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EFFECT OF MULTIPLE AUSTENITIZING
TREATMENTS ON HT-9 STEELS

R.A. Emigh
(M.S. Thesis)

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Lawrence Berkeley Laboratory
University of California
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STEEL**

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ABSTRACT

The effect of multiple austenitizing treatments on the toughness of an Fe-12Cr-1.0Mo-0.5W-0.3V (HT-9) steel was studied. The resulting microstructures were characterized by their mechanical properties, precipitated carbide distribution, and fracture surface appearance. It was proposed that multiple transformations would refine the martensite structure and improve toughness. Optical and scanning electron microscopic observations revealed that the martensite packet structure was somewhat refined by a second austenite transformation. Transmission electron microscopy studies of carbon extraction replicas showed that this multiple step treatment had eliminated grain boundary carbide films seen in single treated specimens on prior austenite grain boundaries. The 0.2% yield strength, tensile strength, and elongation were relatively unchanged, but the toughness measured by fatigue pre-cracked Charpy impact tests increased for the multiple step specimens.

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INTRODUCTION

The long term feasibility of energy production from magnetic fusion reactors will depend in part on plant lifetimes. The structure in closest proximity to the plasma, the first wall/blanket, will see the severest service conditions in terms of radiation damage and thermal cycling. The cost and difficulty of replacing the first wall necessitates that its lifetime be maximized. One of the principal effects of radiation damage on the mechanical properties of metals is a reduction in toughness and an upward shift of the ductile-to-brittle transition temperature (T_b). Should T_b increase to the point where it reaches the service temperature, or the minimum temperature during planned or unplanned shutdowns, the component could fail catastrophically. Therefore, to withstand large doses of radiation the first wall material must begin service with maximum toughness.

The alloy investigated in this research, HT-9, was chosen because of its potential applications in Magnetic Fusion Devices as a first wall/blanket alloy (1). It has been proposed primarily because of its low swelling rate (2) and irradiation creep resistance (3) under neutron irradiation. HT-9 has already been used extensively in European power plants as high temperature piping (4). Its corrosion resistance and high temperature creep resistance make it perfect for applications requiring moderate stress at elevated service temperatures. It also has a low coefficient of thermal expansion and high thermal conductivity, both of which reduce the stresses developed by temperature changes (1).

Unfortunately, the potential usefulness of this steel is limited by irradiation-induced embrittlement which causes an increase in transition temperature (T_b) and a lowering of the Charpy V-notch upper shelf energy (5). It is believed that any improvement in T_b will delay the effects of any irradiation induced increase in T_b . A refinement in the martensite structure is a potential method of improving the alloy's initial toughness. Previous work on 9-12 Ni steels by Kim and Jin (6-9) has produced a successful technique for improving T_b . The procedure involves multiple thermal cycles into the austenite phase field to refine the martensite packet structure. The application of this type of heat-treatment to HT-9 is the purpose of this research.

The commonly specified heat treatment for HT-9 consists of an austenitizing treatment at 1020-1070°C for 30 minutes followed by a temper between 650-800°C for 0.5 to 2 hours (10). Previous research on HT-9 has shown that this heat treatment does not optimize the strength and toughness of this alloy (11). Chin has shown that a particular microconstituent, delta-ferrite, is detrimental to toughness and T_b . From examination of the equilibrium phase diagram (Figure 1) it is apparent that this alloy should transform entirely to austenite upon cooling below 1300°C. In practice, some delta-ferrite grains fail to transform and persist to low temperatures. This is due to a slight inhomogeneity in the distribution of the Cr and Mo, both of which are strong ferrite formers (1). At the interface of this ferrite and the matrix a continuous film of carbides forms and causes a decrease in toughness (11). Chin studied the effect of austenitization temperature on the volume percent of delta-ferrite and interfacial carbides.

He found a large reduction in these microconstituents at 1100°C which corresponded to an improvement in toughness and T_b .

Optical metallography of the as-received plate researched here, showed that it did contain long stringers of delta-ferrite and the associated interfacial carbides (Figure 2). Based on this information, an austenitization treatment of 1100°C for 30 minutes (designated as treatment A) was selected as a baseline. Next, a second 30 minute austenitization treatment at 1100°C was added in an attempt to refine the martensite and carbide structure. This is designated as treatment AA. Since grain growth is fairly rapid at 1100°C (11) it is important to minimize the time spent there. However, at 1050°C grain growth is much slower; therefore it was decided that a second austenitizing treatment of 1050°C for 30 minutes (designated as treatment A') would be examined and is designated specimen AA'. The effect of three austenite transformations was examined by applying an A treatment followed by two A' treatments (specimen AA'A'). In all cases the samples were allowed to air cool and given a temper at 700°C for 2 hours at the completion of all austenitization treatments. The various heat treatments are shown schematically in Figure 3.

EXPERIMENTAL PROCEDURE

A. Material

The alloy tested was HT-9 from ESR Heat #9607RZ of nominal composition Fe-0.2C-11.5Cr-1.0Mo-0.5W-0.3V. The exact composition, as determined by wet chemical analysis, is given in Table 1. The alloy, as-received, was in the form of a rolled plate 0.625 inches (15.88 mm) thick.

B. Heat Treatment

Heat treatments were performed on samples cut from the plate as shown in Figure 4. These were sealed in stainless steel bags to reduce high temperature oxidation. Sample temperatures were monitored with a thermocouple and all heat treatment times were taken after the samples had reached the appropriate temperature. At the completion of each treatment the samples were removed from the steel bags and allowed to air cool. Since this material will be used in thick sections it was believed that air cooling would most closely simulate actual practice and it was selected for this reasoning over a faster quench.

C. Optical Metallography

Optical examination of the as-received and heat treated material was made on a Carl Zeiss Metallograph. Specimens were cut in the longitudinal and transverse orientations from the as-received plate and from Charpy bars for the various heat treatments. They were mounted in Koldmount and ground to 400 grit with water cooling. Next, they were hand polished on Al_2O_3 paper to 0000 and then with diamond polishing paste to $1\mu m$ using kerosene for lubrication. Polishing times were kept to a minimum so that carbides present would not be lost. The heat treated specimens were etched using Viella's reagent (150 ml Ethyl Alcohol, 5 ml HCl, 1 gram picric acid) for 30 to 60 seconds. In addition, a decorating etch (80 ml H_2O , 20 ml HCl, 2 grams ammonium bifluoride, 1 gram potassium metabisulfide) was used on as-received to highlight the delta-ferrite by color staining the interfacial carbides (11). Etching times for this solution were from 15-45 seconds.

D. Grain Size Determination

The prior austenite grain size of all four heat treatments was determined using micrographs taken at 50X. Grain areas were digitized from eight micrographs of each treatment using a CALCOMP 9000 Digitizer. These data were then analysed to give mean grain diameters and standard deviation. The distribution of grain areas is plotted in Figure 5 and the grain size data are given in Table 2.

E. Carbon Extraction Replicas

The following procedure was used to extract precipitated carbides for TEM examination. Optical specimens from each heat treatment were etched for 1 minute with Viella's reagent. Next, a thin carbon film was deposited under vacuum of 10^{-4} torr. The deposited film was then scored with a grid of 2 mm squares and the specimens were submerged in Viella's reagent. As the carbide squares released from the surface they were collected on 200 mesh, 3 mm copper grids. The films were then rinsed thoroughly with ethyl alcohol and allowed to dry. Specimens were then examined at 100kV using a Phillips EM 301 Microscope.

F. Scanning Electron Microscopy

The fracture surfaces of the impact and tensile specimens were examined in a scanning electron microscope. The microscope used was an ISI-DS130 and was operated at 20kV.

G. Charpy Impact Testing

After heat-treatment, standard V-notch Charpy specimens (ASTM Type A, 11) were cut from the samples, machined and ground (Figure 6). The specimens were next notched to a depth of 2 mm and fatigue pre-cracked an additional 1 mm. The specimens were broken using a Charpy impact test machine with a 60 lb (27.3 Kg) hammer. Specimens were submerged in liquid baths of constant temperature for a minimum of 15 minutes. They

were removed from the liquids and fractured within 5 seconds as per ASTM E-23. After fracture, the exact fatigue cracked area was measured using a travelling microscope accurate to ± 0.01 mm. The absorbed energies were then normalized to a constant area of 80 mm^2 (0.124 in^2).

H. Tensile Testing

Tensile testing was performed on an Instron 1332 universal testing machine with 220kN (50kip) capacity. Samples used were subsize flat tensile specimens (Figure 7) with an initial gauge length of 25.4 mm, cut and machined from larger heat-treated blocks. The samples were pulled using a crosshead speed of $6.4 \times 10^{-3} \text{ mm/second}$ ($2.5 \times 10^{-4} \text{ in/second}$). The yield strengths were determined at 0.2% offset as indicated by a clip strain gage. Elongation values were determined using a traveling microscope and a 25.4 mm gauge length. For each heat treatment, two tests were performed at room temperature (25°C).

RESULTS AND DISCUSSION

Microstructure

Optical metallography was performed on as-received, A, AA', AA, and AA'A' specimens. The microstructure of the as-received material (Figure 2) consists of ferrite grains with a small number of delta-ferrite stringers and the associated interfacial carbides. The hardness of this structure was $60R_g$ ($18R_c$). After austenitization, but prior to tempering, the microstructure is almost completely martensitic with a hardness of $52R_c$. During tempering, carbides precipitate out of the martensite primarily on interlath and prior austenite grain boundaries. This reduction of carbon in the martensite drops the hardness to $32R_c$. Optical microscopy reveals that each prior austenite grain has transformed into several packets of martensite (Figure 8). The multiple step treated specimens appear to have a finer martensite structure with more packets per grain. This effect can be seen in Figure 9 which compares the optical microstructure of specimens A and AA'. The martensite microstructure of specimens AA and AA'A' were the same as that of specimen AA'.

Through the use of carbon extraction replicas it was possible to examine the resulting carbide structures of the austenitized and tempered specimens. In all of the heat treatments it was determined, through selected area diffraction, that the carbides present were of the form $M_{23}C_6$. The carbides were observed to lie almost exclusively on

lath boundaries and on prior austenite grain boundaries. In the singly transformed specimens (A) it was observed that there were continuous carbide films along many of the prior austenite grain boundaries (Figure 10). However, this was not seen in the twice transformed specimens (Figure 11 and 12) which exhibited a more uniform distribution of carbides with few or no continuous films. These films, when present, provide a very long, low energy crack path and lead to areas of intergranular fracture. Elimination of these grain boundary films will force fracture to occur more through translath cleavage and less along prior austenite grain boundaries. Since the lath structure is much finer than the prior austenite grain size, the crack is forced to change directions more often, leading to improved toughness.

Mechanical Properties

The mechanical properties were characterized through Charpy impact testing and uniaxial tensile tests. A summary of the tensile data is presented in Table 3, along with the data published by Smidt et.al (5). A comparison of the A and AA' specimens shows that the effect of a second austenitizing treatment is a marginal increase in 0.2% yield strength and ultimate tensile strength along with nearly equal elongation. It is also of interest to compare the HT-9 studied in this research with the Smidt values. The higher yield and tensile strength of our HT-9 can be attributed to two processing variables: 1) the austenitization temperature, and 2) the amount of tempering. The 1100°C austenitizing temperature dissolves carbides more effectively which increases the carbon content of the martensite and raises its hardness.

Increased tempering (higher temperature, longer time) would reduce the strength of this alloy to a level closer to that published by Smidt. If the strength of this alloy is reduced through additional tempering, the toughness and T_b should increase accordingly (13). Therefore any improvement in toughness, without loss of strength, should also exist at lower strength levels.

Fatigue pre-cracked Charpy impact tests were performed on A and AA' specimens at 0°C, 20°C, 50°C, and 100°C. In addition, AA and AA'A' specimens were tested at 0°C, 20°C, and 50°C. The results of these tests are given in Table 4. A plot of the A and AA' results is included as Figure 13. These data show that the second austenitizing treatment has noticeably improved the toughness of this steel. The 40 Joule transition temperature is improved by 25°C and the toughness at 100°C is improved by 15%. This effect is believed to be due to the finer martensite structure and associated carbide structure, as was observed in the studies of the carbide extraction replicas and optical microstructure. Figure 14 compares the Charpy impact values for the AA', AA, and AA'A' specimens. The latter two both show slightly lower toughness than the AA' treatment.

The toughness of this alloy is determined primarily by two microstructural parameters: the prior austenite grain size and the martensite/carbide structure. Previous research on HT-9 has shown that an increase in the prior austenite grain size causes a decrease in impact toughness (13). However, a refinement of the martensite/carbide structure improves toughness, as seen in specimen AA'. It should be noted that the grain size has increased (Table 2) but its effect is outweighed by the improvement gained by the second austenite

transformation. The application of a third transformation step (specimen AA'A') causes an increase in grain size and a slight loss of toughness. Optical metallography reveals no further refinement of the martensite structure. From this it can be concluded that the refinement is completed after two transformations and additional austenitizing treatments will decrease toughness because of grain growth. The AA specimen has the largest grain size by far and, although tougher than the A treatment, has lower toughness than both the AA' and AA'A' treatments (Figure 14). This is consistent with the theory that a second austenitizing treatment improves toughness but that increased grain size decreases it.

Fracture Surface Analysis

The fracture surfaces of the tensile and Charpy specimens were examined using a scanning electron microscope. This was done in order to characterize the fracture mode and examine the micro-features of the fracture. In the case of the tensile specimens the fracture was almost completely ductile rupture in all cases (Figure 15). Some areas of cleavage were seen between ductile regions but the amount was small. In addition, there is considerable secondary cracking of prior austenite grain boundaries especially in the singly transformed specimens. This indicates the general weakness of these interfaces.

The Charpy fracture surfaces for all heat treatments and test temperatures were examined. At 100°C the fracture mode is one composed primarily of ductile-dimple rupture with some areas of translat

cleavage. At this temperature there is a slight difference between the A and AA' treated specimens. The AA' specimens showed fewer areas of cleavage and in the ductile regions they showed more deformation prior to failure (Figure 16).

In the brittle (0°C) mode the fracture is composed of translath cleavage with some areas of intergranular fracture. The difference between the A and AA' is in the number and size of intergranular facets. This effect is readily apparent from the low magnification micrographs shown in Figure 17. The A specimen shows a more intergranular fracture surface with more and larger facets. The AA' specimen shows primarily a translath fracture with a very limited amount of intergranular fracture. In addition, there are areas of the AA' fracture surface that show some amount of ductility (Figure 18) similar to the fracture seen at higher temperatures. By eliminating most of the continuous carbide films on internal boundaries the crack is forced to pass through areas containing fewer carbides.

In the transition region (50°C) the fracture is quasi-cleavage, a combination of translath cleavage and ductile rupture. The principal difference between the A and AA' specimens is in the relative amounts of each type of fracture.

CONCLUSION

In this research the effect of multiple austenitizing treatments on HT-9 has been studied. It was learned, through optical and carbide extraction replication, that a second austenite transformation improves the martensite/carbide structure. The carbide films seen along prior austenite grain boundaries in singly transformed specimens are eliminated by the second transformation. This improves the impact toughness by reducing the amount of intergranular fracture. In addition, it was learned that application of a third austenitizing treatment does not further improve the impact toughness or T_b . From this information the following conclusions are drawn:

1) The ductile-to-brittle transition temperature of HT-9 was improved by 25°C through the application of two austenitization treatments. In addition, the upper shelf impact toughness was improved by 15%. These improvements are the result of two microstructural changes: 1) refinement of the martensite structure and 2) a more uniform distribution of precipitated carbides.

2) Application of a third austenitization treatment does not improve on the mechanical properties achieved by two austenitization treatments.

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Table 1. Elemental analysis of HT-9 plate in weight percent.

C	Cr	Mo	W	V	Ni	Mn	S	P	Si	Fe
.20	12.1	1.04	.45	.28	.51	.57	.003	.016	.17	Bal.

Table 2. Average intersected grain areas of the four heat treatments.

Heat Treatment	Average Grain Diameter (μm)	Standard Deviation	Grains Counted
A	171.	22.	96
AA'	223.	24.	86
AA'A'	245.	17.	77
AA	311.	35.	48

Table 3. Summary of the uniaxial tensile tests performed.

	0.2 % Yield Strength MPa(ksi)	Ultimate Tensile Strength MPa(ksi)	Uniform Elongation %	Total Elongation %	Heat Treatment
A	786(114)	945(137)	6.8	12.8	1100°C/30min + 700°C/2hrs
AA'	800(116)	965(140)	6.6	12.4	1100°C/30min + 1050°C/30min + 700°C/2hrs
Smidt et al	653(95)	823(119)	7.5	16.4	1050°C/30min + 780°C/2.5hrs

Table 4. Summary of the pre-cracked Charpy impact tests performed.

CHARPY IMPACT TOUGHNESS (JOULES)

SPECIMEN	TEMPERATURE (C)			
	0	20	50	100
A	11	13	34	61
AA'	17,18	25	57,58	71
AA	12	22	47	-
AAA'	13	23	51	-

Figure 1. Pseudo-Binary Phase Diagram of Fe-Cr at 0.2% Carbon (14).

XBB 850-9080

Figure 2. Optical micrographs of as-recieved HT-9.

Figure 3. Schematic diagram showing heat treatment times and temperatures

Figure 4. Orientation of test specimens.

Figure 5. Distribution of intersected grain areas counted.

XBL 7910-7195

Figure 6. Charpy impact specimen.

TENSILE SPECIMEN

SCALE 2:1

Figure 7. Pin-loaded flat tensile specimen.

XBB 850-9082

Figure 8. Optical micrographs of austenitized and tempered HT-9 revealing the martensite packed structure (Viella's reagent, 30seconds).

XBB 850-9081

Figure 9. Optical micrographs of specimens A) A and B) AA' (Viella's reagent, 30seconds).

XBB 850-9088

Figure 10. Carbon extraction replica of specimen A.

XBB 850-9089

Figure 11. Carbon extraction replica of specimen AA'.

XBB 850-9090

Figure 12. Carbon extraction replica of specimen AA'.

Figure 13. Plot comparing the pre-cracked Charpy impact toughness of specimens A and AA'.

Figure 14. Plot comparing the pre-cracked Charpy impact toughness of specimens AA, AA', and AA'A'.

XBB 850-9087

Figure 15. Scanning electron micrographs of the fracture surfaces of uniaxial tensile specimens.

XBB 850-9084

Figure 16. Scanning electron micrographs of the fracture surfaces of Charpy impact specimens fractured at 100°C.

XBB 850-9085

Figure 17. Low magnification scanning electron micrographs of the fracture surfaces of Charpy impact specimens fractured at 0°C.

XBB 850-9083

Figure 18. High magnification scanning electron micrographs of the fracture surfaces of Charpy impact specimens fractured at 0°C.