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	Fracture Toughness of High-Cr Steels after Various Thermomechanical Treatments		
	September 2019		
	Thak Sang Byun David A. Collins Timothy G. Lach Choi Jung-Pyung Emily L. Barkley		
	<b>ENERGY</b> Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830		

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# Fracture Toughness of High-Cr Steels after Various Thermomechanical Treatments

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#### Abstract

This research aimed to improve the mechanical properties of high-Cr steels by developing new thermomechanical processes for application to advanced fast reactors. A simultaneous improvement of fracture toughness and strength was specifically targeted in the design of thermomechanical processing for various 9Cr and 12Cr steels. For the structural materials of fusion and fast reactors, the high-chromium steels with fine ferritic/martensitic (FM) structures are favored because of their high creep strength and excellent resistance to high-temperature radiation damage such as void swelling. After the traditional thermomechanical treatment consisting of normalizing, water quenching, and tempering, however, the high-Cr steels show limited mechanical properties at high temperatures, e.g., significant decrease of strength above ~450°C. Since the high-Cr steels are tempered at high temperatures (typically around 750°C), significant coarsening of the lath structure and carbides and annihilation of dislocations occur in the final thermomechanical treatment. It is believed that the high-temperature tempering can maximize the ductility of the FM steels, but their high-temperature strength is reduced and often with high-temperature fracture toughness. It is also likely that such a fully-tempered structure will demonstrate a lowered radiation resistance when compared to the steels with finer microstructures. This research was planned to explore new processing routes that can produce ultrafine microstructures and thus can improve the high-temperature mechanical properties of the high-Cr steels. In this research, three 9Cr steels and two 12Cr steels were selected and a series of new thermomechanical process treatments (TMTs) were designed and applied to the five steels to find the TMT routes that can result in increase of both strength and fracture toughness. It was demonstrated for HT-9 steels that some tailored TMTs increased or maintained the fracture toughness of the high-Cr steels while the treatments could significantly increase their strength to the level comparable to those of nanostructured ferritic alloys. This report compares the fracture toughness data of both 9Cr and 12Cr steels after various thermomechanical treatments with the reference data of similar steels. An hour-long tempering treatment at 600°C with or without a short additional tempering at 750°C is recommended for application to the high-Cr steels for reactor core structures.

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Table 2.	Various thermomechanical processing routes that have been used in this research. The tempering processes include both single-step and double-step tempering treatments, after the same normalization and water quenching treatment

#### **1.0 Introduction**

In the operation of sodium-cooled fast reactors (SFRs), the core structural materials are typically exposed to a wide temperature range of  $310-530^{\circ}$ C and to a high dose (< 200 dpa) at a high flux of fast neutrons (<  $10^{16}$ /s·cm<sup>2</sup>) [1]. Many efforts have been exerted to develop a fast reactor with a higher thermal efficiency and a higher fuel burnup (up to 40%), which equals to ~400 dpa. One of the challenges of achieving the goal is to develop a core material (for cladding and duct) that is able to withstand such a high-dose and high-temperature exposure while in contact with the coolant and the fuel of the reactor [2]. Thus, such a harsh core condition will require a significantly improved performance of core structural materials [2-5]. In general, the core materials for advanced fast reactors require high low-temperature region (< ~430°C) as well as excellent creep and swelling resistances in the higher temperature region [2-4, 6-14].

When compared to the austenitic stainless steels, the quenched and tempered ferriticmartensitic (FM) steels demonstrated distinct advantages in both void swelling resistance and also heat load capability [2-4, 8,9]. Thus far, therefore, the 12Cr-1MoVW (HT-9) steels with tempered martensitic structure have been used as primary core materials for fast reactors not only because they exhibit high resistance to irradiation-induced embrittlement, thermal and irradiation creep, and void swelling but also because they experience little compatibility problem with liquid sodium coolant [2-16]. It is well known that the irradiation-induced embrittlement in lowtemperature (< ~430°C) irradiation, void swelling at very high doses (> 150 dpa), and hightemperature strength above 500°C still limit expansion of the capability of HT-9 steel components to higher doses and higher temperatures. Meanwhile, the 9Cr FM steels are of particular interest because they have smaller radiation-induced ductile-brittle transition temperature (DBTT) shifts as compared with other FM steels [11,30]. Although the 9Cr steels have not been used as reactor core materials so far, those with lower chromium equivalents have generally higher hardenability in quenching, which are capable of producing finer microstructure, than their 12Cr counterpart.

All of these FM steels are basically quenched and tempered (Q&T) steels with high strength and toughness that are obtained primarily by forming fine martensitic/ferritic laths and M<sub>23</sub>C<sub>6</sub>/MC carbide precipitates in the Q&A process. However, after traditional normalizationtempering treatment, the high-Cr steels show limited mechanical properties at high temperatures, e.g., significant decrease of strength above ~450°C. Since the high-Cr steels are tempered at high temperatures (typically around 750°C), significant coarsening of the lath structure and carbides and annihilation of dislocations occur. It is believed that the high-temperature tempering can maximize the ductility of the FM steels, but their high-temperature strength will be reduced by the tempering. It is also likely that such fully-tempered structures will demonstrate a lowered radiation resistance when compared to the steels with finer structures. Radiation effects can be better controlled if controllable microstructural features and size scales can directly involve radiation damage processes such as formation of nanometer scale defect clusters, voids, and helium bubbles, segregation, etc. A principle that has guided this process improvement task is the common knowledge that containing more defect recombination sites or higher defect sink strength is required for higher radiation resistance [17-21]. In this processing development, therefore, refinement of lath structure and precipitates is the key method.

A variety of new thermomechanical processing routes were explored in search of an optimized microstructure that can demonstrate both high strength and high fracture toughness at interested temperatures. In the program, a significantly improved high-temperature mechanical performance has been pursued through process improvement of high-Cr ferritic-martensitic (FM) steels [22,23] and advanced oxide-dispersion strengthened alloys [25-27]. First, we aimed to optimize the thermomechanical processing for two 12Cr steels (with traditional and nitrogenadded chemistries) for significantly increased high-temperature strength and fracture toughness as they are still the most probable candidate for the core materials of the next generation fast reactors. A systematic effort has been made for the processing development and for selecting optimized TMTs. The application of different TMTs to both 9Cr and 12Cr steels was completed considering the guidance from the comprehensive thermodynamics simulation performed earlier in the project. Second, a select set of processing routes that are proven to improve the mechanical properties of 12Cr steels were also applied to three 9Cr steels with different chemistries. Third, the fracture resistance (J-R) tests at selected temperatures were performed for the key TMT conditions. This report presents the results of these tasks and proposes an optimized TMT, after which each of the 9Cr and 12Cr steels can have significantly improved mechanical properties.

## 2.0 Experimental

#### 2.1 Materials and chemistries

To evaluate the effects of various thermomechanical treatments on microstructural and mechanical characteristics, three modified 9Cr-1Mo alloys and two 12Cr-1MoVW (HT-9) alloys were selected and thermomechanically treated. The three 9Cr-1Mo alloy heats, 16094906-1, 16094906-2, and 16094906-3, were provided by other work package at PNNL (led by M. Toloczko) as  $100 \times 100 \times 3$  mm thick plates. The composition of the first heat is close the typical composition for a 9Cr-1Mo steel except for the addition of Ta, but the latter two alloys contain higher nitrogen (0.38% and 0.045%, respectively). Vanadium (0.21%) was added to the 9Cr steel-3. Meanwhile, these two HT-9 plates, 15074631-3 & 15084631-4 (N-added), were supplied by Los Alamos National Laboratory in the form of hot-rolled and heat-treated rectangular plate (330×85×12 mm), which had been cross-rolled twice at 1000°C (once perpendicular and once parallel to the original extrusion direction), normalized (annealed at 1040°C for 30 min and aircooled) and then tempered (annealed at 760°C for 1 hour and air-cooled) [29]. Table 1 lists the chemical compositions of these alloys.

Table I. Chemical comp	positions of $9Cr$ and .	l 2Cr ferritic-mari	tensitic steels wi	ith and without
nitrogen addi	tion. Note the three N	l-added steels, 9C	Cr steel heat-2, 9	PCr steel heat-3,
and 12Cr steel heat-4, contain about 0.04% nitrogen.				

Elements (wt.%)	9Cr Steel Heat-1	9Cr Steel Heat-2 (N- added)	9Cr Steel Heat-3 (N- added)	12Cr Steel (HT-9) Heat-3	12Cr Steel (HT-9) Heat- 4 (N-added)
N	< 0.001	0.038	0.045	0.001	0.044
С	0.12	0.10	0.06	0.20	0.20
S	< 0.001	< 0.001	< 0.001	0.001	0.001
0	0.0076	0.0099	0.0093	0.007	0.007
Cr	9.1	9.1	9.0	11.07	11.42
Mn	0.5	0.5	0.49	0.55	0.56
Мо	1.46	1.42	0.50	1.0	1.0
Ni				0.51	0.52
Р				< 0.01	< 0.01
Si	0.11	0.11	0.10	0.25	0.26
W				0.47	0.48
V			0.21	0.30	0.30
Та	0.087	0.086	0.086		
Fe	88.61	88.64	89.50	85.63	85.20

#### 2.2 Thermomechanical treatments

In this research new thermomechanical processing routes combining a rapid quenching and controlled tempering step(s) were designed and applied to the high-Cr alloys to produce ultrafine microstructures with nanoscale laths and well-dispersed fine carbide particles in the high-Cr steels. In particular, a variety of tempering conditions were designed to test all possible degree of precipitation, i.e., untempered to fully tempered conditions. Figure 1 illustrates the schematics of the thermomechanical processing routes, which indicates that combining different after-quench treatments can yield various processing routes and thus microstructures. Since we aim to improve the mechanical performance of thin core components (for example, ~0.5 mm for fuel cladding and ~3 mm for fuel duct in sodium-cooled reactors), thin coupons ( $\leq 4$  mm) were used to achieve a high cooling rate of 100°C/s or higher, which can produce a nanoscale martensitic lath structure in quenching. In the final step we attempted reduced degrees of tempering, from the traditional full tempering, to produce finer precipitates within the ultrafine lath structure from rapid quenching so that both higher strength and fracture toughness can be achieved.



Figure 1. Schematic of thermomechanical processing: a variety of thermomechanical processing routes can be designed by combining these normalization and tempering components [29]. Multiple single-step tempering and two-step tempering treatments were applied to the thin (2.5–4 mm) coupons. (Note that the controlled rolling or the route (a) are not attempted at this research.)

Table 2 summarizes a few series of thermomechanical treatments (TMTs) consisting of normalization (dissolution of precipitates in the austenite region), rapid quenching in water, and single or two-step tempering. The first step prior to the designed thermal treatments was a hot-rolling process, which consists of multiple heating-rolling steps reduction in each pass, primarily to reduce the thickness of plates to 3 mm for 9Cr alloys or to 2.5–4 mm for 12Cr alloys, with which a rapid quenching is possible in water. The as-rolled (AR) strips or as-normalized plates

were cut into  $\sim 40 \times \sim 50$  mm coupons for further heat treatments. The as-received microstructures were erased by renormalizing all coupons in the same condition to remove the differences from the prior processes. The second step in the TMT was to create a martensitic structure with very fine laths, which is the normalization at 1070°C for 1 hour followed by a rapid quenching in agitated water. After this step, no deforming treatment is applied, considering that the new process will be applied to non-flat components such as cladding tubes.

#	TMT Route	Normalization + Quenching	1 <sup>st</sup> Tempering	2 <sup>nd</sup> Tempering	Approx. Coupon Size in WQ (mm)
1	#AR (As Rolled)	1100°C/30 min & Hot Rolling			
2	#WQ (Water Quench)	1070°C/1h & WQ			40 x 50 x (2.5-4)
3	#WQ-300°C	1070°C/1h & WQ	300°C/1h & AC		40 x 50 x (2.5-4)
4	#WQ-400°C	1070°C/1h & WQ	400°C/1h & AC		40 x 50 x (2.5-4)
5	#WQ-500°C	1070°C/1h & WQ	500°C/1h & AC		40 x 50 x (2.5-4)
6	#WQ-600°C	1070°C/1h & WQ	600°C/1h & AC		40 x 50 x (2.5-4)
7	#WQ-650°C	1070°C/1h & WQ	650°C/1h & AC		40 x 50 x (2.5-4)
8	#WQ-750°C	1070°C/1h & WQ	750°C/1h & AC		40 x 50 x (2.5-4)
9	#WQ-300°C-650°C	1070°C/1h & WQ	300°C/1h & AC	650°C/0.5h & AC	40 x 50 x (2.5-4)
10	#WQ-400°C-650°C	1070°C/1h & WQ	400°C/1h & AC	650°C/0.5h & AC	40 x 50 x (2.5-4)
11	#WQ-500°C-650°C	1070°C/1h & WQ	500°C/1h & AC	650°C/0.5h & AC	40 x 50 x (2.5-4)
12	#WQ-600°C-650°C	1070°C/1h & WQ	600°C/1h & AC	650°C/0.5h & AC	40 x 50 x (2.5-4)
13	#WQ-300°C-750°C	1070°C/1h & WQ	300°C/1h & AC	750°C/0.5h & AC	40 x 50 x (2.5-4)
14	#WQ-400°C-750°C	1070°C/1h & WQ	400°C/1h & AC	750°C/0.5h & AC	40 x 50 x (2.5-4)
15	#WQ-500°C-750°C	1070°C/1h & WQ	500°C/1h & AC	750°C/0.5h & AC	40 x 50 x (2.5-4)
16	#WQ-500°C-650°C-S	1070°C/1h & WQ	500°C/1h & AC	750°C/0.25h & AC	40 x 50 x (2.5-4)
17	#WQ-600°C-750°C	1070°C/1h & WQ	600°C/1h & AC	750°C/0.5h & AC	40 x 50 x (2.5-4)
18	#WQ-600°C-750°C-S	1070°C/1h & WQ	600°C/1h & AC	750°C/0.25h & AC	40 x 50 x (2.5-4)

Table 2. Various thermomechanical processing routes that have been used in this research.The tempering processes include both single-step and double-step temperingtreatments, after the same normalization and water quenching treatment.

Note that the # in front of the TMP routes indicates the heat number (i.e., 1, 2 & 3 for 9Cr steels and 3 & 4 for 12Cr steels)

In the next step, the as-quenched coupons were further heat-treated or tempered before machining into specimens for mechanical testing. The tempering treatments include three groups: (i) single-step tempering for 1 hour at temperatures 300–750°C, in which the highest temperature treatment is equivalent or close to the typical tempering process for most of the ferritic-martensitic steels including HT-9 steels [7,22,23], (ii) two-step tempering consisting of a

lower temperature (300–600°C) tempering for 1 hour and a higher temperature (650°C) tempering for 0.25 or 0.5 hour, and (iii) two-step tempering consisting of a lower temperature (300–600°C) tempering for 1 hour and a higher temperature (750°C) tempering for 0.25 or 0.5 hour. All tempering steps were followed by air-cooling. The first tempering at 300–600°C was to generate fine carbides and other precipitates in the quenched martensite (possibly with small amount of ferrite) structure.

After the thermomechanical processing seven SS-3 subsize tensile specimens were machined from each of the 2.5 to 4 mm thick coupons and seven miniature bend fracture specimens from the each of the thermomechanically treated coupons. As seen in Table 2, the specimens were tested either in the as-rolled (AR) condition, in the as-water quenched (WQ) condition, in 6 single-tempered conditions, or in 10 double-tempered conditions. Both the tensile testing and the fracture testing were carried out at six different temperatures: 25, 200, 300, 400, 500, and 600°C.

#### 2.3 Mechanical testing

In this project more than 400 static fracture resistance (J-R) tests to obtain fracture toughness data were performed in an electromagnetically driven testing machine equipped with an environmentally controlled high temperature furnace. The fracture specimens were miniature (14  $mm \times 4 mm \times 3 mm$ ) bend bars with a 1.5 mm deep notch and a 0.45 mm deep side groove at each side, and all had L-T orientation, in which the loading direction is in the rolling (L) direction and crack extension occurs along the perpendicular (T) direction. Since the plates of 9Cr steels were cross-rolled, no clear directional difference will be observed although the L-T orientation was kept in the 9Cr steel specimens. Precracking to produce sharp crack tip was carried out for all bend bar specimens under a nominal cyclic load of at  $300 \pm 200$  N at 25 Hz until the machined notch extended by 0.3–0.7 mm. Nominal crack length-to-specimen width ratio (a/W) was about 0.5 before the J-R testing. The fracture resistance (J-R) testing was carried out in quasi-static mode at a crosshead speed of 0.3 mm/min with a temperature control within  $\pm 3^{\circ}$ C. For each TMT condition, J-R test was conducted at six (6) temperatures of RT, 200, 300, 400, 500, and 600°C either in argon gas environment or in air. The J-R tests were run in a displacement controlled three-point bending mode, and the static fracture testing and evaluation were performed following the standard procedure in the ASTM Standard E1820-09 [29].



Figure 2. Miniature fracture specimen design: the single edged bend (SEB) fracture specimen for three-point bending (TPB) fracture testing. (Note that the specimen thickness was 2.5 mm for the coupons with < 3mm thickness.)

Since the curve normalization method was applied to the construction of fracture resistance (J-R) curves, the monotonic load-displacement curves, without elastic loading-unloading cycles, were recorded during testing. Testing was terminated when the load measurement increased to a maximum and then decreased to about 55% of the maximum load unless a catastrophic failure occurred before reaching the 55% load point. After each J-R test the tested specimen was heattinted during slow cooling to make a mark for the final crack length before the complete separation of the specimen. Initial and final crack lengths were then measured on optical photographs and used in the calculation of J-R data. In the data analysis procedure to construct the J-Resistance curve (J-integral versus  $\Delta a$  curve), the crack lengths during crack growth (i.e., those between the measured initial and final crack lengths) were calculated using the curve normalization method, which is described in the ASTM Standard E 1820 (section A15). In this work, however, the detailed calculation procedure was further simplified to eliminate the external clip-on gage which is usually attached to measure precise crack mouth opening displacement [16,29]. Two experimental datasets are needed to construct a J-R curve using the normalization method: a load-displacement curve and the initial and final crack lengths. Two interim fracture toughness (J<sub>0</sub>) values were determined at the intersection of the J-R curve and the 0.1 mm and 0.2 mm offset lines of the blunting line. Finally, the J<sub>Q</sub> values data were converted to the stress intensity factor (KJQ) values. The fracture toughness data (KJO) produced in this study remain as interim values (K<sub>JQ</sub>) because the curvature at crack frontline and the limitation imposed by small specimen volume and thickness cannot satisfy some of the standard requirements for the validated fracture toughness (K<sub>IC</sub>).

Finally, it is noted that, although tensile testing has been performed at the same test temperatures selected for the J-R tests and the tensile strength data were used in calculation of J-R curves and fracture toughness values, no tensile data are reported here because the majority of the tensile data were reported in previous report [28] and this report focuses to present the full set

of fracture toughness data for the high-Cr steels from this research. The tensile specimens were the SS-3 dog-bone shaped flat specimens with the gage section dimensions of 7.62 mm  $\times$  0.76 mm  $\times$  1.52 mm (respectively, the length, thickness, and width) and the total length of 25.4 mm. The tensile tests were carried out at room temperature (RT), 200, 300, 400, 500, and 600°C at a displacement rate of 0.5 mm/min, which corresponds to a nominal strain rate of 0.0011/sec. The engineering strength and ductility parameters were obtained from the raw tensile load-displacement and specimen dimension data.

### 3.0 Results and Discussion

# 3.1 Fracture toughness of 12Cr steels after various thermomechanical treatments

Figures 3 and 4 present the fracture toughness (K<sub>JQ</sub>) versus test temperature data over the test temperature range of RT–600°C for the 12Cr steels or HT-9 heat-3 and heat-4, respectively. This testing and evaluation task aims to select a TMT route that can improve both the strength and the fracture toughness of HT-9 steels, or at least either of those without scarifying the other property. In particular, achieving a significant improvement in mechanical properties in the high temperature range of  $> 550^{\circ}$ C is particularly important as this range is where the thermal capability of future fast reactors is expected to be extended. The existing fracture toughness data for the FFTF and INL HT-9 steels are also displayed in the Figures 3 and 4 for the purpose of comparison. Therefore, a reasonable criterion for selecting a new TMT that can improve mechanical properties should be that neither fracture toughness nor strength is decreased form these of reference materials by applying the new TMT.

The fully-tempered ferritic-martensitic steels, including the FFTF and INL HT-9 steels, will show a continuous decrease in fracture toughness with increasing temperature when the steels are tested above room temperature or an upper shelf [30]. Such a test-temperature dependent decrease in the ferritic-martensitic steels is primarily due to the steep decrease of strength with increasing test temperature. In detail, however, a steep decrease or sometimes a local minimum in fracture toughness is found in the elevated temperature region of 200-400°C. Such an additional loss of fracture toughness in the elevated temperature region is known as the effect of dynamic strain aging (DSA) due to the obstruction of dislocation glide by the cloud of interstitial elements such as nitrogen and carbon that follow the stress fields of moving dislocations [12]. Although the DSA induced reduction is usually mild in HT-9 steels and thus its effect is not obvious in the fracture toughness versus temperature curves [30], the fracture toughness versus temperature curve of these steels sometimes show a low value region before a reincrease at higher temperatures. This reincrease of fracture toughness at high temperatures (typically > 400°C) should be primarily due to the increase of ductility beyond the DSA region. Therefore, the temperature dependence of fracture toughness of the fully-tempered HT-9 steels (and 9Cr steels) above room temperature will show a monotonic decrease or a decrease-increase cycle.

It is observed in Figure 3(a) that the room-temperature fracture toughness is generally quite high (i.e., > ~200 MPa $\sqrt{m}$ ) except for a few conditions such as no or low-temperature tempering (AR, WQ-300°C and WQ-400°C). In general, the temperature dependence of fracture toughness above RT is dependent on the degree of tempering: the K<sub>JQ</sub> values of HT-9 steel heat-3 after WQ-400°C, WQ-300°C-650°C, WQ-400°C-650°C, and WQ-600°C-650°C processes monotonically decrease with test temperature; those after WQ-400°C, WQ-500°C, WQ-600°C, and WQ-500°C-650°C decrease and then increase with test temperature. The AR condition resulted in a low RT fracture toughness but it monotonically increased with temperature afterwards. There found a notable case, 3WQ-600°C (and -R), that have yielded significantly improved K<sub>JQ</sub> to the level of 300 and 400 MPa $\sqrt{m}$  at 600°C, which can be positively compared to the typical K<sub>JQ</sub> range of 150–200 MPa $\sqrt{m}$  for the fully tempered HT-9 steels (i.e., FFTF and INL alloys). Since these reference materials commonly show a monotonic decrease of fracture toughness with test temperature, the decrease-increase cycle in fracture toughness should be a useful evidence for an improved mechanical capability.

Figure 3(b) compares the fracture toughness data of the HT-9 heat-3 after two-step tempering, in which the second tempering was at either 650°C or 750°C. Regardless of the differences in the detailed tempering conditions, all of the combinations of tempering steps yielded comparable or higher fracture toughness over the test temperature range when compared to those of the reference HT-9 steels. It is a notable result that the specimens after two tempering treatments,  $500^{\circ}C/1h + 650^{\circ}C/15min$ ,  $600^{\circ}C/1h + 750^{\circ}C/15min$ , are able to maintain their fracture toughness over 200 MPa√m in the high-temperature range. It is a particularly desirable behavior that the fracture toughness of these materials can increase with test temperature in the 500–600°C region, while the materials after other tempering treatments, including the reference cases, experience decrease of fracture toughness with test temperature.



Figure 3. Fracture toughness of 12 Cr steel (HT-9 steel) heat-3 after various thermomechanical treatments, whose final conditions include (a) as-rolled (AR), water-quenched (WQ), single-tempered (1 h) conditions, and (b) double-tempered conditions. Note that R indicates repeated testing and S the second tempering was for 15 minutes instead of typical 30 minutes.



Figure 3 (continued). Fracture toughness of 12 Cr steel (HT-9 steel) heat-3 after various thermomechanical treatments, whose final conditions include (a) as-rolled (AR), waterquenched (WQ), single-tempered (1 h) conditions, and (b) double-tempered conditions. Note that R indicates repeated testing and S the second tempering was for 15 minutes instead of typical 30 minutes.

The fracture toughness data of the HT-9 heat-4 after various TMTs are compared with those of the reference HT-9 steels in Figure 4. The comparison in Figure 4(a) clearly shows that the overall K<sub>JQ</sub> range of the HT-9 heat-4 after hot rolling only or any single-step tempering is slightly lower than the reference data. It is also realized that the fracture toughness of the HT-9 heat-4 is generally lower than that of the HT-9 heat-3. All of the samples tempered at or above 600°C show their fracture toughness either monotonically decreasing from the highest values at room temperature with test temperature or decreasing in low temperature region and then slightly increasing above 300°C. Some cases show temperature transition behavior at  $\leq$  300°C: the K<sub>JQ</sub> values without tempering or after relatively low degrees of tempering, i.e., AR, WA-300°C, WQ-400°C, and WQ-500°C, increase with test temperature from a low toughness range of 60–80





Figure 4. Fracture toughness of 12 Cr steel (HT-9 steel) heat-4 (N-added) after various thermomechanical treatments, whose final conditions include (a) as-rolled (AR), waterquenched (WQ), and single-tempered (1 h), and (b) double-tempered conditions. Note that R indicates repeated testing and S the second tempering was for 15 minutes instead of typical 30 minutes.

The fracture toughness data of the heat-4 after two-step tempering are presented in Figure 4(b). The two two-step tempering routes, WQ-500°C-650°C and WQ-600°C-750°C, resulted in the fracture toughness similar to the reference data. No other tempering route was able to improve fracture toughness with the HT-9 alloy heat-4 composition. Regardless, it is reminded that the strength of the heat-4 either of the two-step tempering treatments was significantly higher than those of fully-tempered cases, and therefore, at least the two TMTs, WQ-500°C-650°C and WQ-600°C-750°C, have achieved significant gains in strength without sacrificing fracture toughness, which can be considered as an improved mechanical property. The results

described above indicate that no clear improvement in fracture resistance can be made with the HT-9 steel composition with nitrogen addition. In fact, the conclusion from the discussion should be that the addition of nitrogen (~0.044%) to the original HT-9 composition is actually detrimental to the fracture resistance of the alloy. The cause for this needs to be further investigated; the addition of nitrogen can form a nitrogen stabilized second phase, which might not be a ductile phase.



Figure 4 (continued). Fracture toughness of 12 Cr steel (HT-9 steel) heat-4 (N-added) after various thermomechanical treatments, whose final conditions include (a) as-rolled (AR), water-quenched (WQ), and single-tempered (1 h), and (b) double-tempered conditions. Note that R indicates repeated testing and S the second tempering was for 15 minutes instead of typical 30 minutes.

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# 3.2 Fracture toughness of 9Cr steels after various thermomechanical treatments

Since only the tempering procedures that could improve the fracture resistance of 12Cr steels were selected for the treatment of 9Cr steels, fracture toughness testing was performed for the limited conditions of three 9Cr steels. The selected TMTs applied to the 9Cr steels were the normalization and water quenching followed by the one-hour tempering at 500°C or 600°C or by the same one-hour tempering plus the second tempering at 650°C or 750°C. In Figures 5 to 7, the fracture toughness data of the three 9Cr steels after these treatments are compared, along with the data for water quenched condition. Some fracture toughness data for other 9Cr alloys such as Eurofer-97 and Mod 9Cr-1Mo were collected from literature [31-35] and given as reference data for comparison. Among the data, the alloy status after the treatment of WQ-600°C (1h)-750°C (0.5h) is considered fully tempered.



Figure 5. Fracture toughness of 9Cr steel-1 after various thermomechanical treatments, whose final conditions include the as-rolled (AR), water-quenched (WQ), single-tempered (1 h), and double-tempered conditions.

The fracture toughness data of the 9Cr steel-1 after these TMTs are compared in Figure 5. First of all, the water quenched material shows the lowest level of fracture toughness throughout the test temperature range. The data after single tempering at 500°C also show relatively lower fracture toughness but are similar to the others with higher degrees of tempering. The three TMTs with higher degrees of tempering, WQ-600°C, WQ-500°C-650°C, and WQ-600°C-750°C, resulted in high fracture toughness data above 150 MPa√m, falling in the range of the reference data for Eurofer-97 and Mod 9Cr-1Mo alloys.

Figure 6 displays the fracture toughness test results for the 9Cr steel-2. Except for the data of the water-quenched material, the fracture toughness data after new TMTs cluster together over the test temperature range regardless of different tempering treatments. Only obvious aberration is the ordinary high value at 600°C for the steel after the WQ-600°C-750°C treatment, which might be due to an excessive ductility introduced to the material. Overall fracture toughness versus temperature behavior of this alloy is highly similar to that of the 9Cr steel-1, which indicates the addition of nitrogen has not affected the mechanical behavior of these alloys.



Figure 6. Fracture toughness of 9Cr steel-2 after various thermomechanical treatments, whose final conditions include the as-rolled (AR), water-quenched (WQ), single-tempered (1 h), and double-tempered conditions.

The 9Cr steel-3 contains relatively smaller amount of molybdenum (0.5% instead of ~1.5% for the other two 9Cr alloys) but additional ~0.21% vanadium and highest amount of nitrogen (0.045%). The fine vanadium carbides and nitrides that might be formed during tempering treatment should be for increasing high temperature strength. The data displayed in Figure 7 indicate, however, that the modification in alloy composition has reduced fracture toughness of the alloy at low temperatures. Both of those single-tempered materials show much lower fracture toughness at room temperature and slightly lower at 200°C; however, the data at higher temperatures are similar to those of other 9Cr alloys. Again, the two double-tempering treatments, WQ-500°C-650°C and WQ-600°C-750°C, resulted in good fracture toughness well within the data range of the reference materials.



Figure 7. Fracture toughness of 9Cr steel-3 after various thermomechanical treatments, whose final conditions include the as-rolled (AR), water-quenched (WQ), single-tempered (1 h), and double-tempered conditions.

#### 4.0 Summary

This research aimed to find a new processing route that can produce an optimized microstructure of each high-Cr steel with improved mechanical properties including excellent high temperature fracture toughness. The research was based on the known observation that finer microstructures usually demonstrate higher resistance to radiation damage as well as better mechanical performance. It was considered that (i) a highly controlled treatment, such as a rapid cooling, which can effectively refine the quenched lath structure, and (ii) the following tempering process, should be feasible for the practical processing of thin core components such as fuel cladding and fuel duct. For this fracture toughness testing campaign, twelve thermomechanical treatments (TMTs) were applied to the two 12Cr alloys, and a select of five TMT routes were applied to the three 9Cr alloys. Fracture toughness tests were carried out over a wide temperature range of 22 - 600°C, and the results were compared with reference data for the 9Cr and 12Cr steels. Listed below are the key observations from the comparison, which aimed to answer to the question whether any of the new TMTs can improve the fracture resistance of the high-Cr steels.

- [1] For the 12Cr (HT-9) steels, the two final TMTs with two-step temping, WQ-500°C-650°C and WQ-600°C-750°C, consistently delivered high fracture toughness over the test temperature range. It is a notable result that the HT-9 heat-3 specimens after two tempering treatments, 500°C/1h + 650°C/15min, 600°C/1h + 750°C/15min, are able to maintain their fracture toughness over 200 MPa√m in the high-temperature range of >200°C. When compared to those of FFTF and INL HT-9 steels, the fracture toughness of the HT-9 steel heat-3 actually improved with those TMT routes but that of the HT-9 steel heat-4 did not show any improvement. The single-step tempering at 600°C also resulted in high fracture toughness for both HT-9 steels.
- [2] Considering the benefit of a higher strength that can be obtained with a lower degree of tempering, it is recommended that the HT-9 steels are tempered at 600°C with or without a short additional tempering at 750°C.
- [3] Similar fracture resistance behavior was observed in the three 9Cr steels. Both of the twostep temperings after water quenching, WQ-500°C-650°C and WQ-600°C-750°C, yielded high fracture toughness with the three 9Cr steel compositions. Comparing with the reference data of Eurofer-97 and Mod 9Cr-1Mo indicates, however, that no improvement of fracture toughness can be attained with the 9Cr steels.
- [4] Addition of nitrogen or other modification in composition did not improve the fracture resistance of the high-Cr steels. That is, the addition of nitrogen (~0.044%) to the original HT-9 composition is actually detrimental to the fracture resistance of the alloy. Similarly, the 9Cr steel-3 contains relatively smaller amount of molybdenum (0.5% instead of ~1.5% for the other two 9Cr alloys) and additional ~0.21% vanadium and highest amount of nitrogen (0.045%), but this compositional modification actually reduced fracture toughness of the alloy, in particular, at low temperatures.

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