differences between the two samples. The 775°C/10h heat-treated sample has a very high density of 20-30 nm sized Nb-rich particles decorating the dislocations, but the 900°C/10h heat-treated sample has very few. The dislocation density after the 900°C/10h heat-treatment also seems to be decreased, but quantitative characterization needs to be performed to confirm that.

Whether the Nb-rich phase on dislocations is the MX phase or the Z-phase is undetermined. Common belief is that the MX phase is a transient phase to Z-phase (Sourmail, 2001). Extensive electron diffraction study would be required to reach a conclusion, which is the next step in the study. On the other hand, the x-ray diffraction study, as presented in section 4.2, does show clear

signals from the MX phase while no indication of the Z-phase. Thus, tentatively speaking, the Nb-rich phase observed in those two samples could be the MX phase. The fact that there are only few MX nano particles on dislocations in the 900°C/10h heat-treated sample leads to the selection of the 775°C/10h as the procedure for heat-treating a large plate of Alloy 709 commercial heat ESR-1100°C condition, as presented in section 5.

Figure 4-7. (Top) BF-STEM image showing the microstructure of the 775°C/10h heat-treated AOD-1100°C sample. (Bottom) EDS element mapping indicating the different phases of the secondary particles.

Figure 4-8. (Top) BF-STEM image showing the microstructure of the 900°C/10h heat-treated AOD-1100°C sample. (Bottom) EDS element mapping indicating the different phases of the secondary particles.

5 Heat treatment of Alloy 709 commercial heat ESR-1100°C plate

Based on these studies, the 775°C/10h protocol was applied to an ESR-1100°C plate at INL. A small piece of sample was sent to ANL for microstructural characterization. The sample was sliced, and prepared separately for micro-hardness test and (S)TEM study. Figure 5-1 shows the hardness values for the as-received ESR-1100°C material and the 775°C/10h heat-treated material, along with data from the AOD-1100°C material (shown previously in Figure 4-2). Unlike the observation in the AOD-1100°C material, which shows significant hardness increase after the heat treatments, the ESR-1100°C material barely shows any increase. Comparison of microstructures between the 775°C/10hr treated AOD-1100°C and ESR-1100°C materials will be presented in section 7, and the hardness results will be rationalized in section 7.

Figure 5-1. Micro-hardness data of the as-received and the heat-treated Alloy 709 AOD-1100°C samples and ESR-1100°C samples.

Figure 5-2 shows the microstructures of the 775°C/10h treated ESR-1100°C sample from STEM. The microstructural features, including the M23C6 precipitates on grain boundaries (not shown in this figure), the MX/M23C6 core/shell particles, the Cr-rich needle-shaped particles, and the Nb-rich nano particles (possibly MX phase or Z-phase) on dislocations, are all similar to the 775°C/10h treated AOD-1100°C material. However, as presented in section 6, there are some significant differences between those two, mainly on the Cr-rich precipitates. Nevertheless, the design goal was achieved by having a high density of nano particles on the dislocations.

Figure 5-2. (Top) BF-STEM image showing the microstructure of the 775°C/10h heat-treated ESR-1100°C sample. (Bottom) EDS element mapping indicating the different phases of the secondary particles.

6 Comparison of heat-treated microstructures

6.1. Comparison of heat-treated microstructures

Figures 6-1 and 6-2 compare the microstructures after the 775°C/10h heat treatment of the AOD-1100°C material and the ESR-1100°C material of the commercial heat of Alloy 709, at lower magnification and at higher magnification, respectively. At lower magnification when multiple grains are in the view, from those two images in Figure 6-1 and many others that are not presented here, it is obvious that there are some features in common: grain boundaries are decorated with M23C6 particles; within the grains, there are a high density of small particles on dislocations and a lower density of large particles scattered homogeneously within the grains. A detailed look of the small precipitates on dislocations (Figure 6-2) reviews that those Nb-rich precipitates, possibly MX phase, are of similar size in both materials, around 20-30 nm. On the other hand, there are also obvious differences.

First of all, the grain boundary precipitates of the AOD-1100°C material are much larger and denser. Second, there are much more needle-like precipitates in the AOD-1100°C material than in the ESR-1100°C material, and those precipitates are also much longer. Third, there is heavy precipitation on the incoherent twin boundaries in the AOD-1100°C material, but much less in the ESR-1100°C material. Overall, the precipitation in the AOD-1100°C material is much more dramatic compared to that in the ESR-1100°C material. One possible explanation is as follows. The ESR is a process of remelting and refining for making high quality ingots. The ingot going through ESR is supposed to have less impurities, such as sulfur, compared to the ingot going through AOD. Impurities are known to be the preferred nucleation sites for precipitation, and therefore, the precipitation in the AOD material is more significant than in the ESR material. Those Nb-rich precipitates on the dislocations are an exception, possibly because dislocations themselves are already preferred nucleation sites.

Figure 6-1. STEM-BF images showing the comparison of microstructures in the 775°C/10h heat-treated AOD-1100°C and ESR-1100°C materials at 5kx magnification.

Figure 6-2. STEM-BF images showing the comparison of precipitates on dislocations in the 775°C/10h heat-treated AOD-1100°C and ESR-1100°C materials at 160kx magnification.

6.2 Implication on mechanical properties

The implication of the precipitation on mechanical properties is as follows. First, as the solutes come out of the solution and form precipitates, solute strengthening is weakened while precipitation hardening is enhanced. When those two mechanisms are at balance, the hardness of the material is not changing much, which possibly explains the micro-hardness results in Figure 5-1 for the ESR-1100°C material. As the precipitation becomes more dramatic, precipitation hardening dominates, and the hardness increases, which possibly explains the micro-hardness results in Figure 5-1 (and Figure 4-2) for the AOD-1100°C material. In the 775°C/10h heat-treated AOD-1100°C, the M23C6 type precipitates on grain boundaries and within the grains show coalescence. M23C6 is a brittle phase, and their coalescence are undesired because it could lead to ductility reduction (Ding et al., 2019.) In this aspect, the less dramatic precipitation of the ESR-1100°C material is a positive improvement over the AOD-1100°C material.

The nano precipitates on dislocations form the pinning sites for dislocation motion, which is the desired mechanism to achieve enhanced creep properties. However, under low temperature (<500°C), low stress service conditions, there are concerns that those precipitates will not be able to form due to the slow kinetics. Having the material being heat-treated using the protocol provided in this study (775°C/10h) to bring out the nano precipitates on dislocations should enhance the creep performance of the Alloy 709 under low temperature, low stress conditions. At higher temperature conditions, the precipitates will be able to form in-service to effectively pin the dislocations. An example is shown in Figure 6-3 for an as-received AOD-1100°C material creep-tested under 600°C/330MPa conditions with a creep life of 1752 hours. Nb-rich precipitates smaller than 10 nm are observed decorating the dislocations. Therefore, the heat treatment protocol may not be necessary for high-temperature creep-type service conditions. However, this assessment is from creep properties only and does not apply to other properties such as fatigue and creep-fatigue.

Figure 6-3. STEM-BF images showing the Nb-rich nano precipitates on dislocations after creep test at 600°C/330MPa of an Alloy 709 AOD-1100°C material (not heat-treated). The insert shows an EDS map of Nb.

7 Summary and Future Work

Heat-treating the commercial heat of Alloy 709 was studied aiming at improving the creep performance of the material at low temperature, low stress conditions. Two protocols, 775°C/10h and 900°C/10h, were selected based on thermodynamic and kinetic modeling, and applied to the as-received AOD-1100°C material. Micro-hardness testing and microstructural characterization were performed. Those experimental studies revealed that similar for both conditions, M23C6 precipitated on grain boundaries and within grain interior. In contrast, after the 775°C/10h treatment, the dislocations are decorated with MX nano particles, while after the 900°C/10h treatment, most of the dislocations are free of MX particles.

Thus it was determined that the 775°C/10h treatment has a better potential to provide enhanced creep properties by pinning the dislocations with nano particles. Following this study, the 775°C/10h treatment was carried out on a large ESR-1100°C plate at INL. Hardness testing and microstructural characterization were performed, and similarities and differences were observed between the two materials being heat-treated under the same protocol. The implication on mechanical properties was briefly discussed, and it was concluded that the heat treatment was beneficial for low temperature, low stress creep type of applications.

Future work involves the determination of the type of precipitates on dislocations (MX or Z-phase) using electron diffraction under TEM. Also, heat treating an ESR-1150°C plate was recently performed at ANL. Characterization will be performed at ANL and mechanical properties testing will be performed at INL.

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Applied Materials Division

Argonne National Laboratory
9700 South Case Avenue
Argonne, IL 60439

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