



(51) International Patent Classification:

C22C 30/00 (2006.01) F22B 37/10 (2006.01)
C21D 1/26 (2006.01) G21C 1/08 (2006.01)

(21) International Application Number:

PCT/CA2016/050104

(22) International Filing Date:

5 February 2016 (05.02.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/112,879 6 February 2015 (06.02.2015) US

(71) Applicant: **ATOMIC ENERGY OF CANADA LIMITED / ÉNERGIE ATOMIQUE DU CANADA LIMITEE** [CA/CA]; Chalk River Laboratories, Chalk River, Ontario K0J 1J0 (CA).

(72) Inventors: **TAPPING, Robert L.**; P.O. Box 338, Chalk River, Ontario K0J 1J0 (CA). **STAEHLE, Roger W.**; 22 Red Fox Road, North Oaks, Minnesota 55127-6331 (US). **ARIOKA, Koji**; c/o Institute of Nuclear Safety Systems, 64 Sata, Mihama-cho, Mikata-gun, Fukui 919-1205 (JP).

(74) Agent: **BERESKIN & PARR LLP/S.E.N.C.R.L., S.R.L.**; 40 King Street West, Suite 4000, Toronto, Ontario M5H 3Y2 (CA).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: NICKEL-CHROMIUM-IRON ALLOYS WITH IMPROVED RESISTANCE TO STRESS CORROSION CRACKING IN NUCLEAR ENVIRONMENTS

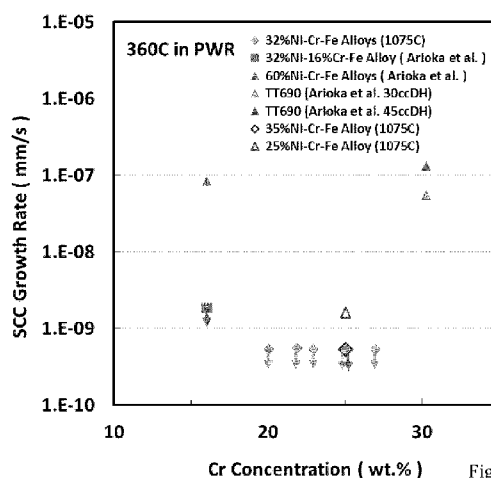


Figure 27A

(57) Abstract: A Ni-Cr-Fe alloy with improved resistance to stress corrosion cracking in nuclear environments, the alloy comprising 23-28 wt% Cr, 25-35 wt% Ni, < 0.03 wt% C, < 0.70 wt% Si, < 1.0 wt% Mn, < 0.015 wt% S, > 0.35 wt% Ti, 0.15-0.45 wt% Al, < 0.75 wt% Cu, and balance Fe and incidental impurities. The alloy may be used in steam generator tubing of a nuclear reactor. A method of producing an article includes: providing the alloy as disclosed herein; forming the alloy into the article by cold working the alloy to 20%; and heat treating the article.

- 1 -

**TITLE: NICKEL-CHROMIUM-IRON ALLOYS WITH IMPROVED
RESISTANCE TO STRESS CORROSION CRACKING IN NUCLEAR
ENVIRONMENTS**

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application No. 62/112,879 filed on February 6, 2015, the entire contents of which are hereby incorporated herein by reference.

FIELD

[0002] The present disclosure relates to materials science and corrosion engineering.

BACKGROUND

[0003] The following paragraphs are not an admission that anything discussed in them is prior art or part of the knowledge of persons skilled in the art.

[0004] Nickel-chromium-iron Alloy 800 (UNS N08800), as currently used in nuclear and other applications, has good corrosion resistance, especially resistance to stress corrosion cracking (SCC).

[0005] However, as reactor and other industrial plants age, and are considered for extended life beyond the original design lifetime, it is desirable to decrease susceptibility to SCC further.

INTRODUCTION

[0006] The following is intended to introduce the reader to the detailed description that follows and not to define or limit the claimed subject matter.

[0007] In an aspect of the present disclosure, a Ni-Cr-Fe alloy with improved resistance to stress corrosion cracking in nuclear environments may have between about 23 and 28 wt% Cr. In some examples, the alloy may have between about 24 to 27 wt% Cr, or about 25 wt% Cr. In some examples, the

- 2 -

alloy may have between about 25 and 35 wt% Ni, or between about 32 and 35 wt% Ni.

[0008] In some particular examples, the alloy may have about 32 wt% Ni and about 25 wt% Cr, or about 25 wt% Ni and about 25 wt% Cr, or about 35 wt% Ni and about 25 wt% Cr, or about 32 wt% Ni and about 27 wt% Cr. The alloy may further have: < 0.03 wt% C; < 0.70 wt% Si; < 1.0 wt% Mn; < 0.015 wt% S; > 0.35 wt% Ti; between 0.15 and 0.45 wt% Al; < 0.75 wt% Cu; < 0.03 wt% N; > 12 Ti/C; and balance substantially Fe.

[0009] The alloy may be used in a nuclear reactor. The alloy may be used in steam generator tubing of a nuclear reactor.

[0010] In an aspect of the present disclosure, a method of producing an article may include: providing the alloy as disclosed herein; forming the alloy into the article; and heat treating the article. In some examples, the step of heat treating may consist of solution annealing the article at at least about 1000°C for at least about 3 minutes, or between about 1050°C to 1100°C for at least about 3 minutes, or at about 1075°C for about 1 hour.

[0011] The method may further include, after the step of heat treating, rapidly cooling the article. The step of forming may include cold working the article to about 20%. After the step of heat treating, the article may have an average grain size of about 100µm.

[0012] Other aspects and features of the teachings disclosed herein will become apparent, to those ordinarily skilled in the art, upon review of the following description of the specific examples of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The drawings included herewith are for illustrating various examples of apparatuses and methods of the present disclosure and are not intended to limit the scope of what is taught in any way. In the drawings:

Figure 1 is a drawing of a compact tension (CT) specimen;

- 3 -

Figure 2 is an image of a CT specimen with fatigue pre-crack before testing;

Figure 3A is a graph showing crack growth vs. cavity formation for cold-worked (CW) carbon steel in creep and SCC conditions;

Figure 3B is a graph showing crack growth vs. cavity formation rates for CW Alloy 600 (UNS N06600) and Alloy 690 (UNS N06690);

Figure 4A is a graph showing temperature, conductivity and dissolved hydrogen vs. time in pressurized water reactor (PWR) primary water at 360°C (20%CW, 32%Ni-27%Cr-Fe, 1075°C x 1h W.C.);

Figure 4B is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 360°C (20%CW, 35%Ni-25%Cr-Fe, 1075°C x 1h W.C.);

Figure 4C is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 360°C (20%CW, 25%Ni-25%Cr-Fe, 1075°C x 1h W.C.);

Figures 5A and 5B show fracture surfaces after testing in PWR primary water at 360°C (20%CW, 32%Ni-27%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 6A and 6B show fracture surfaces after testing in PWR primary water at 360°C (20%CW, 35%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 7A and 7B show fracture surfaces after testing in PWR primary water at 360°C (20%CW, 25%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figure 8A is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 340°C (20%CW, 32%Ni-27%Cr-Fe, 1075°C x 1h W.C.);

- 4 -

Figure 8B is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 340°C (20%CW, 35%Ni-25%Cr-Fe, 1075°C x 1h W.C.);

Figure 8C is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 340°C (20%CW, 25%Ni-25%Cr-Fe, 1075°C x 1h W.C.);

Figures 9A and 9B show fracture surfaces after testing in PWR primary water at 340°C (20%CW, 32%Ni-27%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 10A and 10B show fracture surfaces after testing in PWR primary water at 340°C (20%CW, 35%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 11A and 11B show fracture surfaces after testing in PWR primary water at 340°C (20%CW, 25%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figure 12A is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 320°C (20%CW, 32%Ni-27%Cr-Fe, 1075°C x 1h W.C.);

Figure 12B is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 320°C (20%CW, 35%Ni-25%Cr-Fe, 1075°C x 1h W.C.);

Figure 12C is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 320°C (20%CW, 25%Ni-25%Cr-Fe, 1075°C x 1h W.C.);

Figures 13A and 13B show fracture surfaces after testing in PWR primary water at 320°C (20%CW, 32%Ni-27%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

- 5 -

Figures 14A and 14B show fracture surfaces after testing in PWR primary water at 320°C (20%CW, 35%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 15A and 15B show fracture surfaces after testing in PWR primary water at 320°C (20%CW, 25%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figure 16A is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 290°C (20%CW, 32%Ni-27%Cr-Fe, 1075°C x 1h W.C.);

Figure 16B is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 290°C (20%CW, 35%Ni-25%Cr-Fe, 1075°C x 1h W.C.);

Figure 16C is a graph showing temperature, conductivity and dissolved hydrogen vs. time in PWR primary water at 290°C (20%CW, 25%Ni-25%Cr-Fe, 1075°C x 1h W.C.);

Figures 17A and 17B show fracture surfaces after testing in PWR primary water at 290°C (20%CW, 32%Ni-27%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 18A and 18B show fracture surfaces after testing in PWR primary water at 290°C (20%CW, 35%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 19A and 19B show fracture surfaces after testing in PWR primary water at 290°C (20%CW, 25%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 20A, 20B and 20C show scanning electron microscope (SEM) images of the surface after testing on the bottom of the CT specimens;

Figures 21A, 21B, 21C, 21D, 21E, 21F, 21G, 21H, 21I and 21J show Auger electron spectroscopy (AES) mapping of the cross section after testing on the bottom of the CT specimens;

- 6 -

Figures 22A, 22B and 22C show SEM images of the cross section after testing on the bottom of the CT specimens;

Figures 23A and 23B show fracture surfaces after testing in air at 460°C (20%CW, 32%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 24A and 24B show fracture surfaces after testing in air at 440°C (20%CW, 32%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 25A and 25B show fracture surfaces after testing in air at 425°C (20%CW, 32%Ni-25%Cr-Fe, 1075°C x 1h W.C.) (12.5mm^t);

Figures 26A and 26B show fracture surfaces after testing in air at 445°C (19%CW, 34%Ni-22%Cr-Fe, 1065°C x 10m A.C.) (11mm^t);

Figure 27A is a graph showing SCC growth rate vs. Cr concentration for alloys in PWR primary water at 360°C;

Figures 27B and 27E are graphs showing SCC growth rate vs. Cr concentration for alloys in PWR primary water at 320°C;

Figures 27C and 27D are graphs showing SCC growth rate vs. Cr concentration for alloys in PWR primary water at 290°C;

Figures 28A and 28B are graphs showing SCC growth rate vs. 1/T for alloys in PWR primary water;

Figures 29A and 29B show SEM images of the surface after testing on the bottom of the CT specimens;

Figure 30A is a graph showing parabolic law vs. 1/T for alloys in PWR primary water;

Figure 30B is a graph showing SCC initiation time vs. 1/T for alloys in PWR primary water;

Figure 30C is a graph showing crack growth rate vs. 1/T for alloys in PWR primary water; and

Figure 30D is a graph showing discharged vacancies vs. time for two sizes of grains.

- 7 -

DETAILED DESCRIPTION

[0014] Various apparatuses or methods will be described below to provide an example of an embodiment of each claimed invention. No embodiment described below limits any claimed invention and any claimed invention may cover apparatuses and methods that differ from those described below. The claimed inventions are not limited to apparatuses and methods having all of the features of any one apparatus or method described below, or to features common to multiple or all of the apparatuses or methods described below. It is possible that an apparatus or method described below is not an embodiment of any claimed invention. Any invention disclosed in an apparatus or method described below that is not claimed in this document may be the subject matter of another protective instrument, for example, a continuing patent application, and the applicant(s), inventor(s) and/or owner(s) do not intend to abandon, disclaim or dedicate to the public any such invention by its disclosure in this document.

[0015] The present disclosure relates to optimizing the material specification of Alloy 800 to give reliable SCC resistance in initiation and propagation during long term exposures, for example, to at least 80 years in Canada Deuterium Uranium (CANDU) reactor and PWR primary systems. Materials considered herein are modifications of Alloy 800 with different concentrations of Cr and Ni. The measured SCC growth rates were compared with rates obtained previously for Alloys 690 (61% Ni) and 316 (10% Ni) in PWR primary water. Furthermore, measured SCC growth rates were compared with other test results of alloys with variations of nickel and chromium.

[0016] Firstly, the effects of nickel and chromium concentrations on intergranular stress corrosion cracking (IGSCC) was investigated. The following alloys with higher Cr concentrations and cold-worked to 20% (20%CW) were examined: 32%Ni-27%Cr-Fe; 35%Ni-25%Cr-Fe; and 25%Ni-25%Cr-Fe.

[0017] Secondly, the temperature dependence of SCC growth of steam generator (SG) tubing in a range of operating temperatures was examined. The

- 8 -

above-noted Ni-Cr-Fe alloys with higher Cr concentration were examined at 290°C, 320°C, 340°C and 360°C.

[0018] Thirdly, the role of cavity formation on SCC initiation of carbon steel for long terms at high temperatures was considered, and the rate of cavity formation was measured. Then, the results were compared with results for Alloy 690 to compare the SCC initiation resistance of the Ni-Cr-Fe alloys described herein, considering life beyond 60 years. An alloy of 20%CW solution annealed 32%Ni-25%Cr-Fe (1075°C x 1 h W.C.) was examined in the range of temperatures between 425°C and 460°C. The results were compared with the results obtained previously to examine the effect of Cr concentration and the effect of heat treatment on the rate of cavity formation in air. Furthermore, a Ni-Cr-Fe alloy specimen with fine grains was tested at 445°C to confirm its reproducibility of the result obtained at 460°C, and to examine the grain size effect considering steam generator tubing with fine grain size.

[0019] For applications where increased resistance to corrosion (SCC in particular) is required, such as in nuclear power plants or similar applications where material integrity is important, any increase in materials performance whilst remaining within specification limits, that are similar to the materials currently in use, is important, and hence useful. Alloys of the present disclosure may provide significantly improved resistance to SCC compared to Alloy 800 alloys currently available. Thus, the alloys of the present disclosure may be useful for applications where Alloy 800 is currently used, and potentially other applications where Ni-Cr and austenitic stainless steels are used.

[0020] Alloys of the present disclosure may provide improved corrosion resistance, which becomes an economic benefit if the improved material reduces instances of component failure and results also in longer life of materials and components in service. Thus, alloys of the present disclosure may have commercial benefits for manufacturers of Ni-Cr-Fe alloys, and in particular for suppliers of materials to the nuclear industry, and potentially also to the suppliers of materials for all other applications that use Alloy 800 or related materials.

- 9 -

[0021] The experimental procedures are now described as follows.

[0022] Chemical compositions of test materials are summarized in Table 1. Mechanical properties of test materials were measured at room temperature and 320°C; the results from annealed and ~20% cold rolled materials are summarized in Tables 2 and 3.

Material	Ni	Cr	C	Si	Mn	P	S	Ti	Al	Cu	Fe	N	Ti/C
	wt%												
32Ni-20Cr	32.45	20.03	0.030	0.30	0.38	<0.002	0.001	0.42	0.28	0.45	Bal.	0.003	15.6
32Ni-23Cr	32.37	22.95	0.030	0.30	0.37	<0.002	0.001	0.42	0.29	0.46	Bal.	0.003	14.5
32Ni-25Cr	32.57	24.99	0.029	0.29	0.42	0.001	0.001	0.40	0.37	0.39	Bal.	0.004	15.4
34Ni-22Cr	34.10	21.90	0.020	0.23	0.50	<0.005	0.002	0.58	0.014	0.42	Bal.	<0.01	19.3
25Ni-25Cr	24.97	25.03	0.029	0.39	0.40	0.004	0.003	0.42	0.33	0.37	Bal.	-	14.5
35Ni-25Cr	34.97	25.05	0.028	0.29	0.40	0.004	0.003	0.42	0.33	0.37	Bal.	-	15.0
32Ni-27Cr	32.46	26.97	0.028	0.28	0.40	0.004	0.003	0.42	0.33	0.39	Bal.	-	15.0
Exemplary Spec.	25-35	23-27	<0.03	<0.7	<1.0	-	<0.015	>0.35	0.15-0.45	<0.75	Bal.	<0.03	>12

Table 1. Ni-Cr-Fe alloy chemical compositions

- 10 -

Material	Heat treatment	Cold work (%)	Yield Stress (MPa)	Tensile Stress (MPa)	Elongation (%)	Hv (1 kg)
32Ni-20Cr	1075°C x 1h	20	579	627	23	223
32Ni-23Cr	1075°C x 1h	20	590	649	23	221
32Ni-25Cr	1075°C x 1h	20	601, 607	658, 663	25, 26	226
34Ni-22Cr	1065°C x 10m	19	-	-	-	254, 274
25Ni-25Cr	1075°C x 1h	20	605, 592	651, 651	20, 22	227
35Ni-25Cr	1075°C x 1h	20	610, 603	675, 667	22, 21	236
32Ni-27Cr	1075°C x 1h	20	633, 610	684, 675	22, 25	239

Table 2. Mechanical properties at room temperature

Material	Heat treatment	Cold work (%)	Yield Stress (MPa)	Tensile Stress (MPa)	Elongation (%)
32Ni-20Cr	1075°C x 1h	20	502	531	20
32Ni-23Cr	1075°C x 1h	20	510	542	18
32Ni-25Cr	1075°C x 1h	20	520, 524	549, 552	18, 18
34Ni-22Cr	1065°C x 10m	19	-	-	-
25Ni-25Cr	1075°C x 1h	20	520	541	15
35Ni-25Cr	1075°C x 1h	20	519, 540	561, 567	17, 16
32Ni-27Cr	1075°C x 1h	20	526, 531	556, 564	16, 17

Table 3. Mechanical properties at room temperature at 320°C

[0023] Specimens were machined as 0.5T compact tension type (0.5T CT) with 12.5mm thicknesses. Specimens were prepared using ~20% cold rolled materials in the T-L orientation, i.e., crack growth direction parallel to the rolling direction as shown in Figure 1. A fatigue pre-crack of about 2 mm was produced using a load ratio ($R = K_{\min}/K_{\max} = 0.1$) with 8 Hz and at a $K_{\min}$ below

- 11 -

the stress intensity for testing. An example of the CT specimen with fatigue pre-crack before testing is shown in Figure 2.

[0024] Rates of SCC growth were measured in the range of temperatures between 290°C and 360°C in PWR primary water using 20% cold rolled CT specimens. The specimens were broken after testing by fatigue in air. The fracture surfaces were analyzed using SEM to determine the crack morphology and the depth of IGSCC. Maximum IGSCC depths were determined using SCC depth data that are measured from at least four points. SCC crack growth rate was calculated by equation (1):

$$IGSCC \text{ growth rate } \left(\frac{mm}{s} \right) = \frac{\text{Maximum IGSCC depth (mm)}}{\text{Exposure time (s)}} \quad (1)$$

[0025] Tests were performed under constant load conditions without dynamic loading in the test environment at 360°C, 340°C, 320°C and 290°C. The initial K value was 30MPa^{1/2} in all cases.

[0026] Rates of SCC growth were measured in test facilities at 360°C, 340°C, 320°C and 290°C in typical PWR primary water, which contains boric acid (H₃BO₃, 500ppm as B), lithium hydroxide (LiOH, 2ppm as Li), and dissolved hydrogen (DH, ~30 cc/kg H₂O). The concentration of hydrogen was adjusted by bubbling an appropriate gas pressure through the solution in the storage tank at room temperature before the solution is pumped into the autoclaves; hydrogen and oxygen were measured at ambient temperatures using a hydrogen and oxygen gas monitor. Dissolved oxygen was controlled to less than 5ppb through the testing.

[0027] The depth of intergranular corrosion was measured by SEM observation in cross sectional view using focussed ion beam (FIB) of the bottom of CT specimens to characterize the Cr concentration and temperature with peak. Film analyses by AES were performed on specimens after testing in PWR primary water at 290°C, 320°C, 340°C and 360°C. These measurements provided information on the cause of the measured temperature dependence.

[0028] Good correlations have been reported previously between rates of cavity formation and creep crack growth in gas with carbon steel as shown in

- 12 -

Figure 3A. Similar correlations have also been performed on Alloy 690 and Alloy 600 as shown in Figure 3B. Then, the rate of cavity formation was assumed from the results of measured rates of creep crack growth in air considering the correlation between rates of creep crack growth and cavity formation shown in Figures 3A and 3B. SCC initiation caused by cavity formation was correlated with the rate of cavity formation.

[0029] Rates of creep crack growth were measured at 425°C, 440°C and 460°C in air using ~20% cold rolled CT specimens of solution annealed 32%Ni-25%Cr-Fe alloy (1075°C x 1h W.C.). Furthermore, 19%CW 34%Ni-22%Cr (1065°C x 10m A.C.) with fine grains was tested at 445°C to confirm the reproducibility of the results at 460°C to examine effects of grain size. Tests were performed under constant load conditions without dynamic loading in the test environment. The initial K value was 40MPam^{1/2} in all cases. Specimens were broken by fatigue in air after testing. The fracture surfaces were analyzed using SEM to determine the crack morphology and the depth of creep crack. Maximum creep crack depth was determined using creep crack depth data that are measured from at least four points. Creep crack growth rate was calculated by equation (2):

$$\text{Creep crack growth rate } \left(\frac{\text{mm}}{\text{s}} \right) = \frac{\text{Maximum creep crack depth (mm)}}{\text{Exposure time (s)}} \quad (2)$$

[0030] These results were compared with other data to assess effects of Cr concentration and carbide precipitation on the rate of cavity formation. Results were compared with those of Alloy 690 to compare the SCC initiation resistance caused by cavity formations between the Ni-Cr-Fe alloys described herein and Alloy 690.

[0031] The test results are now described as follows.

[0032] Test conditions of test 1 at 360°C are summarized in Figures 4A, 4B and 4C. Test duration in test 1 was 5,233 h. Water chemistries of the test environments were well controlled during testing. After testing, the specimens were broken by fatigue in air to determine the depth of SCC and fracture

- 13 -

morphologies. The observed results of the fracture surfaces of test specimens are shown in Figures 5A, 5B, 6A, 6B, 7A and 7B.

[0033] No trace of SCC was observed in the test specimens of 35%Ni-25%Cr-Fe alloy and 32%Ni-27%Cr-Fe alloy after 5,233 h exposures in PWR primary water at 360°C, as shown in Figures 5A, 5B, 6A and 6B. These results show excellent SCC growth resistance of these alloys at 360°C in PWR primary water, for example, as compared with Alloy 690 in the range of specification of Ni concentration of Alloy 800 currently available (32 to 35%Ni). One very local and shallow IGSCC was observed in the 20%CW 25%Ni-25%Cr-Fe alloy. The maximum rate of SCC growth was $\sim 1.6 \times 10^{-9}$ mm/s based on the destructive observations shown in Figure 7B.

[0034] Test conditions of test 2 at 340°C are summarized in Figures 8A, 8B and 8C. Test duration in test 2 was 5,233 h. Water chemistries of the test environments were well controlled during the testing. After testing, the specimens were broken by fatigue in air to determine the depth of SCC and the fracture morphologies. The observed results of the fracture surfaces of the specimens are shown in Figures 9A, 9B, 10A, 10B, 11A and 11B.

[0035] No trace of SCC was observed in the test specimens after 5,233 h exposures in PWR primary water at 340°C, as shown in Figures 9A, 9B, 10A, 10B, 11A and 11B. These results show excellent SCC growth resistance of the alloys.

[0036] Test conditions of test 3 at 320°C are summarized in Figures 12A, 12B and 12C. Test duration in test 3 was 6,609 h. Water chemistries of the test environments were well controlled during the testing. After testing, the specimens were broken by fatigue in air to determine the depth of SCC and the fracture morphologies. The observed results of the fracture surfaces of test specimens are shown in Figures 13A, 13B, 14A, 14B, 15A and 15B.

[0037] No trace of SCC was observed in the test specimens after 6,609 h exposures in PWR primary water at 320°C, as shown in Figures 13A, 13B, 14A, 14B, 15A and 15B. These results show excellent SCC growth resistance

- 14 -

of the alloys, for example, as compared with 20%CW Alloy 690 TT (T-L), also at 320°C in PWR primary water.

[0038] Test conditions of test 4 at 290°C are summarized in Figures 16A, 16B and 16C. Test duration in test 4 was 6,155 h. Water chemistries of the test environments were well controlled during the testing. After testing, the specimens were broken by fatigue in air to determine the depth of SCC and the fracture morphologies. The observed results of the fracture surfaces of test specimens are shown in Figures 17A, 17B, 18A, 18B, 19A and 19B.

[0039] No trace of SCC was observed in all of the test specimens after 6,155 h in PWR primary water at 290°C, as shown in Figures 17A, 17B, 18A, 18B, 19A and 19B. These results show excellent SCC growth resistance of the alloys also at 290°C in PWR primary water.

[0040] To consider mechanisms of SCC growth in PWR primary water, film analyses were performed using alloy specimens after testing in PWR primary water at 290°C, 320°C, 340°C and 360°C. Surface oxidation behaviors after testing are shown in Figures 20A, 20B and 20C. Intergranular corrosion was observed after testing at 290°C and 320°C in alloys with low Cr concentrations less than 22%Cr, as shown in Figure 20A, 20B and 20C. However, there was no trace of intergranular corrosion in alloys with Cr concentrations more than 23%. Accordingly, SEM observations and AES analyses of cross sectional views were performed to examine the temperature dependence with peak of IGSCC growth after sampling by FIB, as shown in Figures 21A, 21B, 21C, 21D, 21E, 21F, 21G, 21H, 21I and 21J. SEM observations of cross sectional views were performed to assess the mechanisms of Cr concentration dependence on SCC growth resistance; samples of alloys were used with different Cr concentrations after tests at 290°C, as shown in Figures 22A, 22B and 22C.

[0041] Intergranular corrosion was observed in alloys with low Cr concentration less than 23% tested at 320°C and 290°C. No clear evidence of intergranular corrosion was observed in alloys tested at higher temperatures more than 340°C. No clear evidence of intergranular corrosion was observed in

- 15 -

alloys with high Cr concentration of more than 25% after testing at 290°C, 320°C, 340°C, and 360°C.

[0042] To examine the effect of material characteristics on SCC initiation caused by cavity formation, considering long term reliability more than 60 years in high temperature water, rates of cavity formation were measured from the results of creep crack growth using 20%CW CT specimens of solution annealed 32%Ni-25%Cr-Fe alloy (1075°C x 1h W.C.) at 425°C, 440°C and 460°C in air. Then, the results were compared with results of 20%CW Alloy 690 TT to compare the crack initiation resistance caused by cavity formation. The reproducibility of 19%CW 34%Ni-22%Cr-Fe alloy (1065°C x 10m A.C.) with fine grains was tested at 445°C to examine the effects of grain size, for example, in steam generator tubing.

[0043] Test durations were between 4,030 h and 9,590 h. After testing, the specimens were broken by fatigue in air to determine the depth of creep cracking and the fracture morphologies. The results of observations on fracture surfaces are shown in Figures 23A, 23B, 24A, 24B, 25A, 25B, 26A and 26B.

[0044] Intergranular crack growth was observed in almost all specimens tested at 460°C, 445°C, and 440°C, as shown in Figures 23A, 23B, 24A, 24B, 26A and 26B. However, no crack growth was observed in solution annealed 32%Ni-25%Cr-Fe alloy tested at 425°C after 9,590 h in air, as shown in Figures 25A and 25B. Measured maximum rates of creep crack growth of solution annealed 32%Ni-25%Cr-Fe alloy tested at 440°C ($\sim 1.6 \times 10^{-8}$ mm/s) was about 50 times slower than that of Alloy 690 TT with the same grain size ($\sim 100\mu\text{m}$). About 10 times more rapid rate of creep crack growth was observed in 34%Ni-22%Cr-Fe alloy with fine grains ($\sim 20\mu\text{m}$) compared with solution annealed 32%Ni-25%Cr-Fe alloy with large grains ($\sim 100\mu\text{m}$). Furthermore, more than 50 times rapid rate of creep crack growth was observed in carbide precipitated 32%Ni-25%Cr-Fe alloy than solution annealed 32%Ni-25%Cr-Fe alloy.

[0045] The SCC growth resistance of Ni-Cr-Fe alloys described herein with Cr concentrations more than 25% in PWR primary water was measured. The results are summarized as a function of Cr concentration in Figures 27A,

- 16 -

27B, 27C, 27D and 27E, together with existing results for Ni-16%Cr-Fe alloys and Alloy 690 TT. The dependencies on temperature of SCC growth are summarized in Figures 28A and 28B, together with existing results for Ni-16%Cr-Fe alloys and Alloy 690 TT.

[0046] There was no trace of SCC observed in 32%Ni-25%Cr-Fe alloy, 32%Ni-27%Cr-Fe alloy, and 35%Ni-25%Cr-Fe alloy in the range of temperatures between 290°C and 360°C. The results showed that temperature dependencies of SCC growth with peak was not observed for Cr concentrations more than 25%. Excellent SCC growth resistance in Ni-Cr-Fe alloys with more than 25% Cr concentrations were observed relative to Alloy 690 TT in the range of temperatures between 290°C and 360°C in PWR primary water. The peak of the SCC growth rate of the Ni-Cr-Fe alloys seems to be in the range of temperatures between 320°C and 290°C, judging from results obtained for 32%Ni-16%Cr-Fe alloy, as shown in Figure 28A.

[0047] Samples were examined with the SEM after testing at 290°C. Intergranular corrosion was observed in 32%Ni-Cr-Fe alloys with 16%, 20%, 22%, and 23% Cr after testing at 290°C in PWR water without the application of stress, as shown in Figures 29A and 29B. No trace of intergranular corrosion was observed in the 32%Ni-25%Cr-Fe and 32%Ni-27%Cr-Fe alloys. The thickness of the inner layer may be influenced by the Cr concentrations in alloys. These results suggest that intergranular corrosion may produce some influence on IGSCC growth for Ni-Cr-Fe alloys, judging from the similar trend of dependence of Cr concentration both on SCC growth and intergranular corrosion, as shown in Figures 28A and 29B.

[0048] Samples were examined with the SEM after testing at 290°C, 320°C, 340°C, and 360°C. Furthermore, AES analyses were performed to determine the dependence of temperature on film compositions. The results of these observations are shown in Figures 21A, 21B, 21C, 21D, 21E, 21F, 21G, 21H, 21I, 21J, 22A, 22B and 22C. As shown, the thicknesses of inner oxide layers appear to be thicker after testing at high temperature than low temperatures. Moreover, the thicknesses of specimens with high Cr

- 17 -

concentrations appear to be greater than specimens having lower Cr concentrations, even at 290°C. The parabolic law constant was calculated according to equation (3) to confirm this trend more clearly. The results are summarized in Figure 30A.

$$\text{Thickness of inner layer (mm)} = (K_p \cdot \text{time})^{1/2} \quad (3)$$

Wherein:

K_p = parabolic law constant (mm^2/s); and

time = exposure time (s).

[0049] Intergranular corrosion appears to occur at low temperatures less than 320°C in 32%Ni-Cr-Fe alloys with Cr concentrations less than 23%. Furthermore, the susceptibility of the alloys to intergranular corrosion appears to decrease at temperatures higher than 340°C. Moreover, significant dependencies of film compositions on temperature were not observed. The inner layer consisted mainly of Cr-rich oxide. On the other hand, the outer layer mainly consisted of Ni- and Fe-rich oxides.

[0050] Dependencies on temperature with peak of the parabolic law constant were observed in alloys with low Cr concentration in the range between 16% and 23%. This trend is similar to the temperature dependence of SCC growth with peak of Alloy 800. Furthermore, higher parabolic law constants were observed in alloys with higher Cr concentrations, including 25% at 290°C. This trend is also similar to the dependence of Cr concentration on SCC growth of Alloy 800 at 290°C.

[0051] These results suggest that intergranular corrosion may play a role in IGSCC growth, judging from the similar trend of dependence of temperature both on SCC growth and intergranular corrosion. Furthermore, measured temperature dependencies of intergranular corrosion susceptibilities with peak may be related to the kinetics of the inner oxide layer considering the similar dependence of temperature.

- 18 -

[0052] SCC initiation behavior caused by cavity formation of 20%CW TT690, MA600 and carbon steel was examined, as shown in Figure 30B. The dependencies of several influences on rates of cavity formation of the alloys were examined to compare with Alloy 690 TT. For this, the effects of the following characteristics were examined: comparison of rates of cavity formation with Alloy 690 TT; effect of carbide precipitation on rates of cavity formation; effect of grain size on rate of cavity formation; and effect of Cr concentration on rates of cavity formation.

[0053] As shown in Figures 3A and 3B, a good correlation was observed between rate of creep crack growth and cavity formation because the rate limiting processes of creep cracking are assumed to be proportional to the rate of cavity formation. Therefore, firstly, the measured rate of creep crack growth in solution treated Ni-Cr-Fe alloy with 25%Cr was compared with the results for other alloy specimens with different Cr concentrations. Then, the effect of Cr concentration on the rate of cavity formation could be determined. Secondly, the measured rates of solution treated Ni-Cr-Fe alloy were compared with the results of carbide precipitated alloy to determine the effect of carbide precipitation on the rate of cavity formation. Thirdly, the measured rates in solution treated Ni-Cr-Fe alloy with large grains (~100µm) were compared with the results of solution treated 34Ni-22Cr-Fe alloys with fine grains (~20µm) to determine the effect of grain size on the rate of cavity formation. Finally, the measured rates of cavity formation were compared with the results for Alloy 690 TT to understand the SCC initiation resistance caused by cavity formation. All results are summarized in Figure 30C.

[0054] Firstly, it should be appreciated that carbide precipitation may accelerate cavity formation, by providing nucleation sites for cavities, thereby enhancing the rate of cavity formation near the carbides. Evidence for this correlation includes the rapid crack growth in carbide precipitated alloy in a double heat treatment at 1075°C x 1h + 900°C x 1h. In general, solution annealed alloy in a single high temperature heat treatment is better for the Ni-Cr-Fe alloys described herein so as to not precipitate carbides.

- 19 -

[0055] Secondly, rapid cavity formation may occur in material with small grains, for example, SG tubing relative to thick components such as control rod drive mechanism (CRDM) housings. An estimated crack initiation time for Alloy 690 TT with large grains may be about 100 years at operating temperature (320°C), based on an extrapolated value in Figure 30B. However, if the effect of grain size from the data is used to assess the SCC initiation time of SG tubing with fine grains, the estimated time may decrease by a factor of ten. Consequently, the estimated SCC initiation time may be about 10 years. However, the degree of cold work may alter these influences.

[0056] Accordingly, the rate of intergranular crack growth may be about 100 times slower for solution annealed 32%Ni-25%Cr-Fe than for Alloy 690 TT. Furthermore, carbide precipitated 32%Ni-25%Cr-Fe alloy may be about 100 times faster than for solution annealed 32%Ni-25%Cr-Fe alloy. These results suggest that carbide precipitation strongly decreases the resistance of SCC initiation caused by cavity formation in the Ni-Cr-Fe alloys described herein. Precipitated carbides may provide initiation sites for cavity formations. Therefore, high temperature final heat treatments, such as 1075°C followed by rapid cooling, to reduce carbide precipitation are desirable for SCC initiation resistance caused by cavity formation. A ten times more rapid rate of intergranular crack growth (rate of cavity formation) was observed in solution annealed alloy with fine grain (~20µm) than solution annealed alloy with large size of grain (~100µm), as shown in Figure 30C. The main cause of the effect of grain size may be the difference of the magnitude of discharged vacancies from small grains, judging from the calculated results shown in Figure 30D. This suggests that about ten times shorter SCC initiation time is produced by cavity formation with the smaller grains.

[0057] The estimated SCC initiation time caused by cavity formation of 20%CW Alloy 690 TT with large size of grains (~100µm) is estimated to be about 100 years, based on the extrapolated value at 320°C, as shown in Figure 30B. Taking into account the grain size effect described above, the estimated SCC initiation time with fine grains may be assumed to be about ten years,

- 20 -

although other effects, such as degree of cold work may be considered. No significant effect of Cr concentration on the rate of cavity formation was observed in the range of Cr concentration between 20% and 25%.

[0058] In conclusion, measured SCC growth rates of Ni-Cr-Fe alloys with between 25 and 27 wt% Cr were very slow at temperatures between 320°C and 360°C, compared with SCC growth rates of Alloy 690. Given that the results for alloys having 27 wt% Cr were so clearly good, it is believed that alloys having up to 28 wt% Cr, and possibly more, may also exhibit an improved resistance to stress corrosion cracking in nuclear environments. Regarding the mechanism of dependence of Cr concentration in IGSCC growth, intergranular corrosion may play a role on the susceptibility of IGSCC growth in PWR primary water. Regarding the mechanism of dependence of temperature with peak on IGSCC growth for Ni-Cr-Fe alloys, intergranular corrosion may play a role on the susceptibility of IGSCC growth for Ni-Cr-Fe alloys in PWR primary water.

[0059] Furthermore, Ni-Cr-Fe alloys described herein produced excellent crack initiation resistance relative to Alloy 690 from the point of view of resistance of cavity formation. Lower cavity formation rates may yield an initiation rate for Ni-Cr-Fe alloys described herein that is about 100 times less than an initiation rate for Alloy 690. However, a significant increase in rates of cavity formation may occur with carbide precipitation and small grain sizes. Therefore, a high temperature final heat treatment followed by rapid cooling may produce a low rate of cavity formation for the Ni-Cr-Fe alloys described herein.

[0060] The heat treatment of the Ni-Cr-Fe alloys described herein may be carried out at a temperature of at least 1000°C, for a minimum of 3 minutes, and followed by rapid water cooling. More particularly, the heat treatment may be carried out in the range of 1050-1100°C. The intent for the Ni-Cr-Fe alloys is to avoid carbide precipitation, which may occur below 1050°C. There may be no specified maximum time because the total time may be determined by the thickness of the material, and thus how long it takes the material to get to

- 21 -

temperature. Once at temperature, a time of 3 minutes or possibly more may be required. For example, for SG tubing, a thin wall (e.g., 1mm) means that 3 minutes (the time it takes to go through an annealing furnace) may be appropriate. Maximum times may depend on material thicknesses, initial conditions, etc., and may be optimized according to product specifications, including grain size, surface cleanliness, hardness, etc.

[0061] While the above description provides examples of one or more methods or apparatuses, it will be appreciated that other methods or apparatuses may be within the scope of the accompanying claims.

- 22 -

CLAIMS

We claim:

1. A Ni-Cr-Fe alloy with improved resistance to stress corrosion cracking in nuclear environments, wherein the alloy has between about 23 and 28 wt% Cr.
2. The alloy of claim 1, wherein the alloy has between about 24 to 27 wt% Cr.
3. The alloy of claim 1, wherein the alloy has about 25 wt% Cr.
4. The alloy of any one of claims 1 to 3, wherein the alloy has between about 25 and 35 wt% Ni.
5. The alloy of any one of claims 1 to 4, wherein the alloy has between about 32 and 35 wt% Ni.
6. The alloy of claim 1, wherein the alloy has about 32 wt% Ni and about 25 wt% Cr.
7. The alloy of claim 1, wherein the alloy has about 25 wt% Ni and about 25 wt% Cr.
8. The alloy of claim 1, wherein the alloy has about 35 wt% Ni and about 25 wt% Cr.
9. The alloy of claim 1, wherein the alloy has about 32 wt% Ni and about 27 wt% Cr.
10. The alloy of any one of claims 1 to 9, wherein the alloy has:
 - < 0.03 wt% C;
 - < 0.70 wt% Si;
 - < 1.0 wt% Mn;
 - < 0.015 wt% S;
 - > 0.35 wt% Ti;

- 23 -

between 0.15 and 0.45 wt% Al;
< 0.75 wt% Cu;
< 0.03 wt% N;
> 12 Ti/C; and
balance substantially Fe and incidental impurities.

11. Use of the alloy of any one of claims 1 to 10 in a nuclear reactor.
12. Use of the alloy of any one of claims 1 to 10 in steam generator tubing of a nuclear reactor.
13. A method of producing an article, the method comprising:
 - providing the alloy of any one of claims 1 to 10;
 - forming the alloy into the article; and
 - heat treating the article.
14. The method of claim 13, wherein the step of heat treating consists of solution annealing the article at at least about 1000°C for at least about 3 minutes.
15. The method of claim 13, wherein the step of heat treating consists of solution annealing the article at between about 1050°C to 1100°C for at least about 3 minutes.
16. The method of claim 13, wherein the step of heat treating consists of solution annealing the article at about 1075°C for about 1 hour.
17. The method of any one of claims 13 to 16, further comprising, after the step of heat treating, rapidly cooling the article.
18. The method of any one of claims 13 to 17, wherein the step of forming comprises cold working the article to about 20%.
19. The method of any one of claims 13 to 18, wherein, after the step of heat treating, the article has an average grain size of about 100µm.

- 24 -

20. An apparatus or a method comprising any combination of one or more of the features described above and/or claimed above and/or illustrated in the drawings.

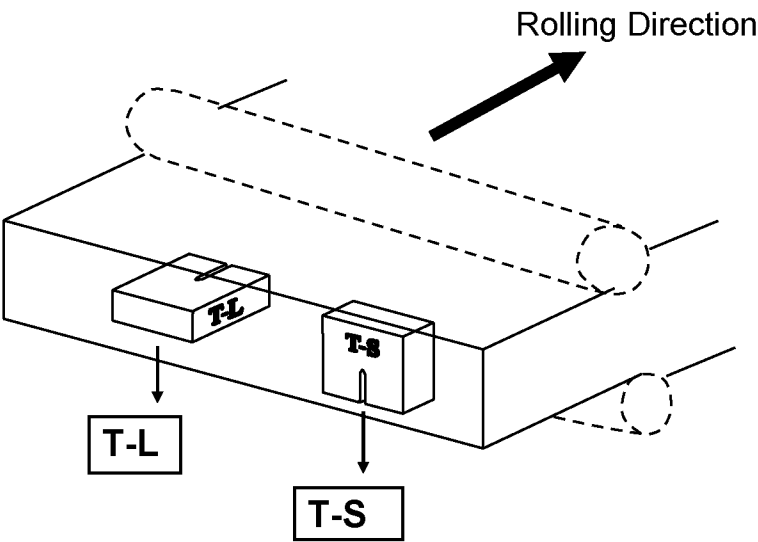


Figure 1

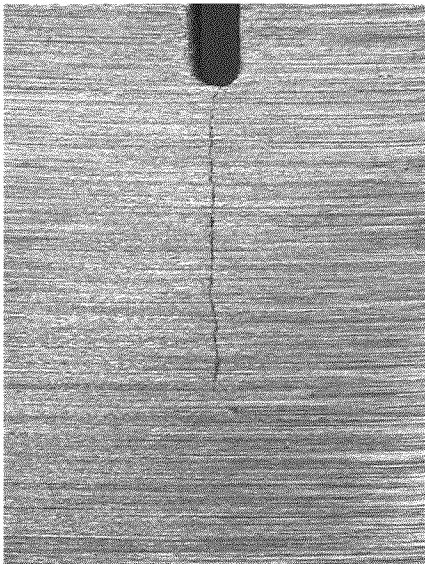


Figure 2

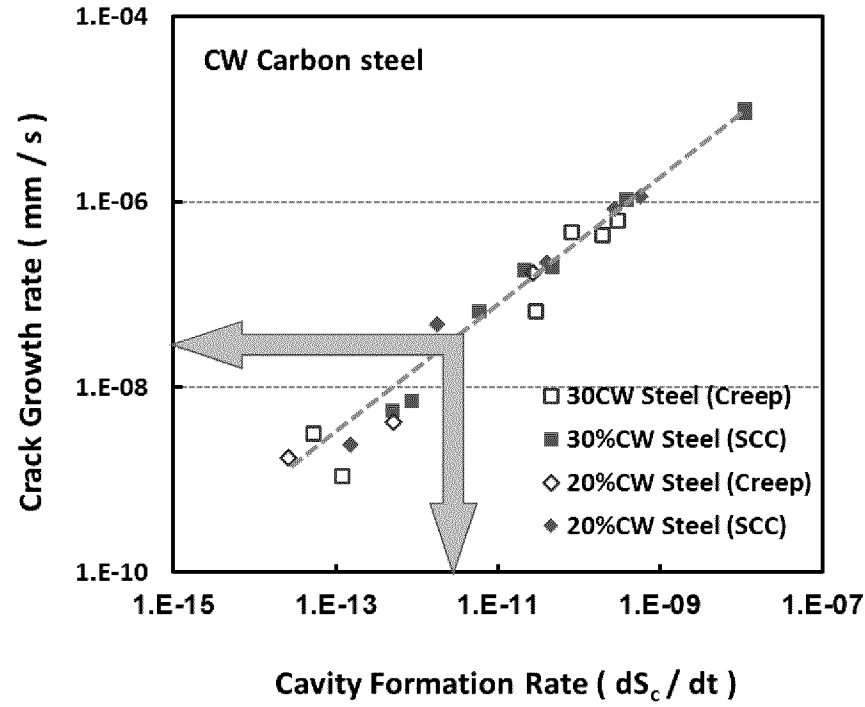


Figure 3A

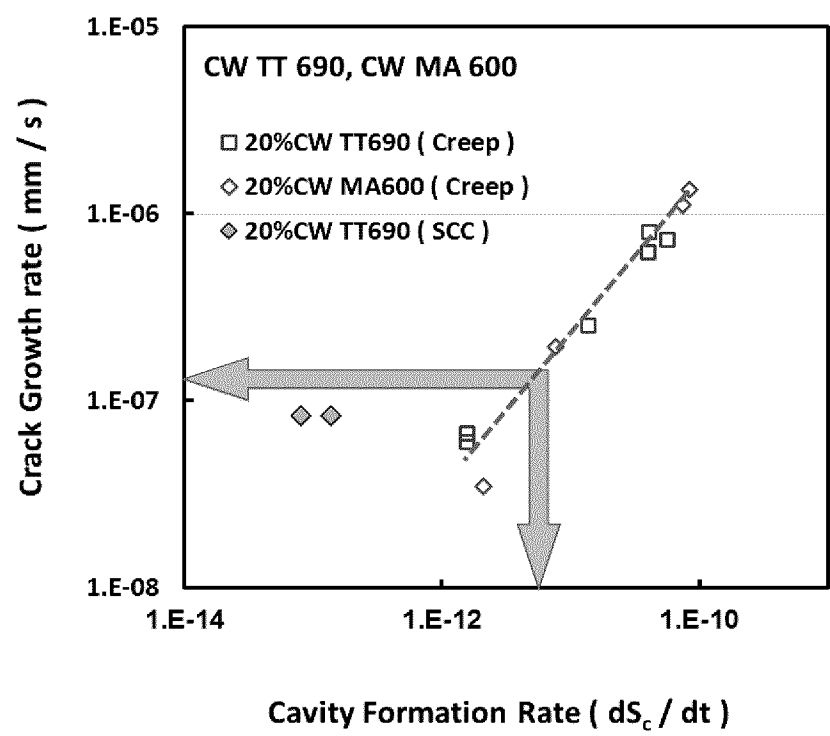


Figure 3B

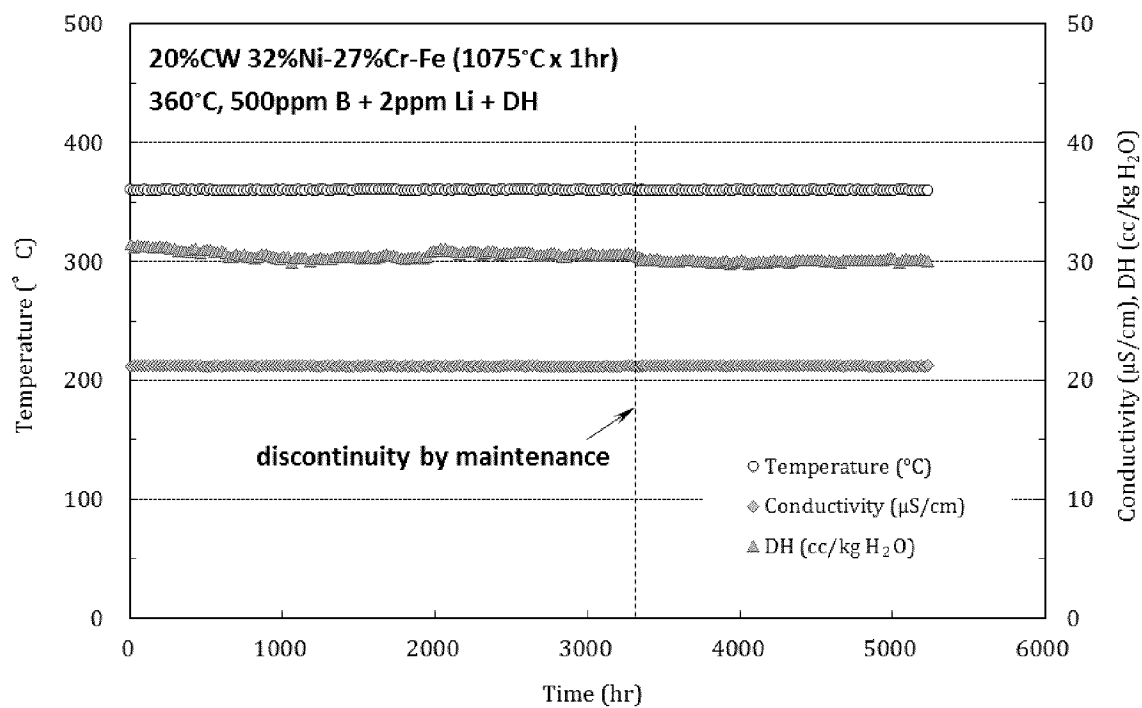


Figure 4A

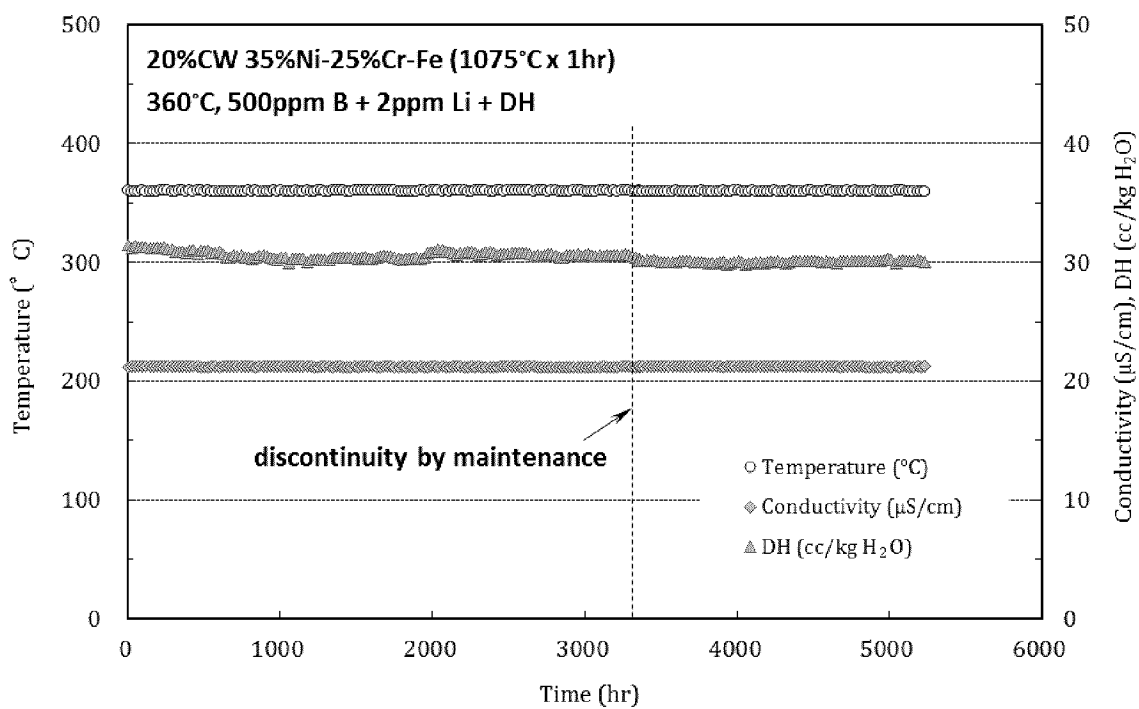


Figure 4B

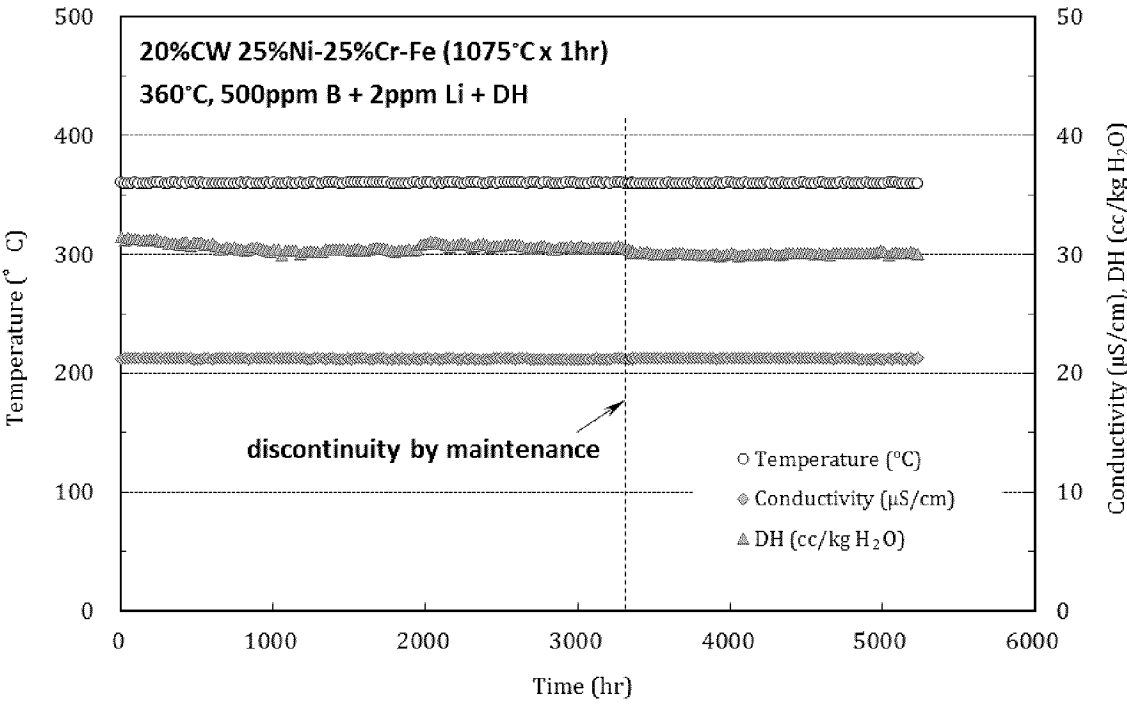


Figure 4C

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G27Cr32NiC2-4 (12.5mm ³)	20%CW (TL) 32% Ni-27% Cr Model Alloy 1075°C x 1 hr W.C.	360°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.2

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.00	2.00	2.02	1.99	2.11	2.19	2.43	2.63	2.73	2.75	2.28

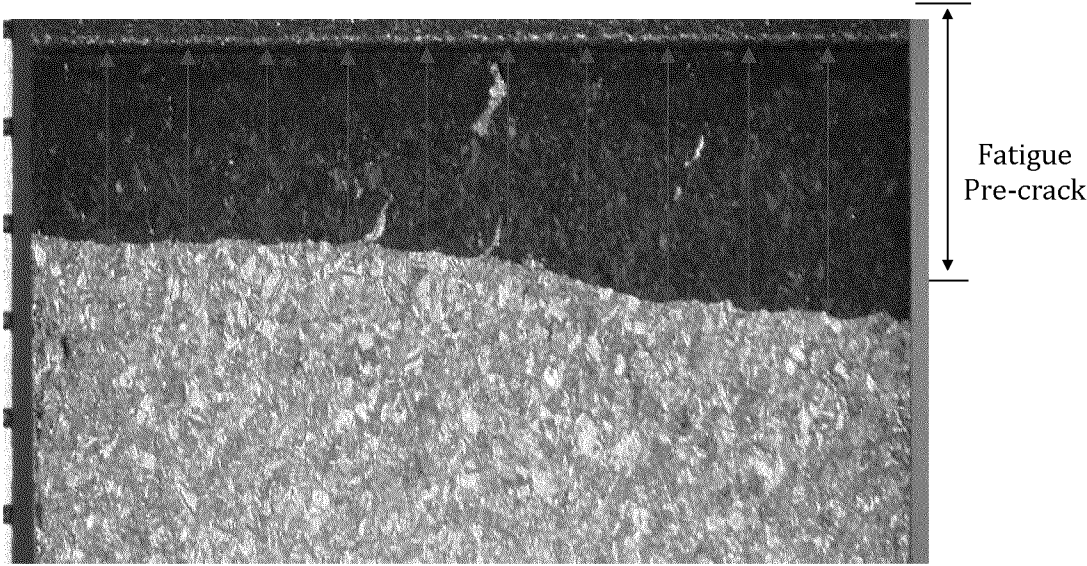
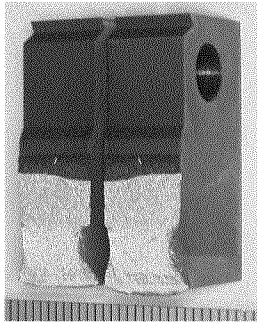
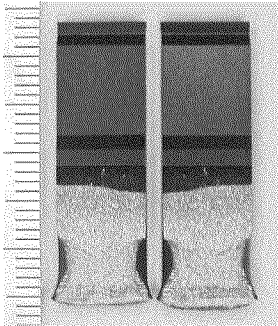


Figure 5A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G27Cr32NiC2-4 (12.5mm ⁴)	20%CW (TL) 32% Ni-27% Cr Model Alloy 1075°C x 1 hr W.C.	360°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.2

Depth of SCC (mm)	Average (mm)
no crack	—

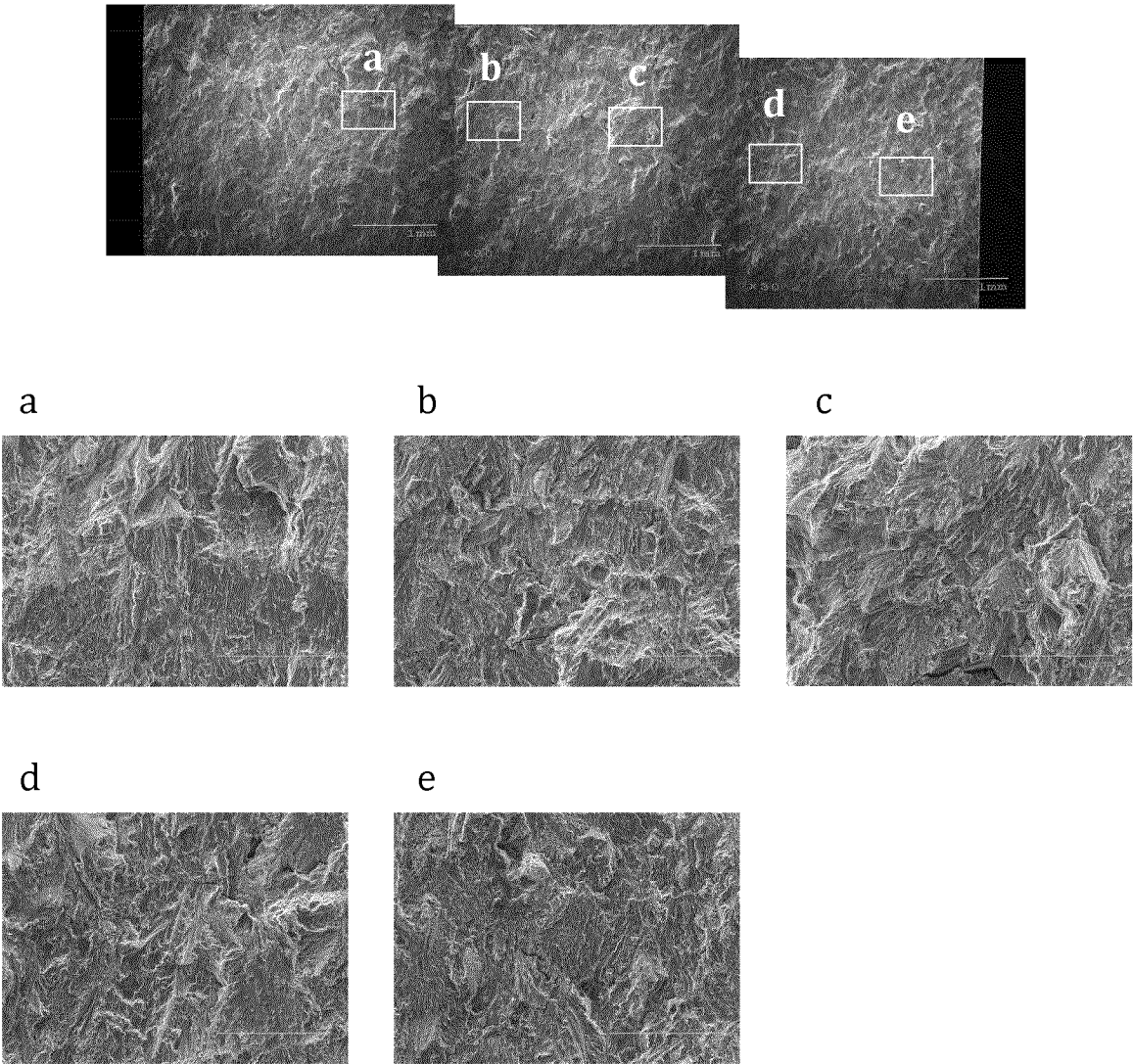


Figure 5B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr35NiC2-4 (12.5mm ^t)	20%CW (TL) 35% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	360°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.2

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.23	2.31	2.32	2.32	2.37	2.31	2.38	2.38	2.39	2.25	2.33

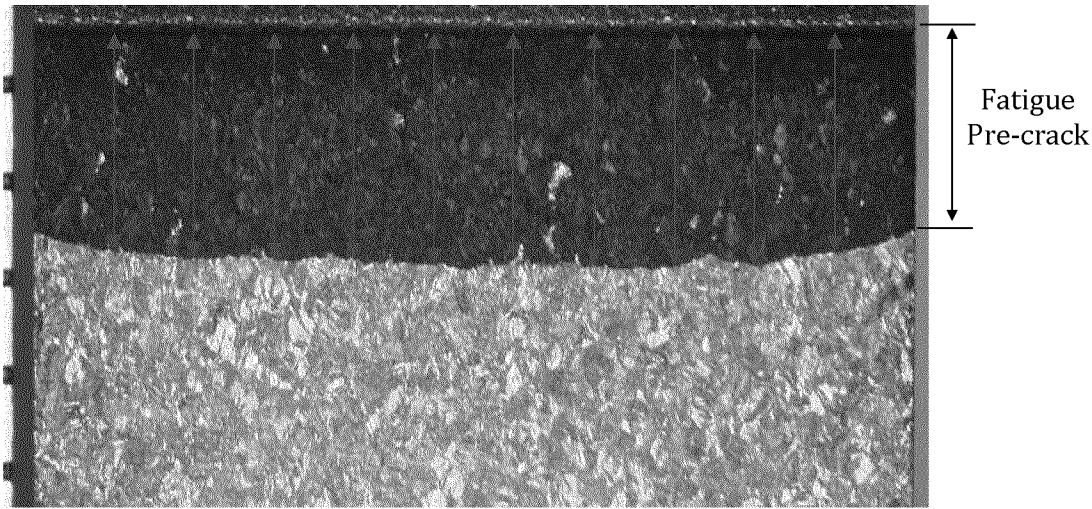
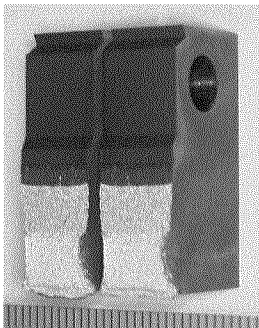
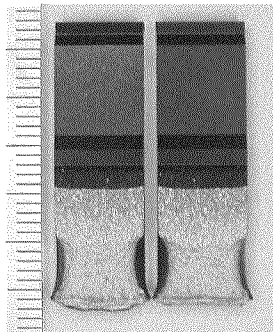


Figure 6A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr35NiC2-4 (12.5mm ^t)	20%CW (TL) 35% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	360°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.2
Depth of SCC (mm)				Average (mm)
no crack				—

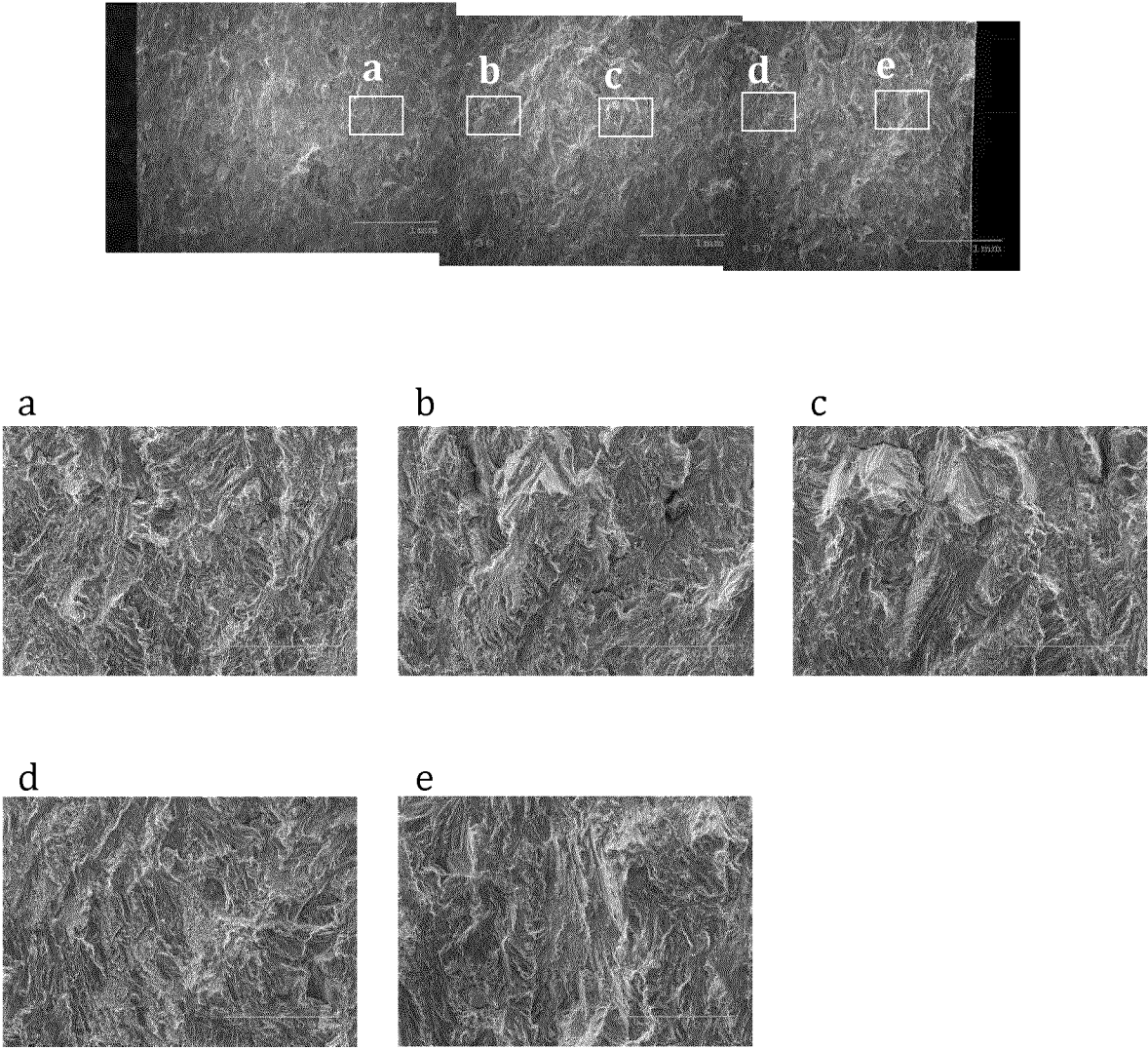


Figure 6B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr25NiC2-4 (12.5mm ^t)	20%CW (TL) 25% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	360°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.2

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.29	2.39	2.43	2.54	2.63	2.57	2.40	2.37	2.36	2.41	2.44

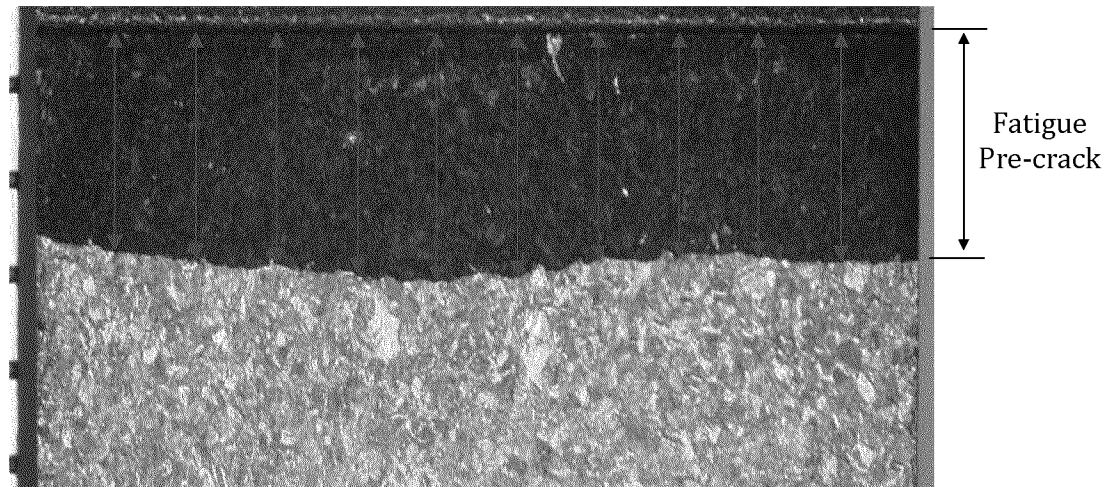
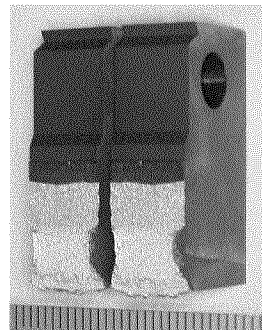
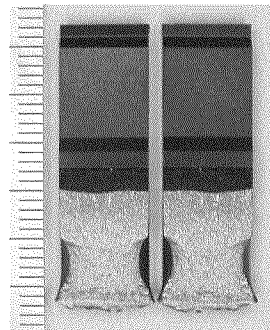


Figure 7A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr25NiC2-4 (12.5mm ^t)	20%CW (TL) 25% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	360°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.2
Depth of SCC (mm)				Average (mm)
no crack				—

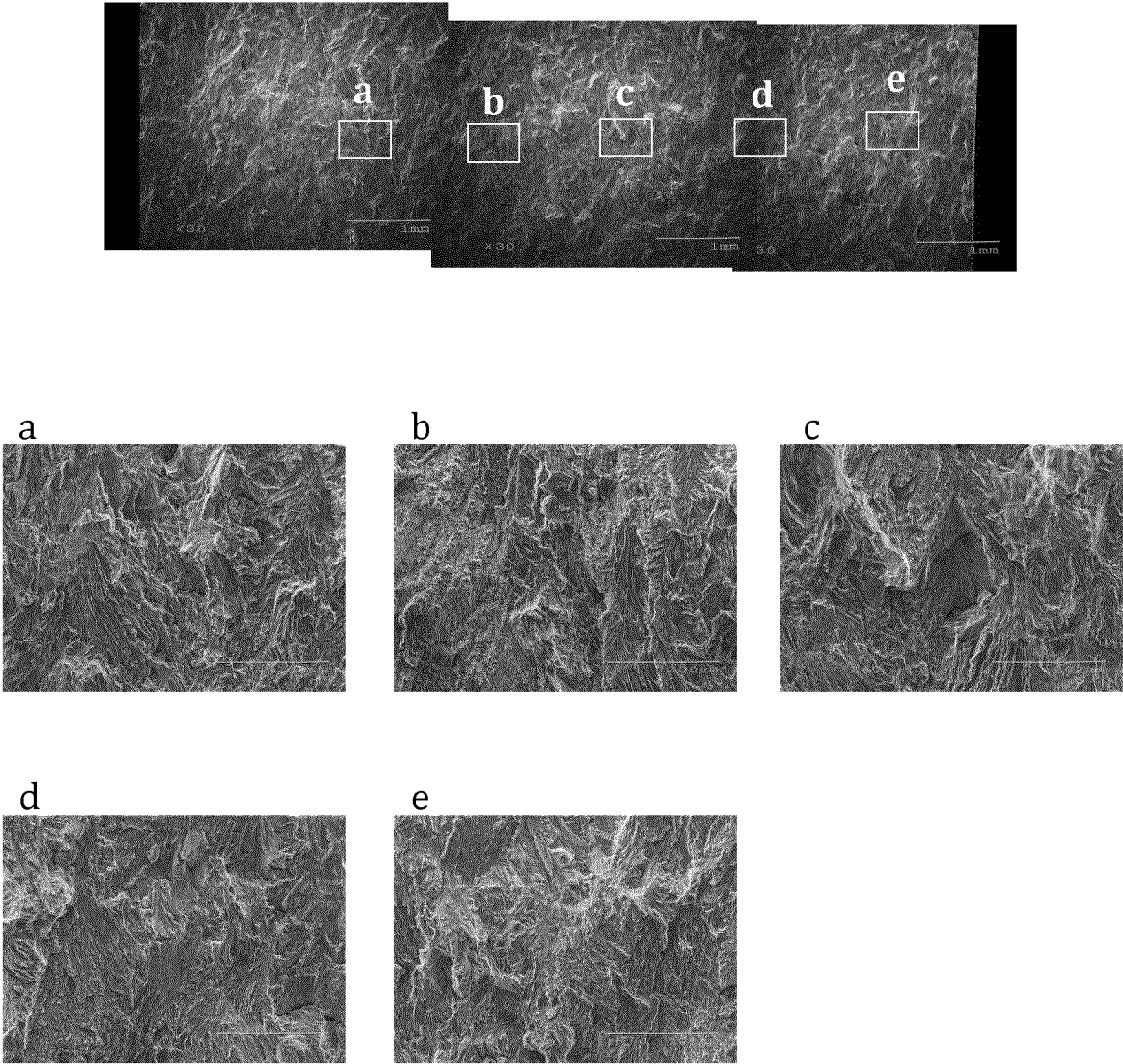


Figure 7B

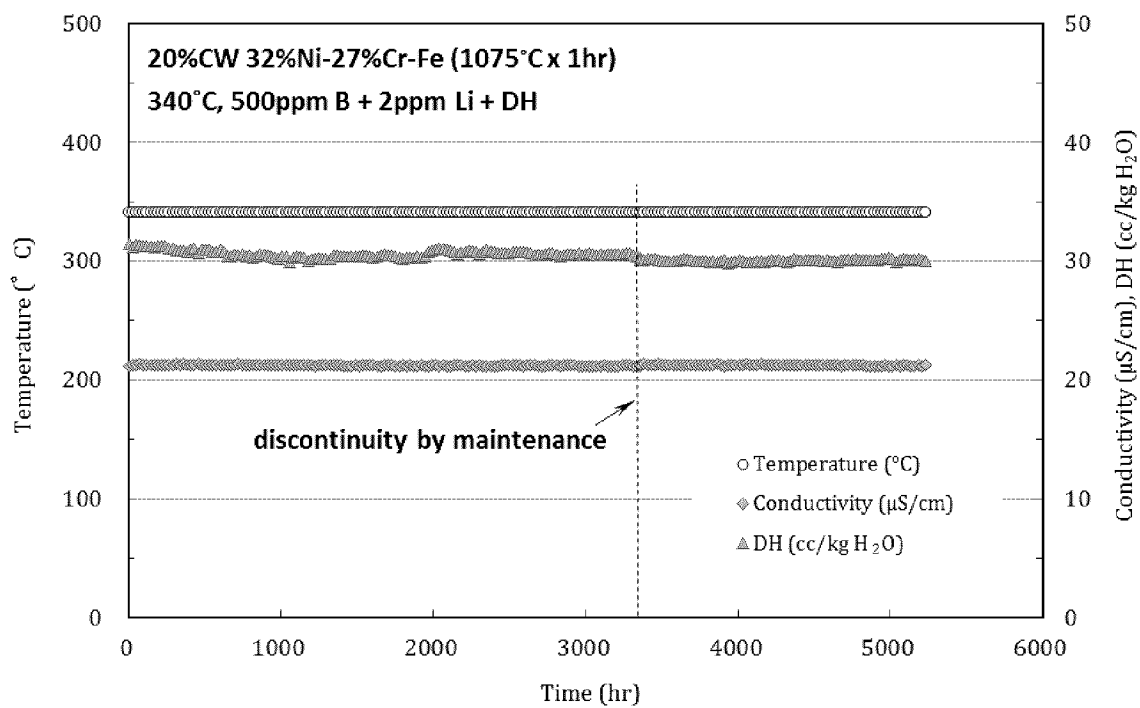


Figure 8A

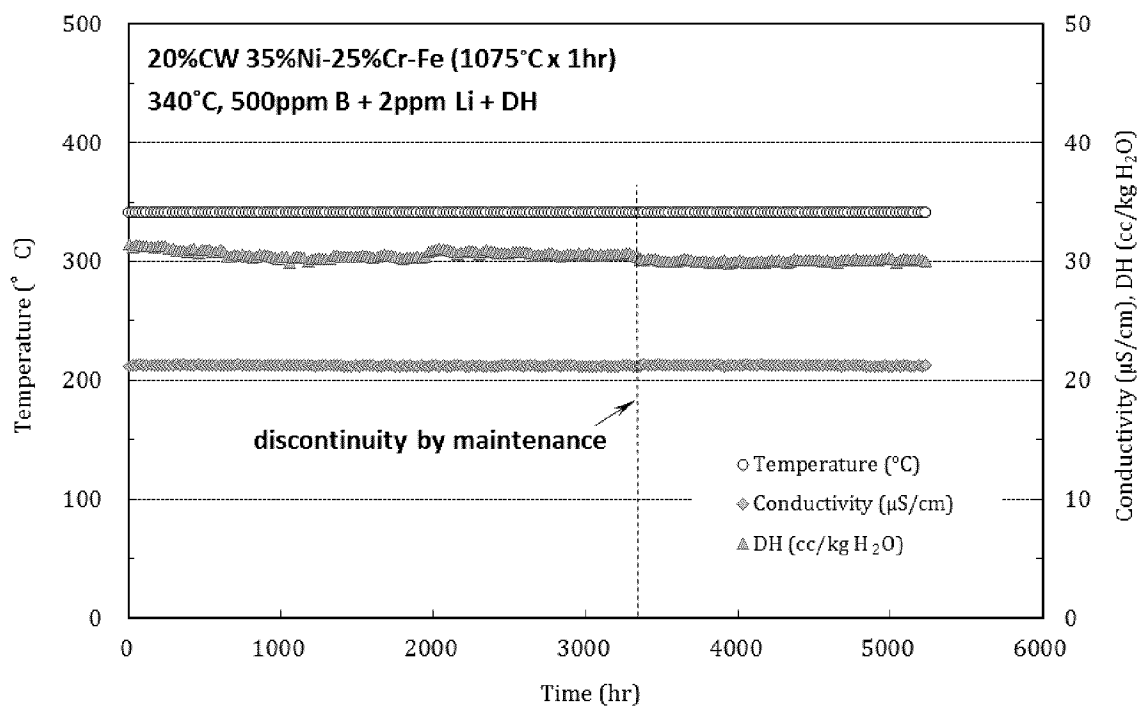


Figure 8B

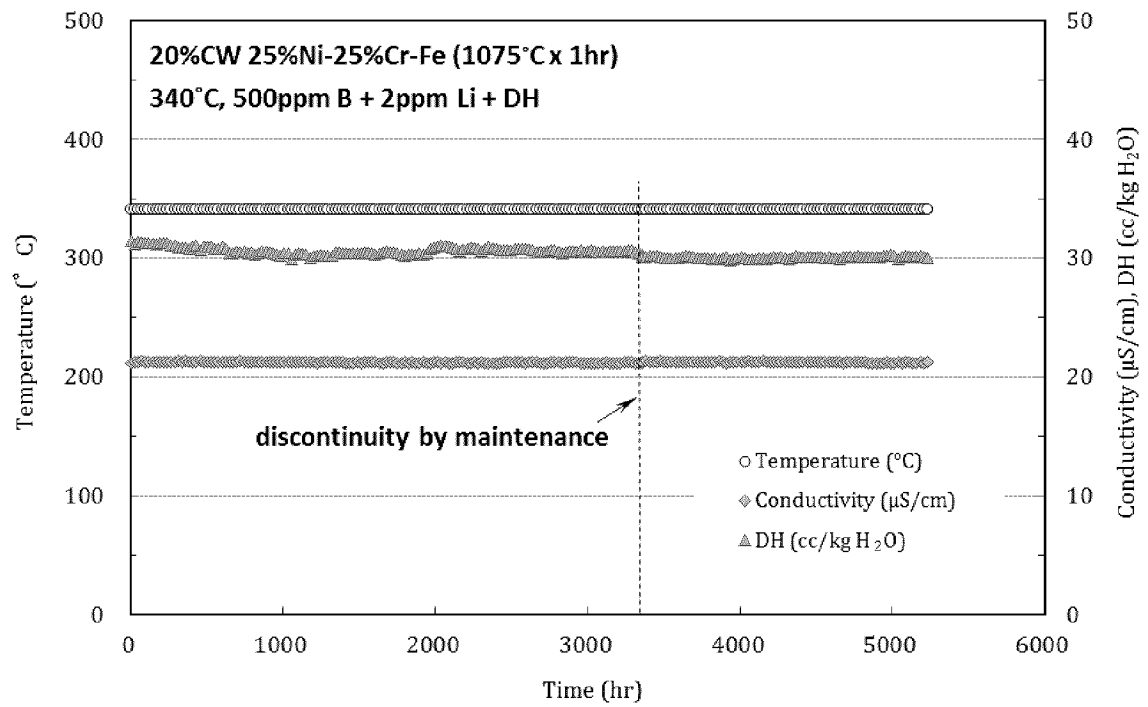


Figure 8C

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G27Cr32NiC2-3 (12.5mm ^t)	20%CW (TL) 32% Ni-27% Cr Model Alloy 1075°C x 1 hr W.C.	340°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.3

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.43	2.46	2.44	2.43	2.50	2.54	2.61	2.59	2.52	2.48	2.51

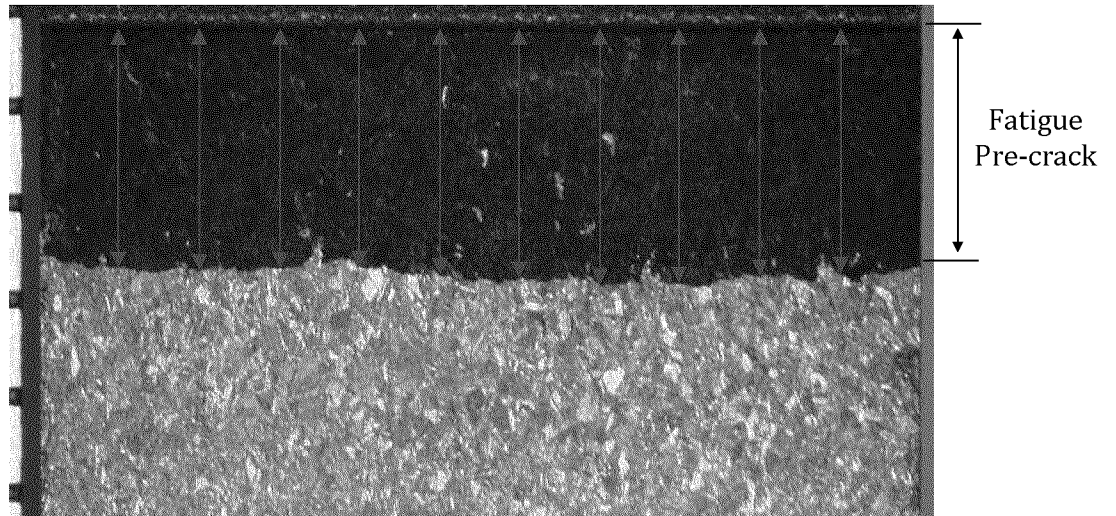
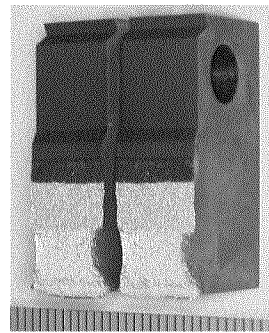
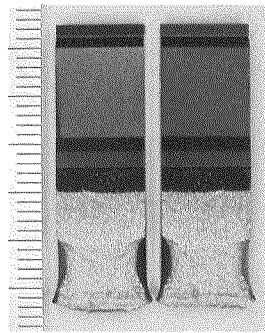


Figure 9A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G27Cr32NiC2-3 (12.5mm ^t)	20%CW (TL) 32% Ni-27% Cr Model Alloy 1075°C x 1 hr W.C.	340°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.3
Depth of SCC (mm)				Average (mm)
no crack				—

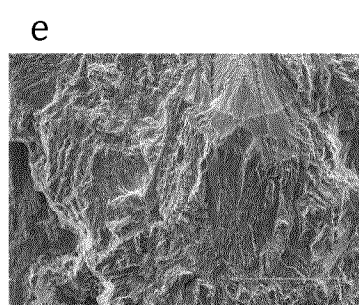
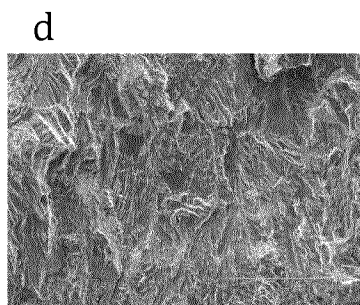
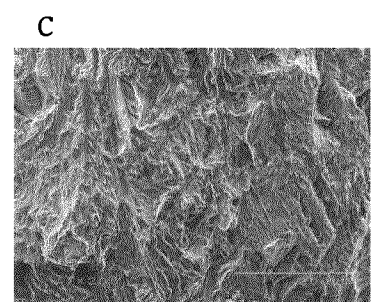
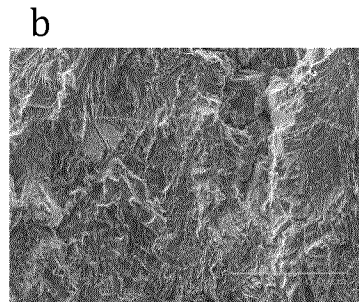
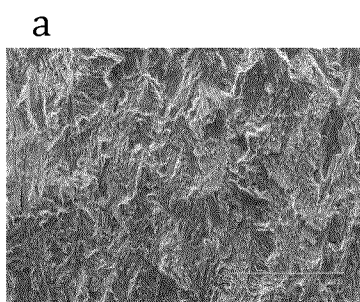
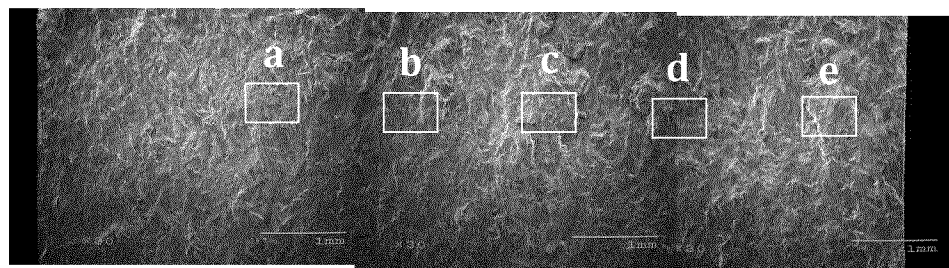


Figure 9B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr35NiC2-3 (12.5mm ^t)	20%CW (TL) 35% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	340°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.3

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.83	2.81	2.71	2.51	2.47	2.38	2.32	2.27	2.21	2.08	2.46

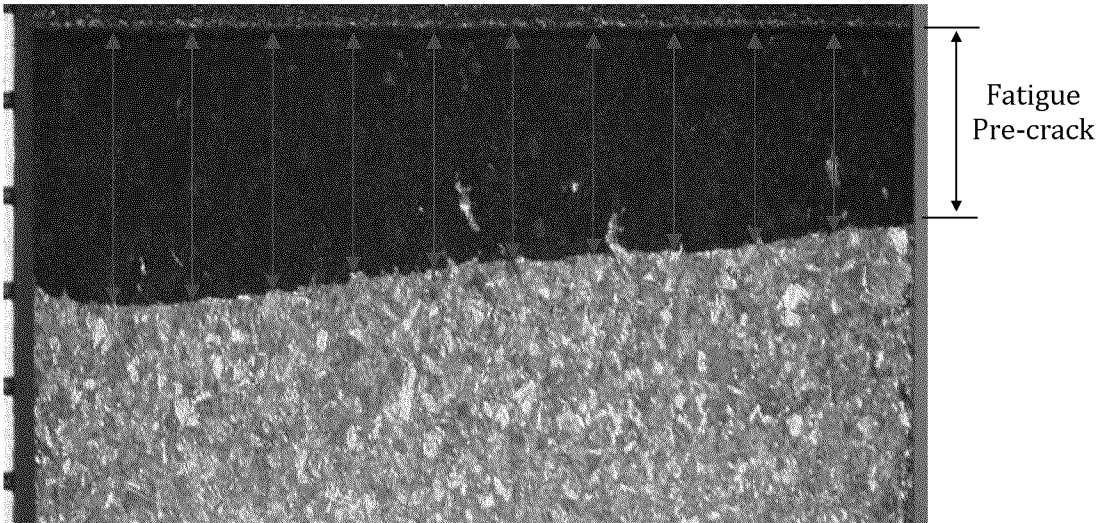
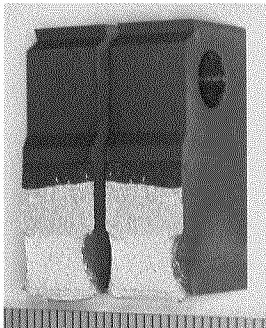
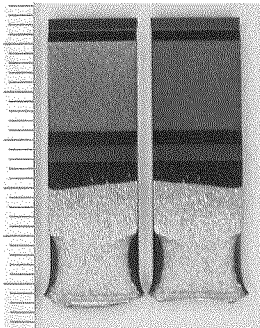


Figure 10A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr35NiC2-3 (12.5mm ^t)	20%CW (TL) 35% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	340°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.3
Depth of SCC (mm)				Average (mm)
no crack				—

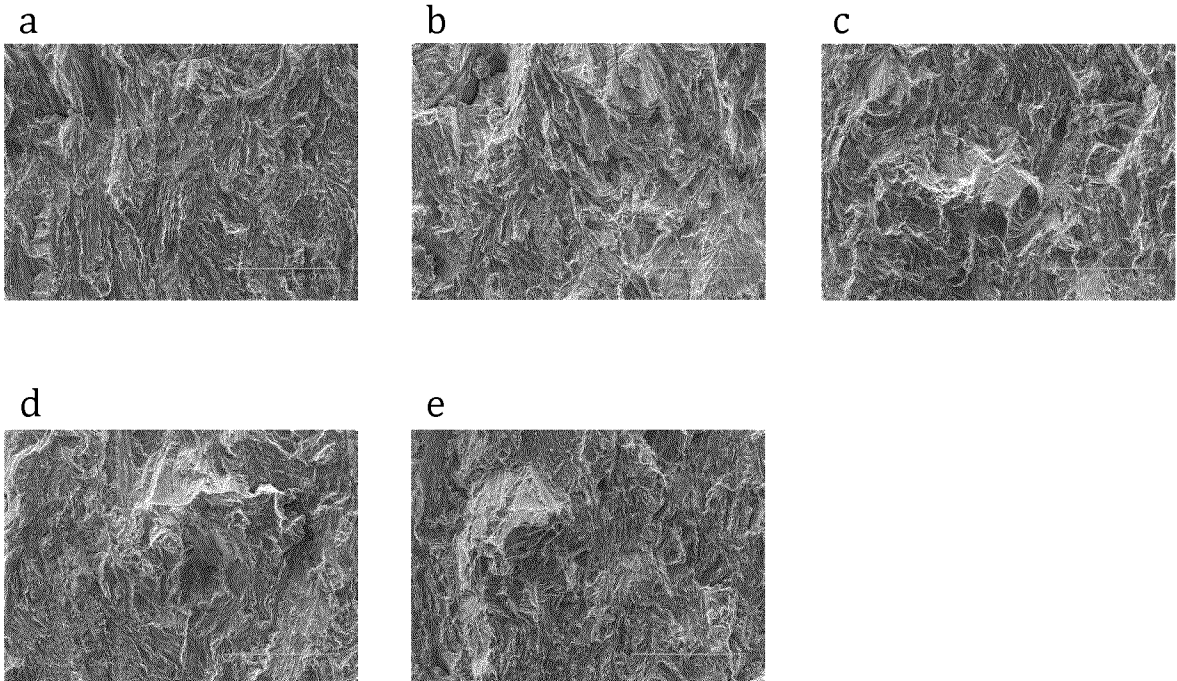
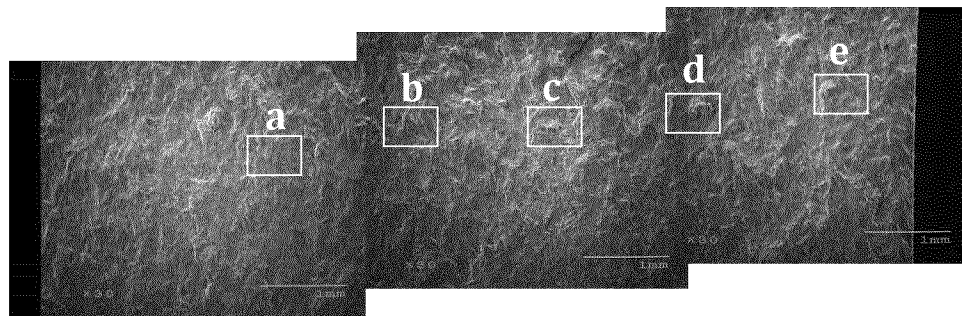


Figure 10B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr25NiC2-3 (12.5mm ^t)	20%CW (TL) 25% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	340°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.3

Depth of fatigue Pre-crack (mm)										Average depth(mm)
3.12	3.17	3.14	3.04	2.82	2.73	2.57	2.39	2.18	2.13	2.73

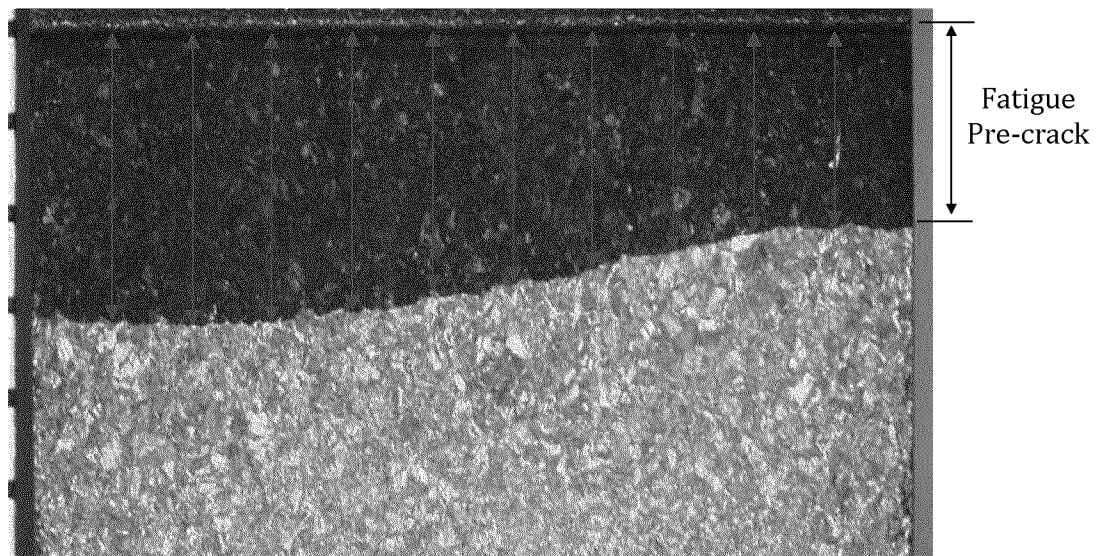
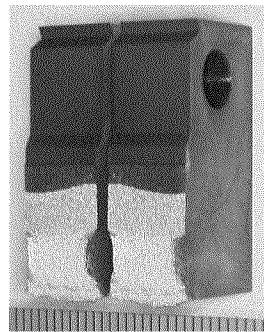
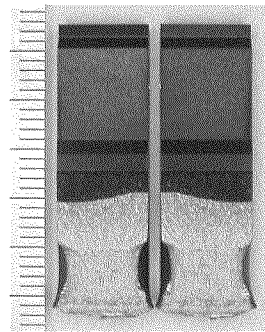


Figure 11A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr25NiC2-3 (12.5mm ^t)	20%CW (TL) 25% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	340°C 500ppm B 2ppm Li 2.75ppm DH	30	5,233.3
Depth of SCC (mm)				Average (mm)
no crack				—

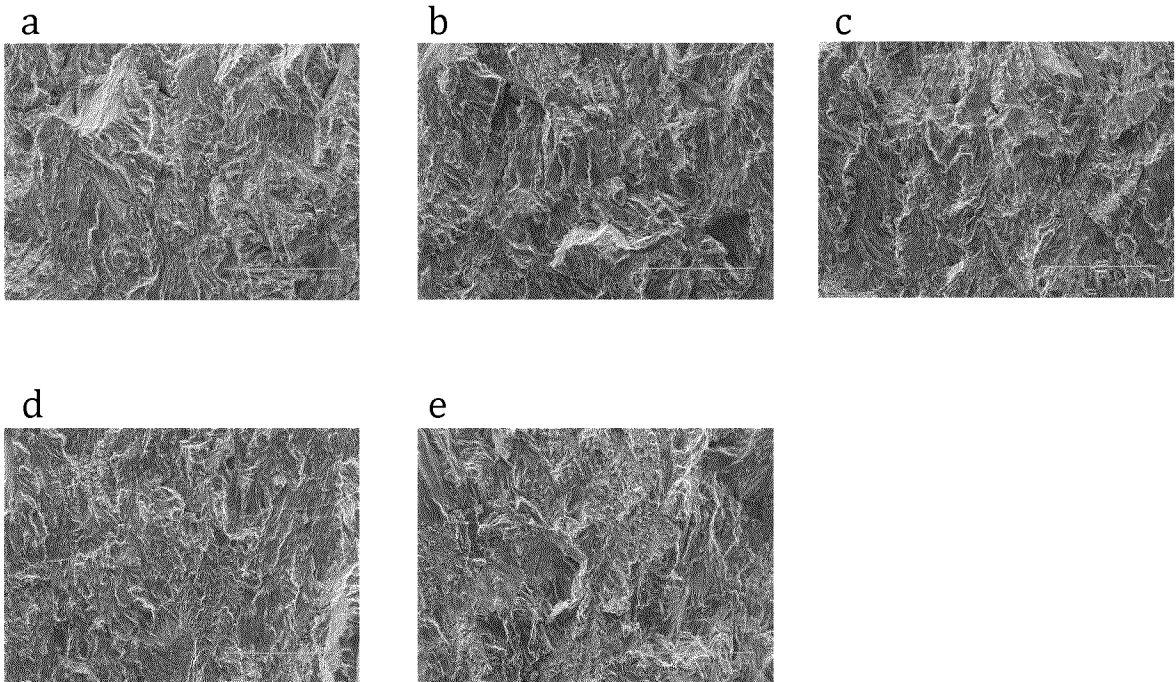
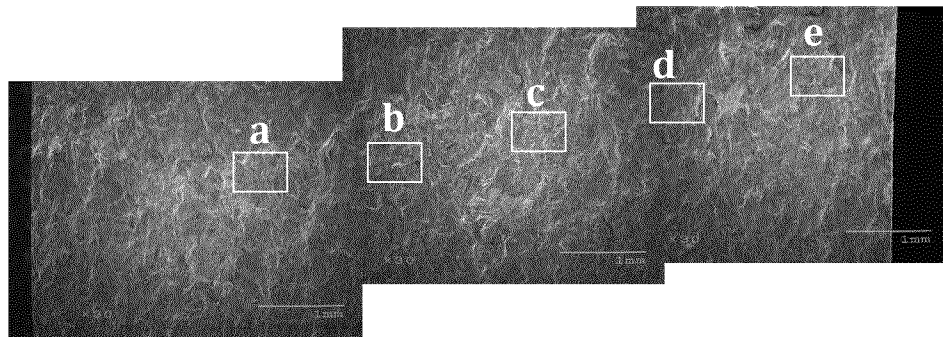


Figure 11B

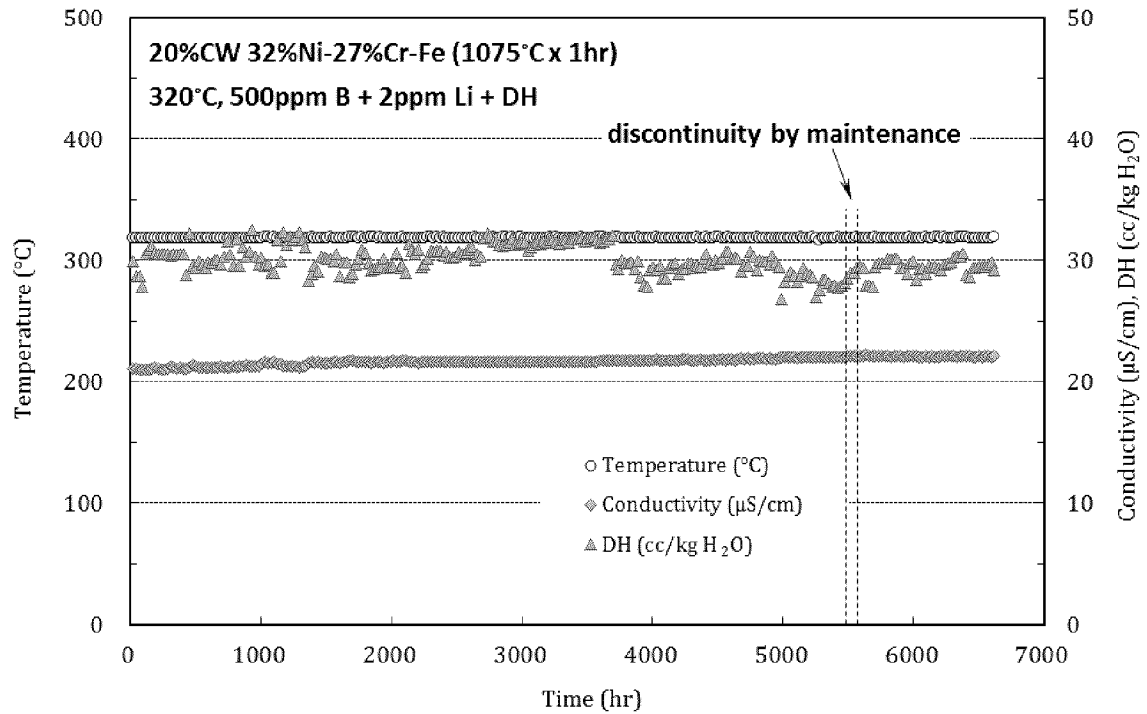


Figure 12A

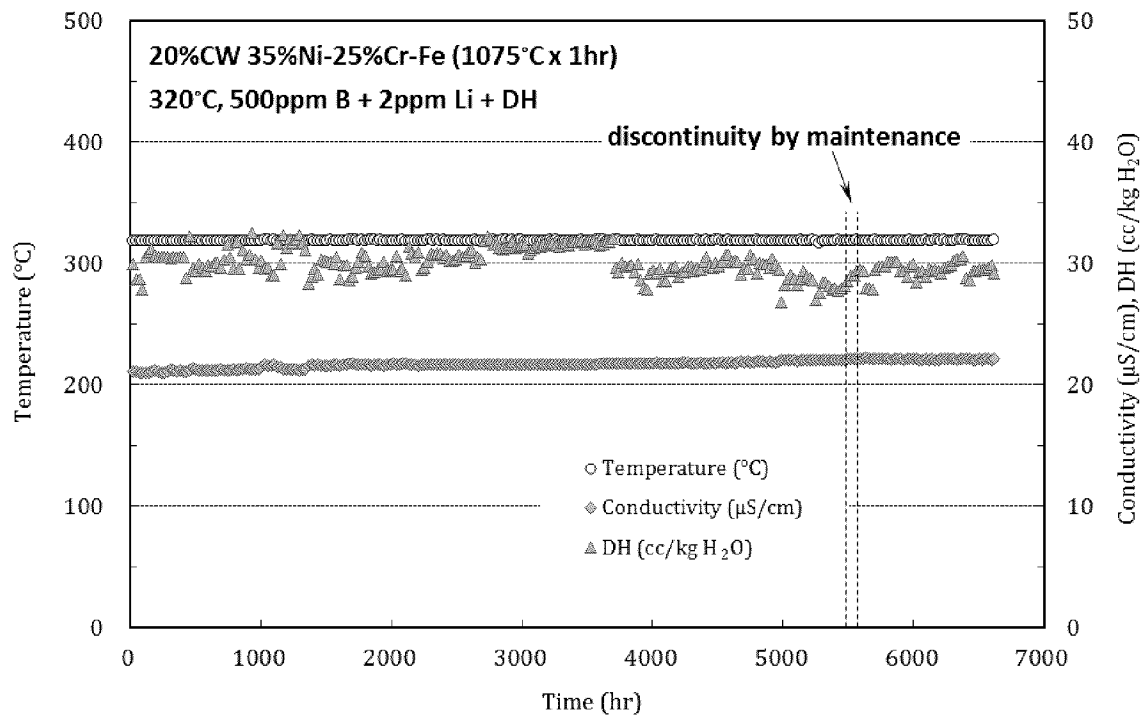


Figure 12B

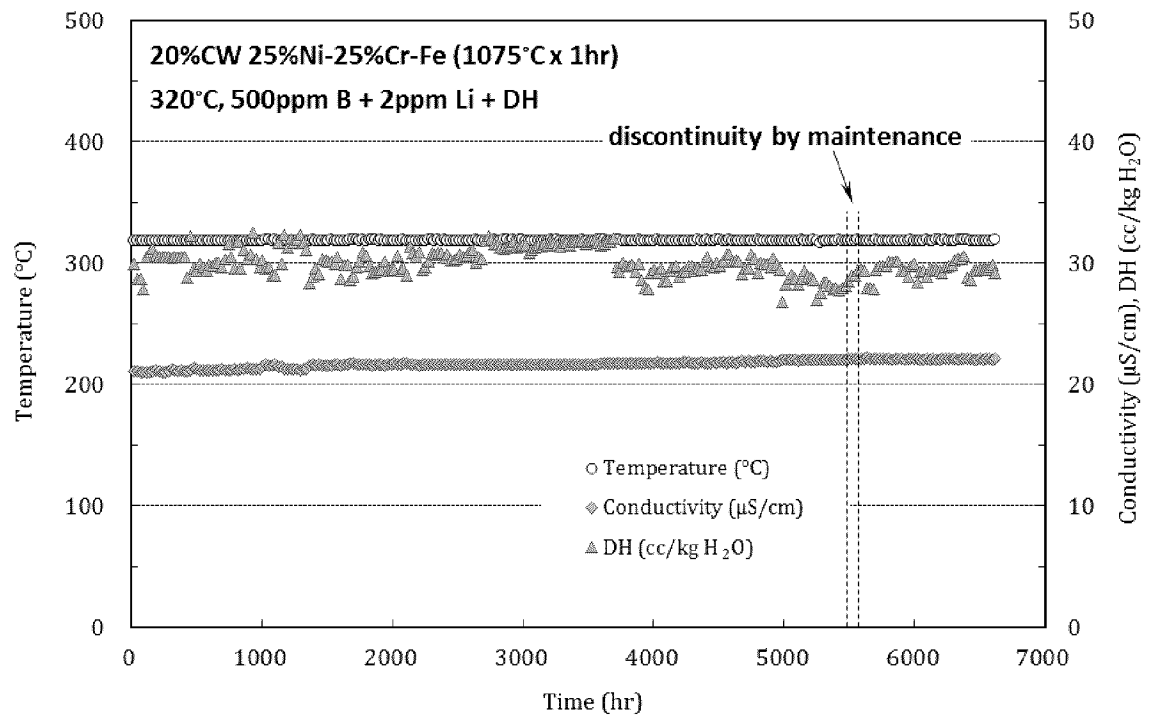


Figure 12C

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G27Cr32NiC2-1 (12.5mm ^t)	20%CW (TL) 32% Ni-27% Cr Model Alloy 1075°C x 1 hr W.C.	320°C 500ppm B 2ppm Li 2.75ppm DH	30	6,609.2

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.13	2.11	2.13	2.11	2.29	2.34	2.54	2.62	2.59	2.74	2.36

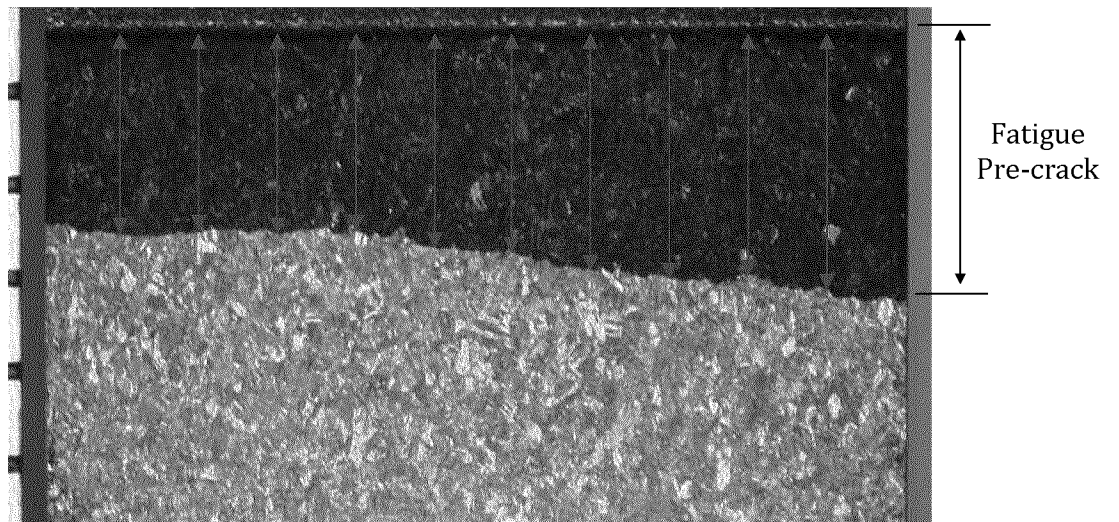
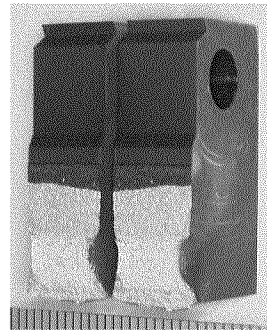
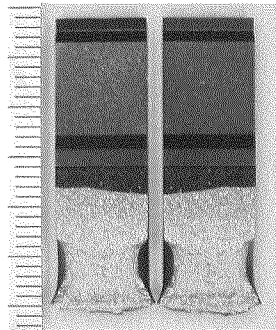


Figure 13A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G27Cr32NiC2-1 (12.5mm ^t)	20%CW (TL) 32% Ni-27% Cr Model Alloy 1075°C x 1 hr W.C.	320°C 500ppm B 2ppm Li 2.75ppm DH	30	6,609.2
Depth of SCC (mm)				Average (mm)
no crack				—

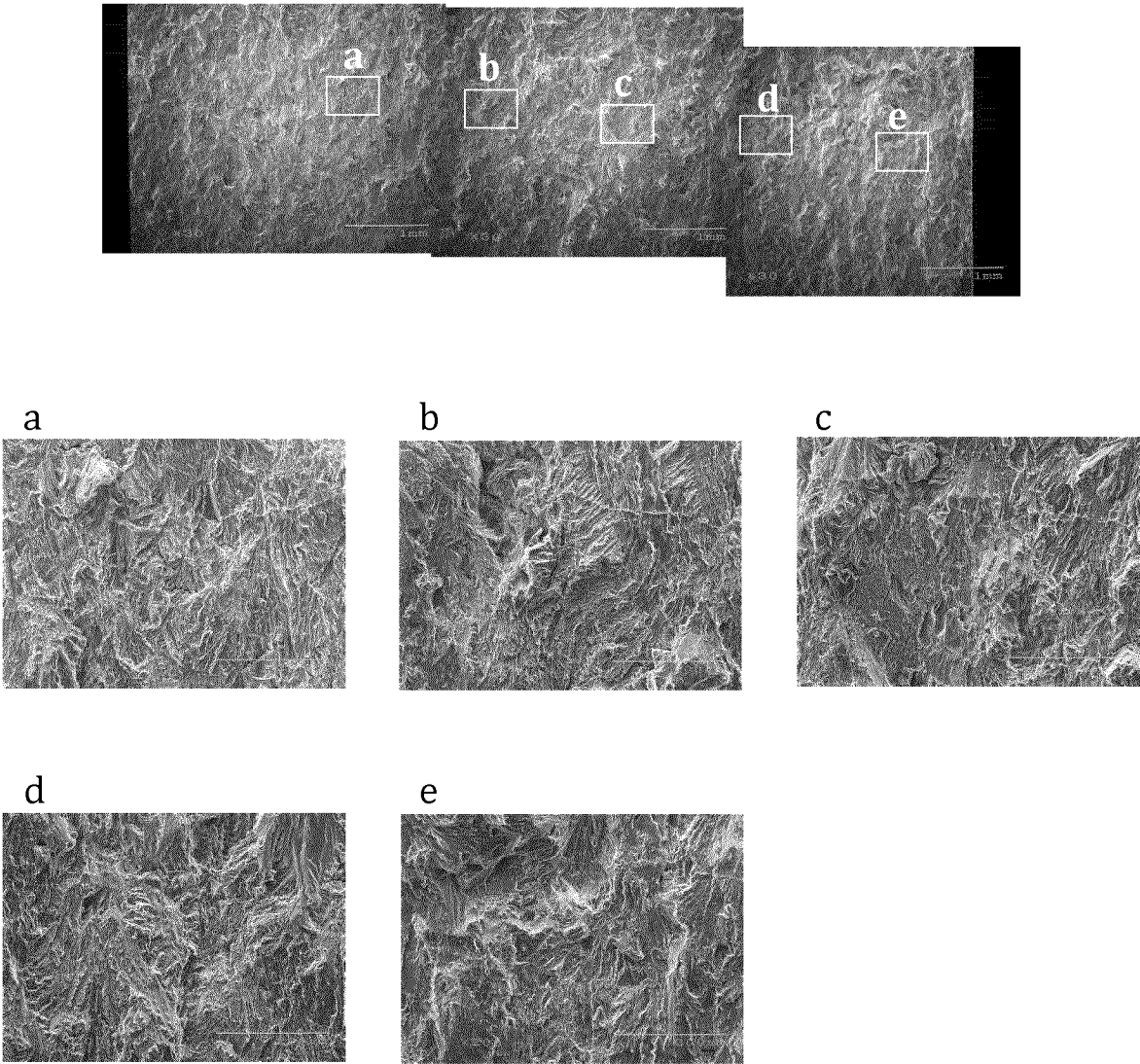


Figure 13B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr35NiC2-1 (12.5mm ^t)	20%CW (TL) 35% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	320°C 500ppm B 2ppm Li 2.75ppm DH	30	6,608.5

Depth of fatigue Pre-crack (mm)										Average depth(mm)
3.24	3.20	3.07	3.07	2.97	2.82	2.65	2.47	2.31	2.25	2.80

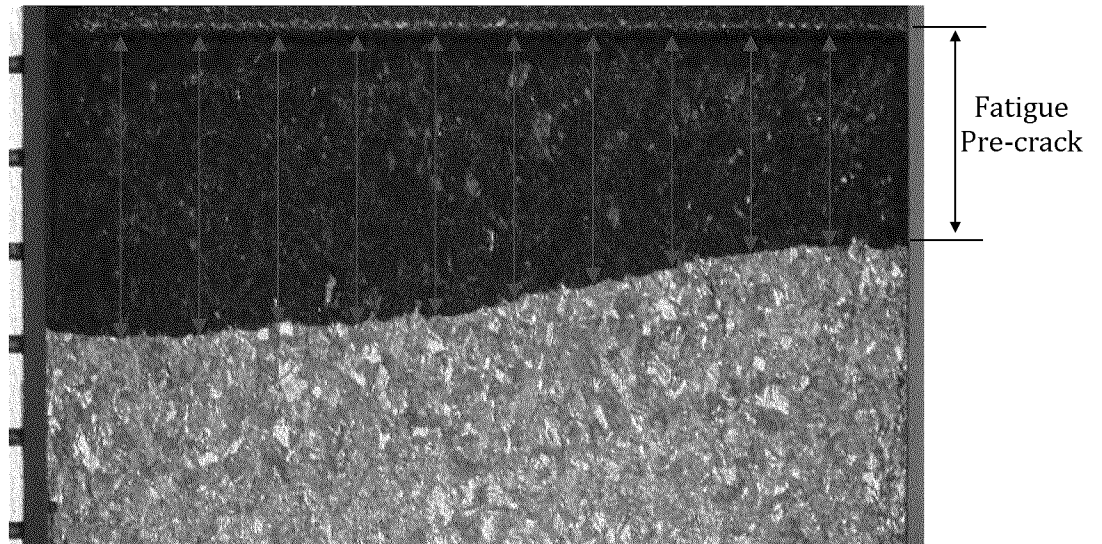
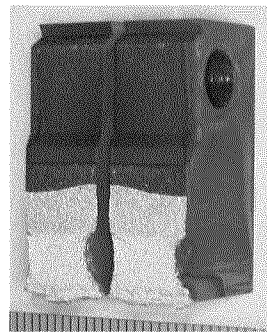
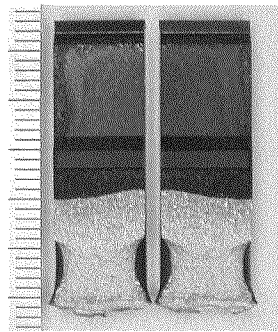


Figure 14A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr35NiC2-1 (12.5mm ^t)	20%CW (TL) 35% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	320°C 500ppm B 2ppm Li 2.75ppm DH	30	6,608.5
Depth of SCC (mm)				Average (mm)
no crack				—

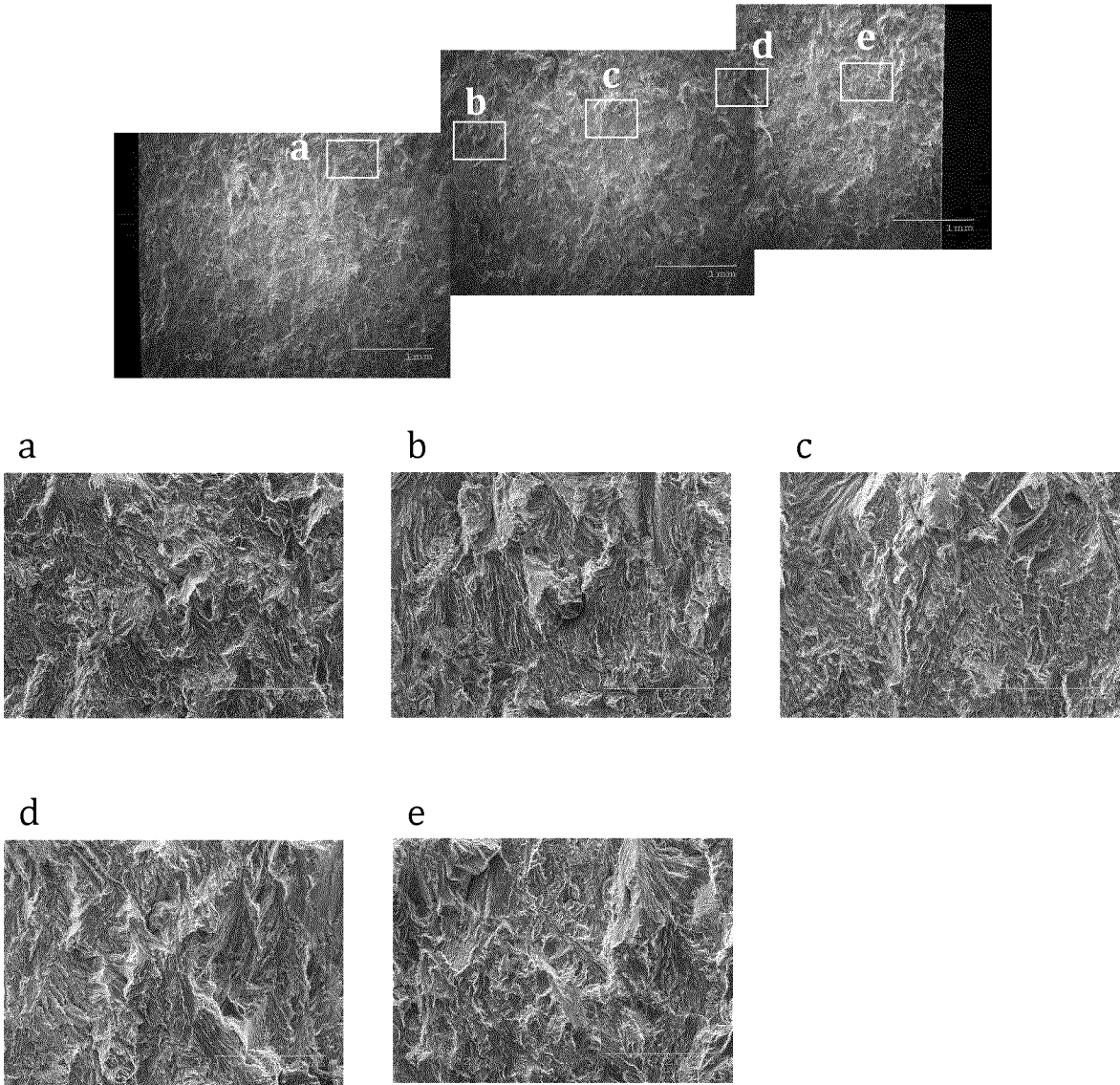


Figure 14B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr25NiC2-1 (12.5mm ^t)	20%CW (TL) 25% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	320°C 500ppm B 2ppm Li 2.75ppm DH	30	6,608.5

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.52	2.55	2.59	2.58	2.51	2.50	2.43	2.34	2.23	2.18	2.44

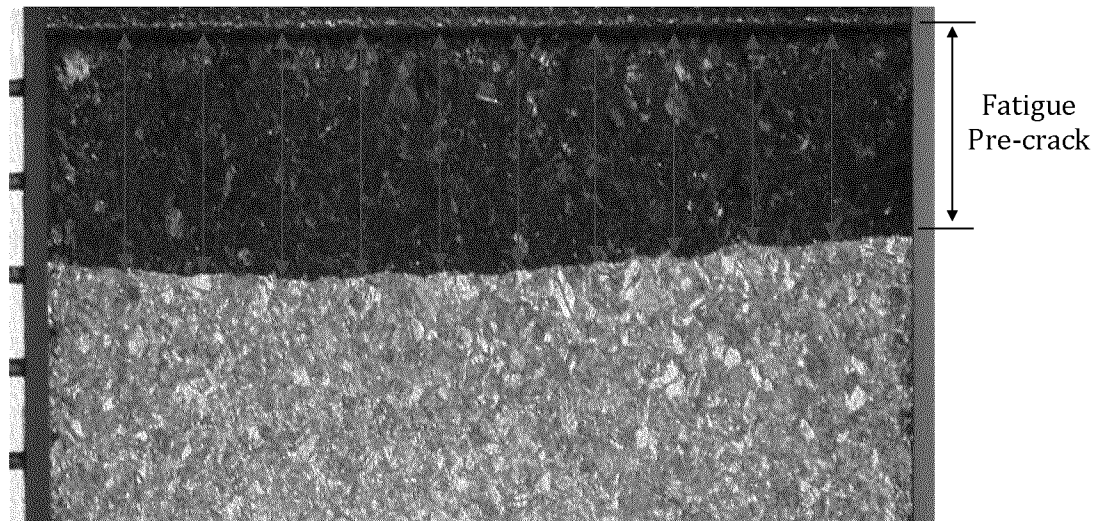
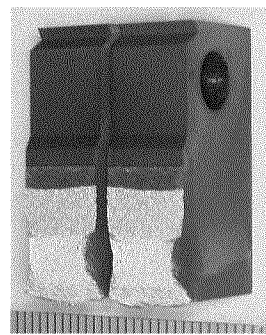
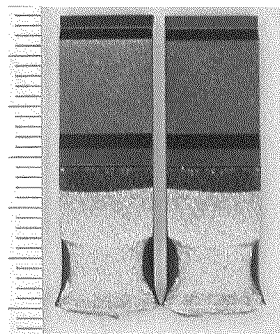


Figure 15A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr25NiC2-1 (12.5mm ^t)	20%CW (TL) 25% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	320°C 500ppm B 2ppm Li 2.75ppm DH	30	6,608.5
Depth of SCC (mm)				Average (mm)
no crack				—

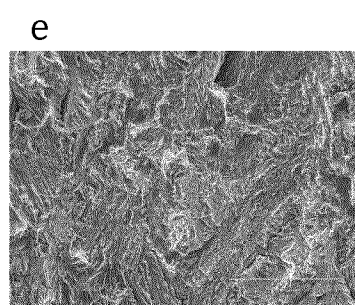
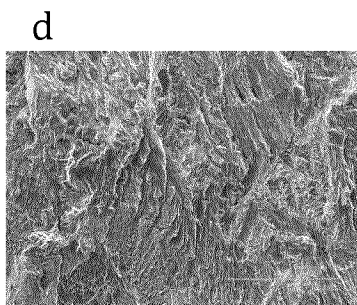
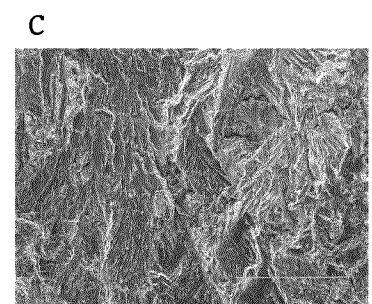
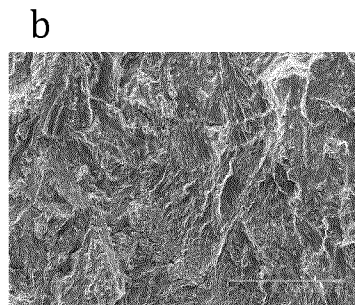
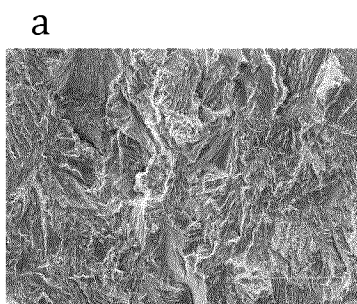
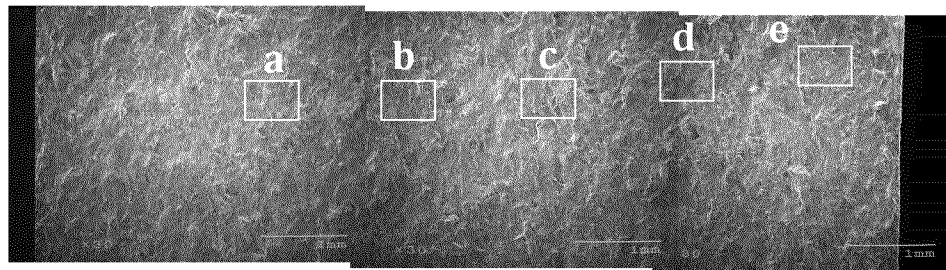


Figure 15B

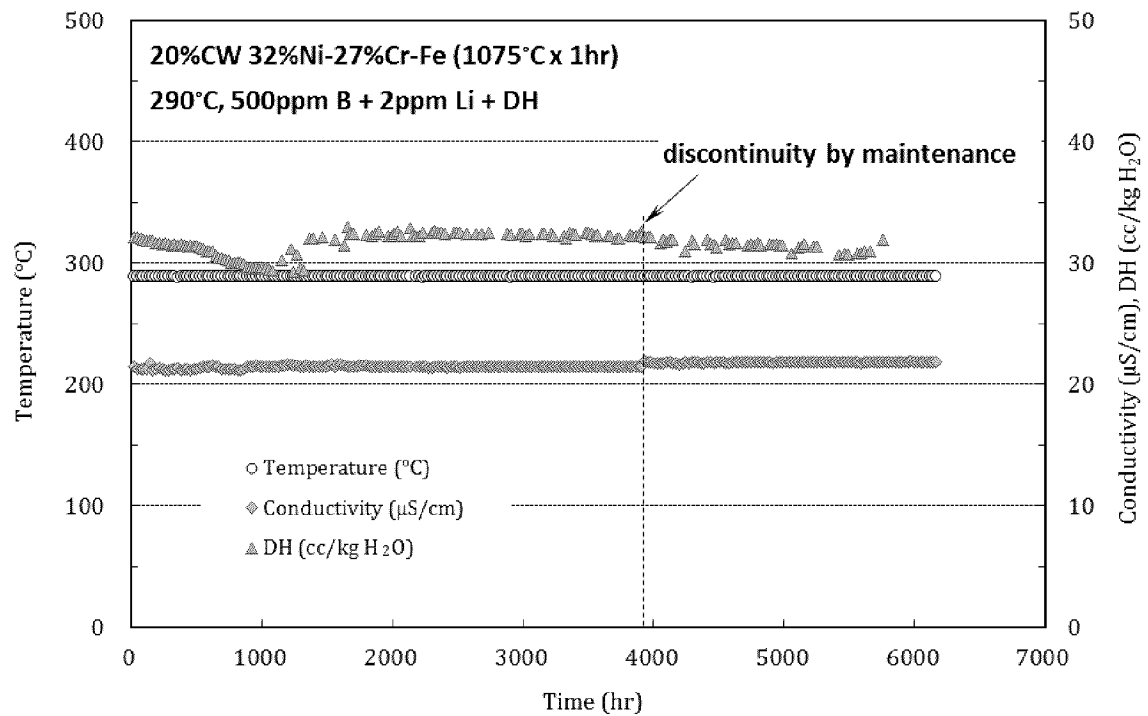


Figure 16A

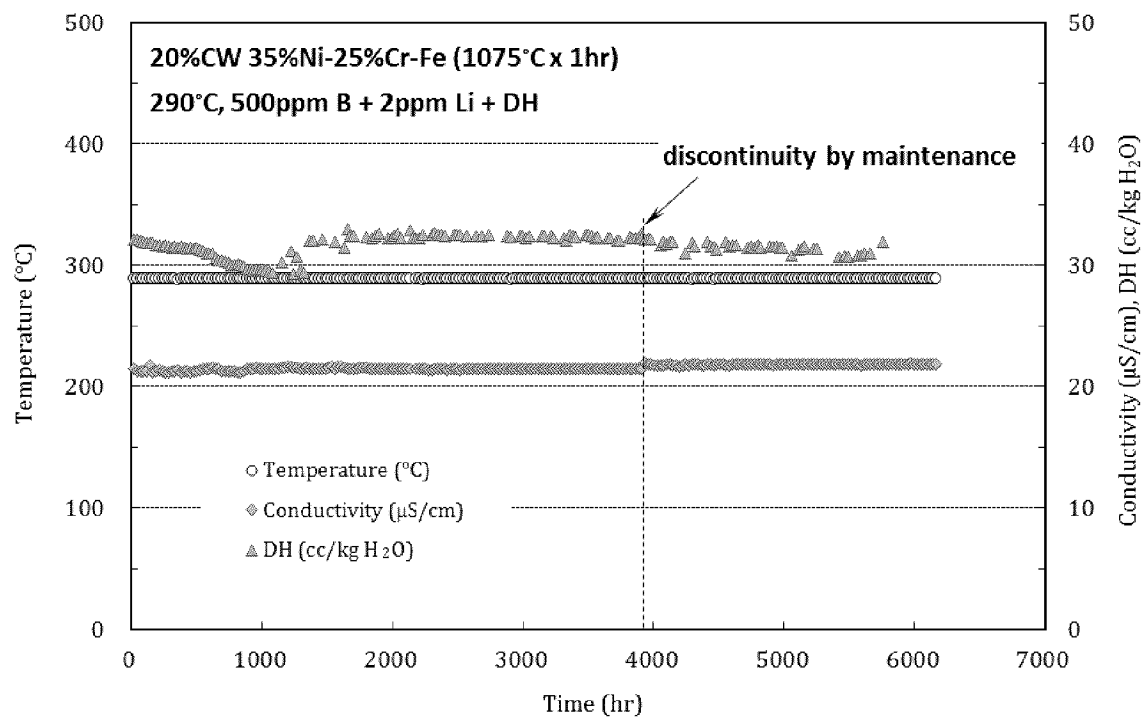


Figure 16B

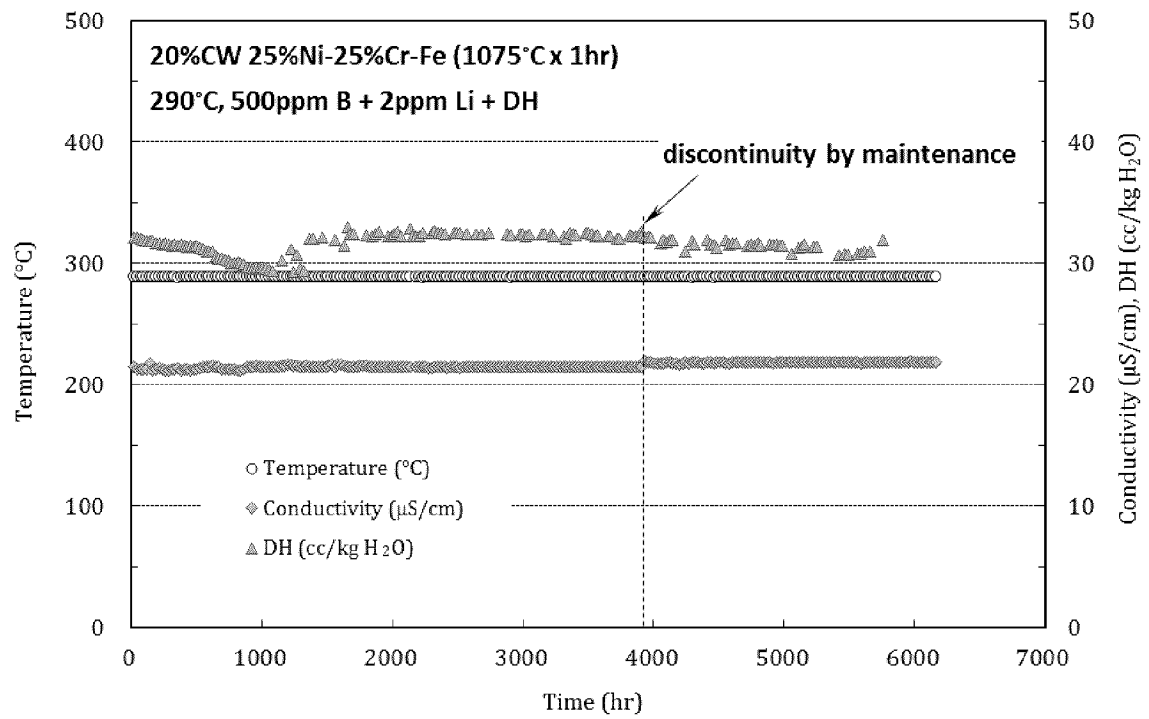


Figure 16C

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G27Cr32NiC2-2 (12.5mm ^t)	20%CW (TL) 32% Ni-27% Cr Model Alloy 1075°C x 1 hr W.C.	290°C 500ppm B 2ppm Li 2.75ppm DH	30	6,154.5

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.44	2.39	2.42	2.34	2.27	2.18	2.34	2.37	2.24	2.22	2.32

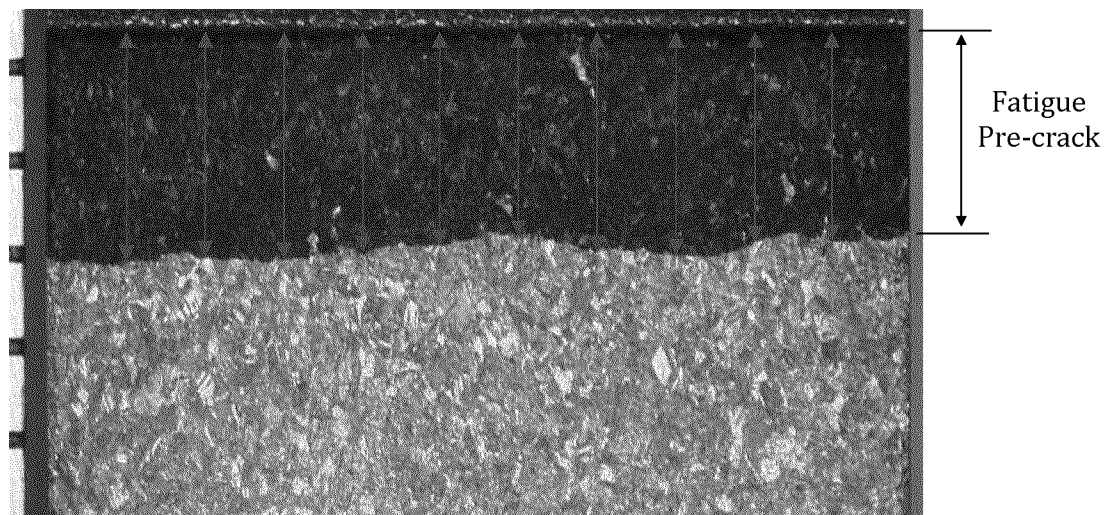
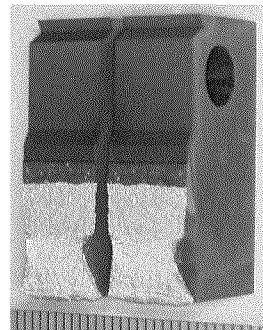
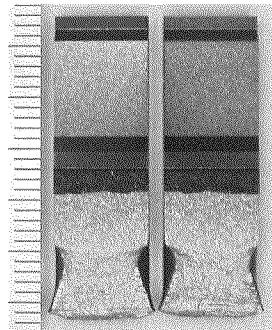


Figure 17A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G27Cr32NiC2-2 (12.5mm ^t)	20%CW (TL) 32% Ni-27% Cr Model Alloy 1075°C x 1 hr W.C.	290°C 500ppm B 2ppm Li 2.75ppm DH	30	6,154.5
Depth of SCC (mm)				Average (mm)
no crack				—

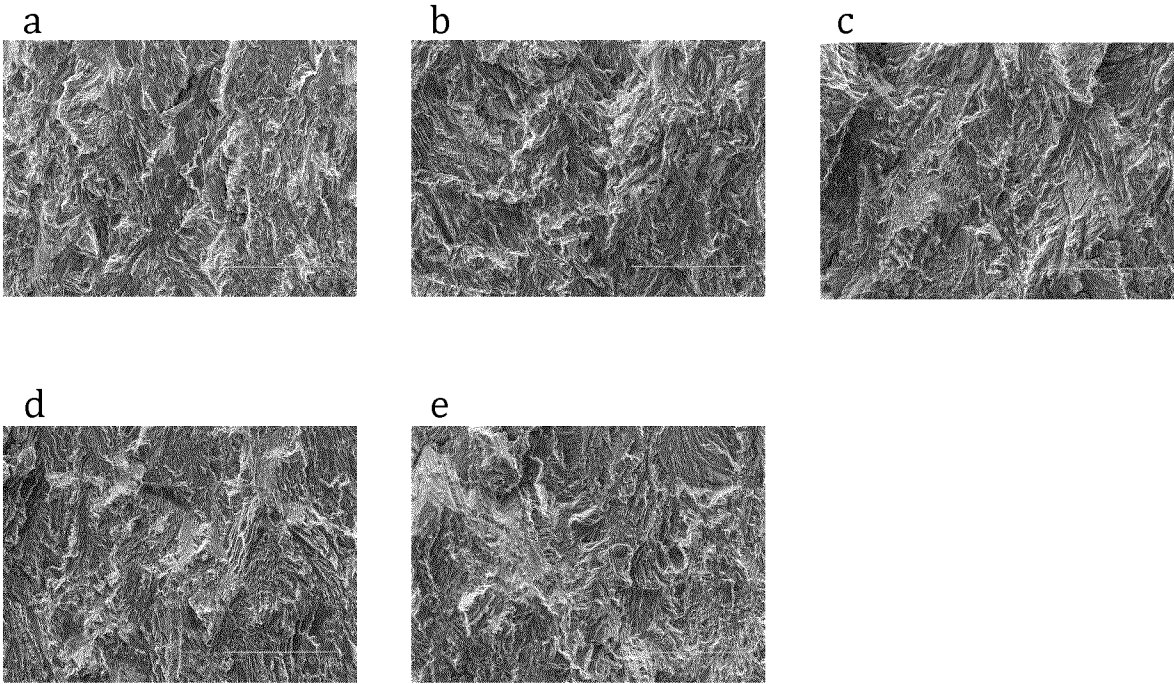
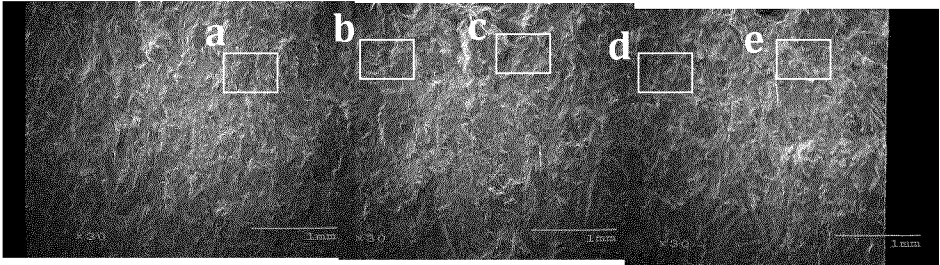


Figure 17B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr35NiC2-2 (12.5mm ^t)	20%CW (TL) 35% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	290°C 500ppm B 2ppm Li 2.75ppm DH	30	6,154.6

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.45	2.51	2.56	2.50	2.44	2.36	2.34	2.16	2.14	2.07	2.35

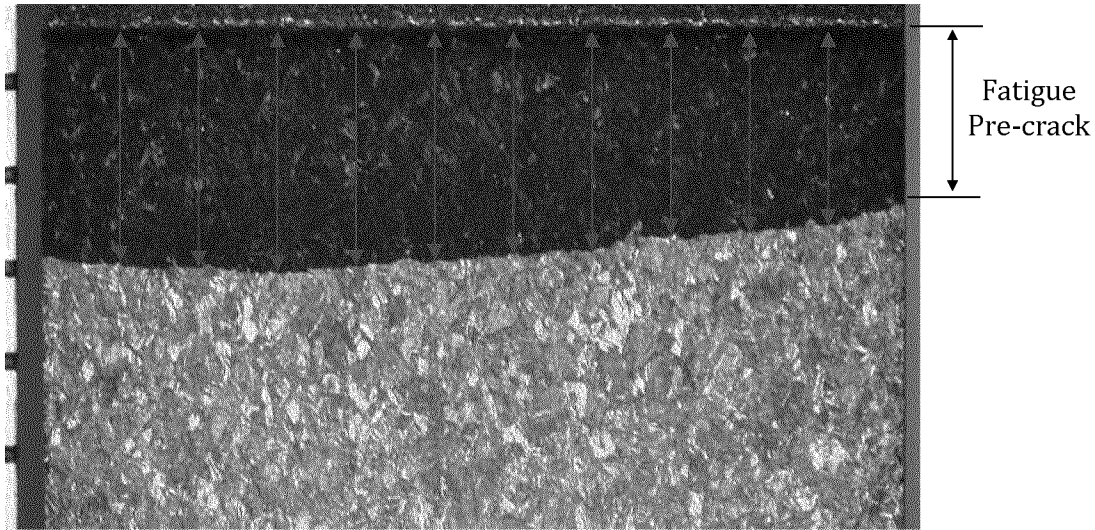
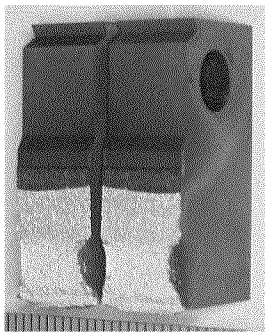
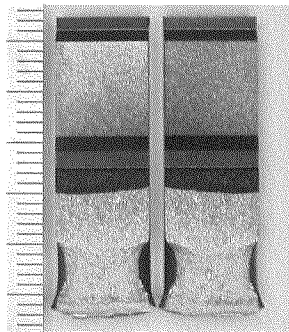


Figure 18A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr35NiC2-2 (12.5mm ^t)	20%CW (TL) 35% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	290°C 500ppm B 2ppm Li 2.75ppm DH	30	6,154.6
Depth of SCC (mm)				Average (mm)
no crack				—

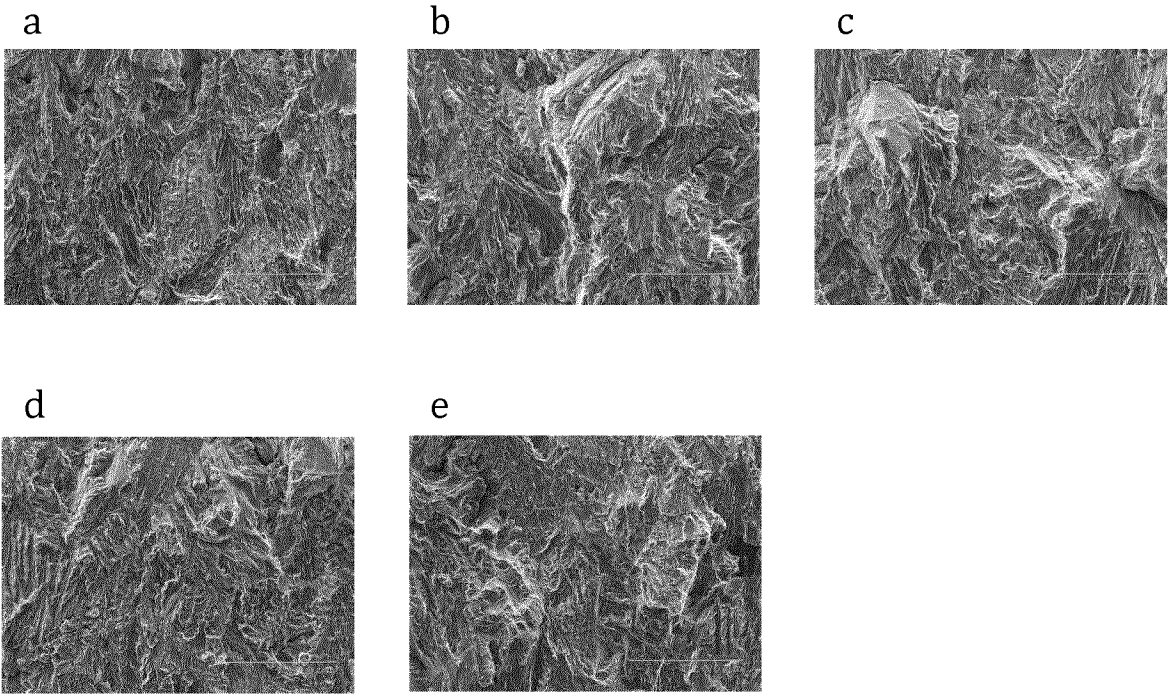
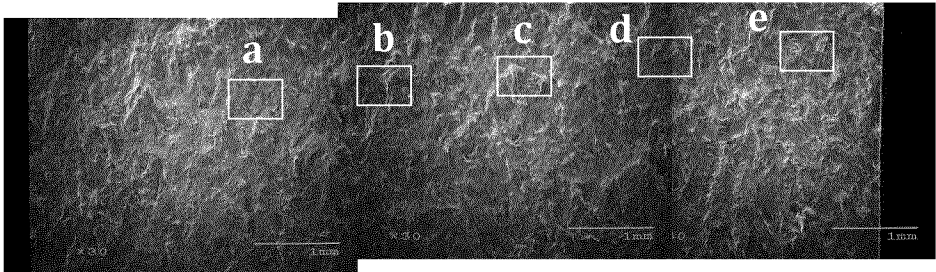


Figure 18B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr25NiC2-2 (12.5mm ^t)	20%CW (TL) 25% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	290°C 500ppm B 2ppm Li 2.75ppm DH	30	6,154.6

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.05	2.12	2.26	2.42	2.49	2.50	2.46	2.26	2.14	2.12	2.28

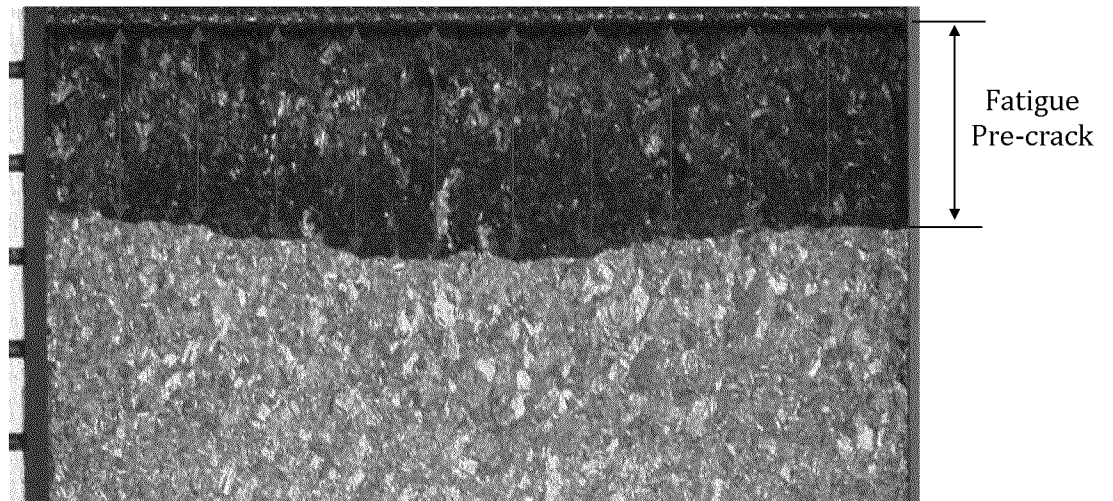
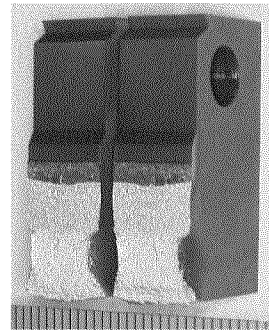
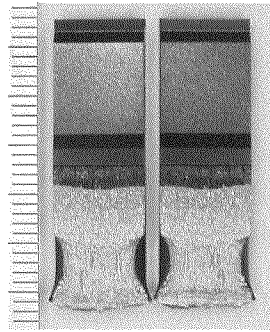


Figure 19A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr25NiC2-2 (12.5mm ^t)	20%CW (TL) 25% Ni-25% Cr Model Alloy 1075°C x 1 hr W.C.	290°C 500ppm B 2ppm Li 2.75ppm DH	30	6,154.6
Depth of SCC (mm)				Average (mm)
no crack				—

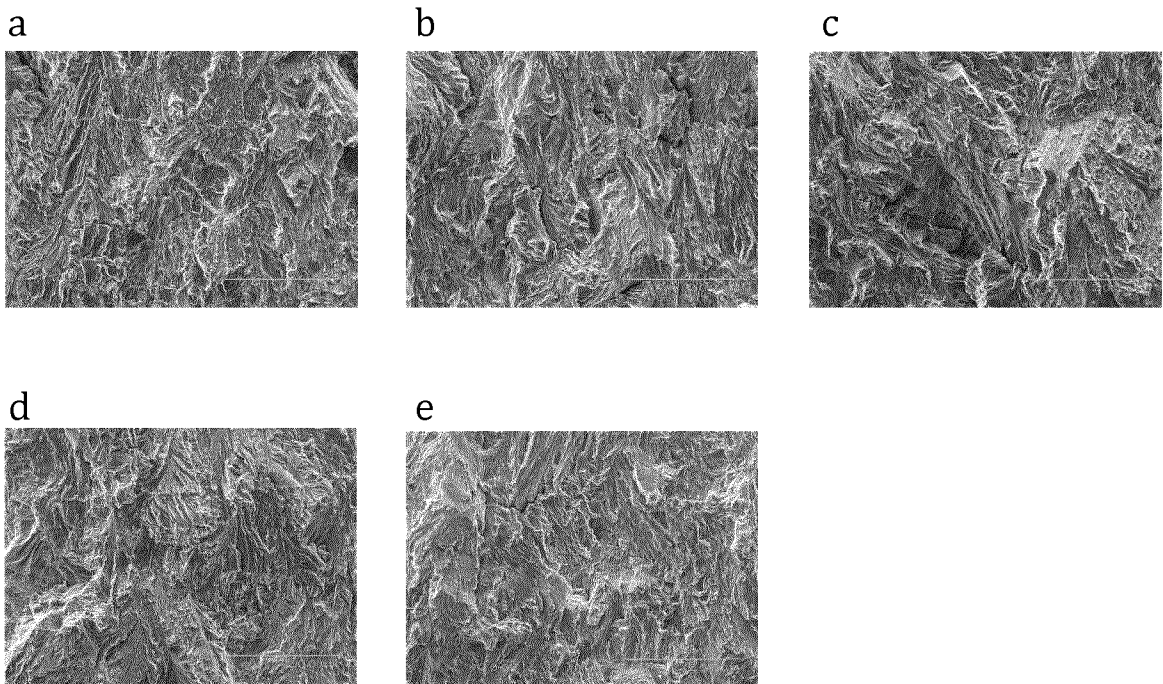
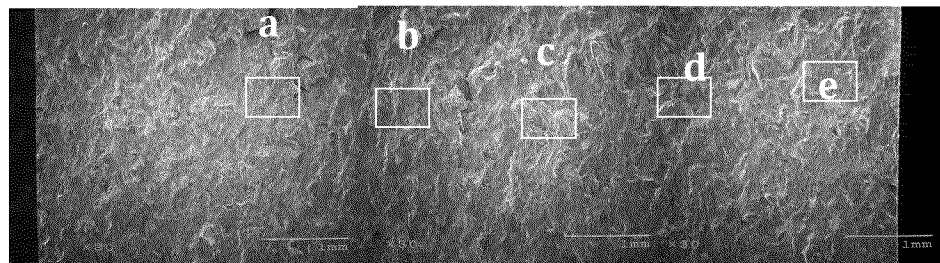
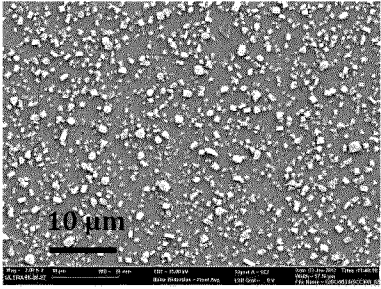
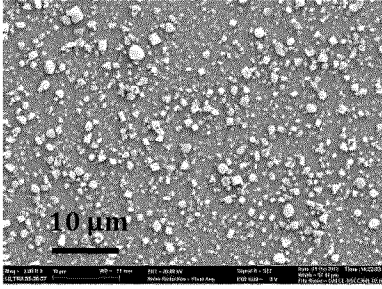
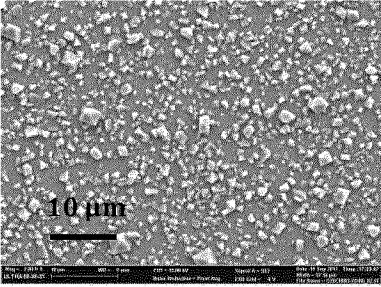
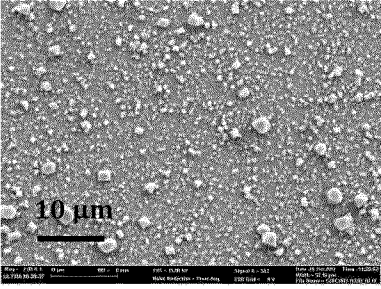
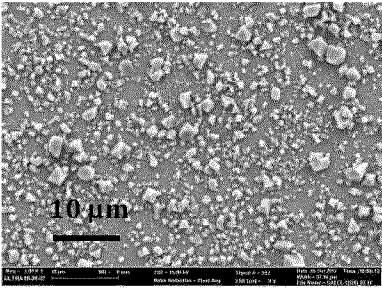
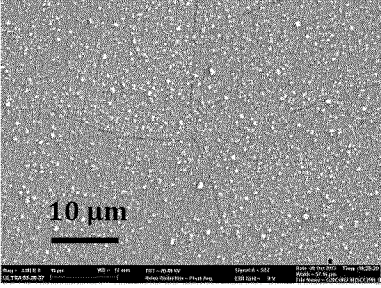
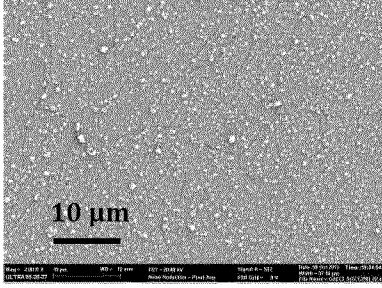
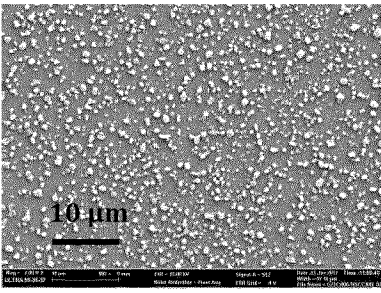
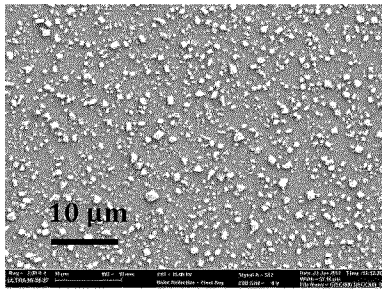
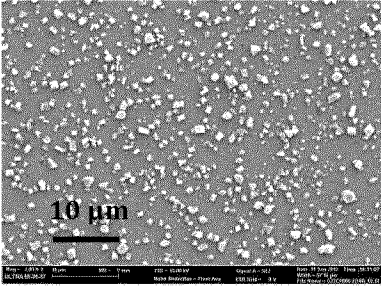
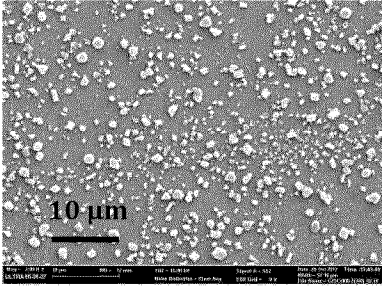
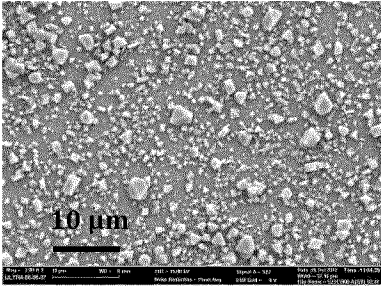
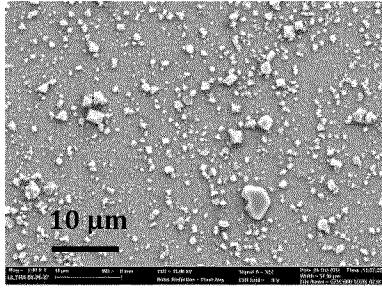
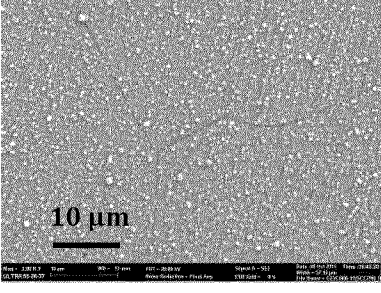
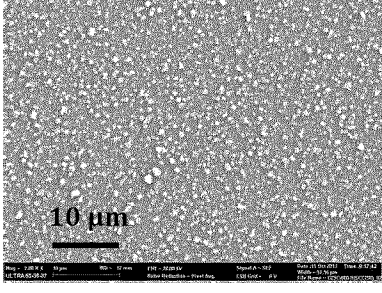


Figure 19B

Test Temperature (°C)	Heat treatment : 1075°C x1hr_W.C.	Heat treatment : 1065°C x10min_A.C.
	32%Ni-20%Cr	32%Ni-22%Cr
360	(5,252.6hr) 	(4,988.7hr) 
340	(5,824.7hr) 	—
320	(7,242.2hr) 	(5,637.5hr) 
290	(4,988.8hr) 	(4,973.7hr) 

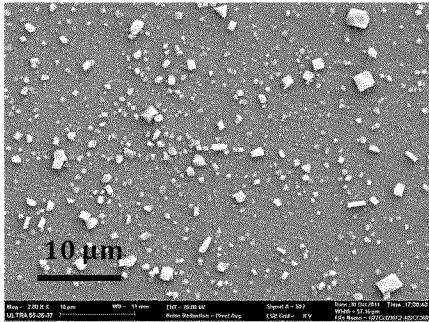
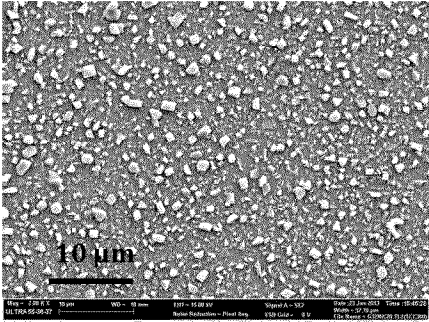
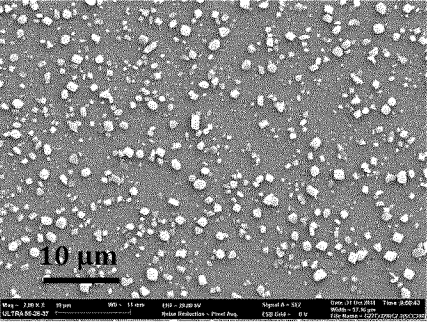
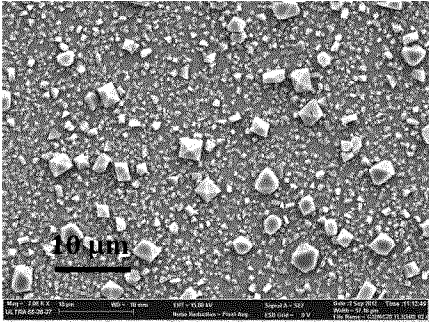
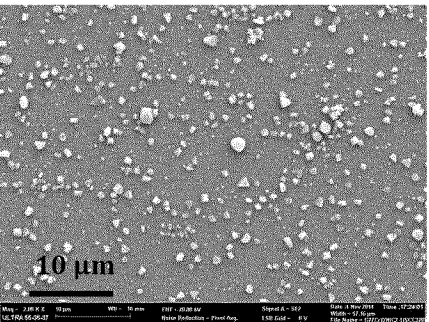
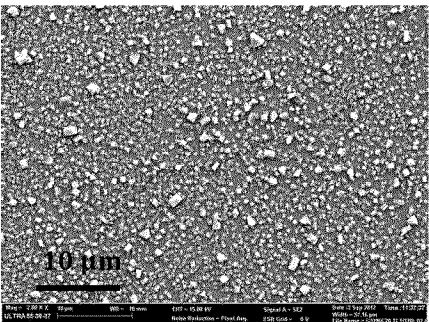
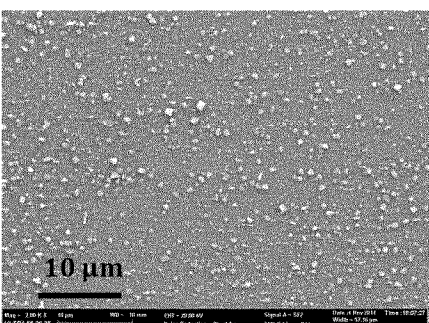
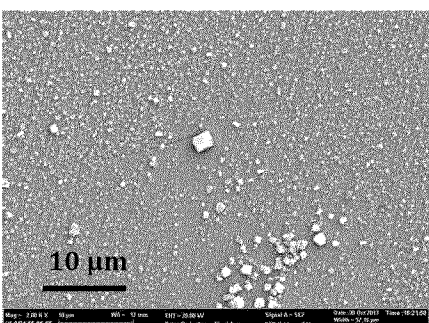
() : Test Duration

Figure 20A

Test Temperature (°C)	Heat treatment : 1075°C x1hr_W.C.	Heat treatment : 1075°C x1hr_W.C.
	32%Ni-23%Cr	32%Ni-25%Cr
360	(5,252.6hr) 	(5,252.6hr) 
340	(5,824.7hr) 	(5,252.6hr) 
320	(5,637.5hr) 	(6,311.8hr) 
290	(4,973.7hr) 	(4,973.7hr) 

(): Test Duration

Figure 20B

Test Temperature (°C)	Heat treatment : 1075 °C x 1hr_W.C.	
	32%Ni-27%Cr	32%Ni-16%Cr
360	(5,233.2hr) 	(1,488.3hr) 
340	(5,233.3hr) 	(5,824.8hr) 
320	(6,609.2hr) 	(1,361hr) 
290	(6,14.5hr) 	(4,467.3hr) 

(): Test Duration

Figure 20C

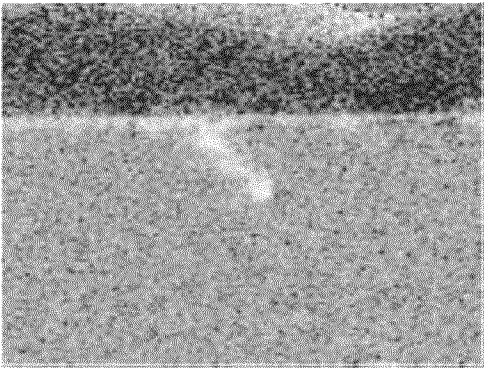
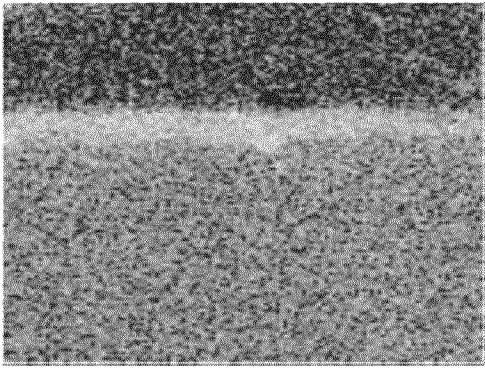
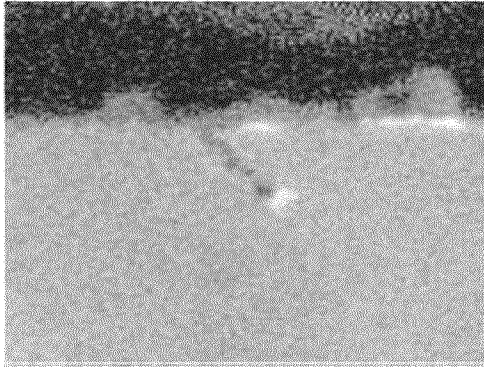
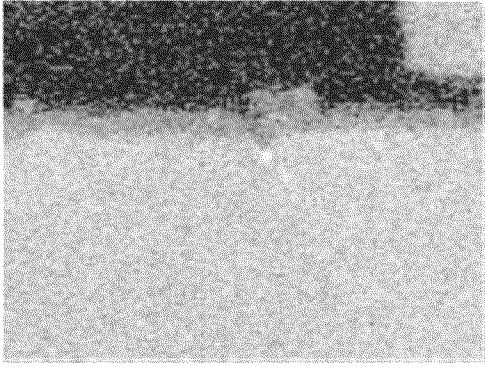
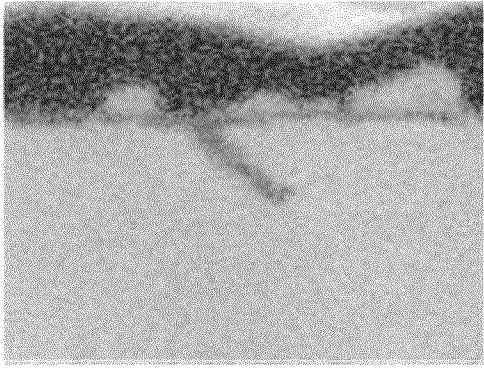
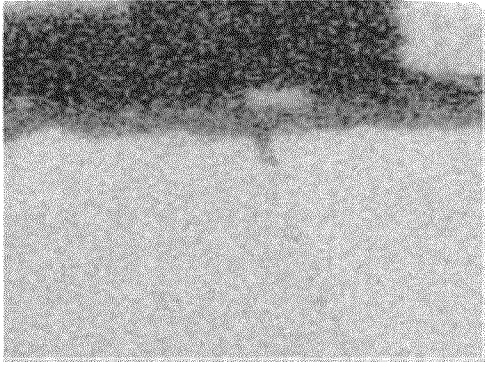
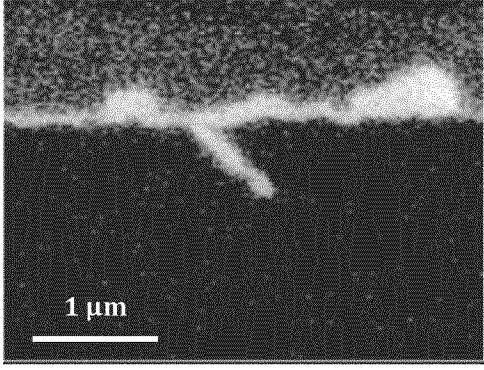
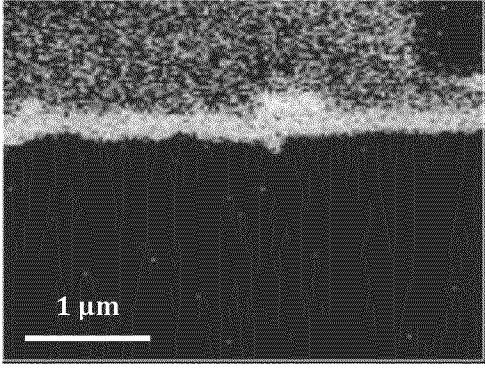
Material : 32%Ni-16%Cr		
	Test Temperature(°C)	
	360	340
Cr		
Ni		
Fe		
O		

Figure 21A

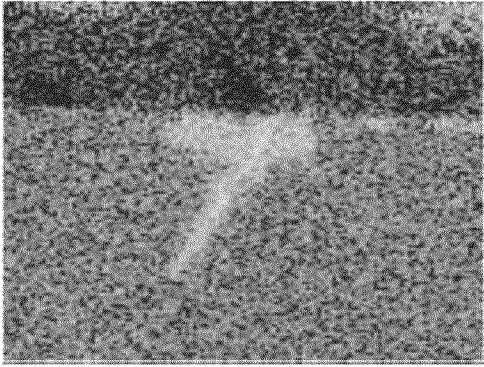
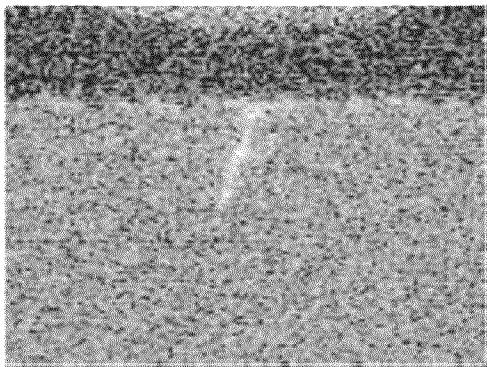
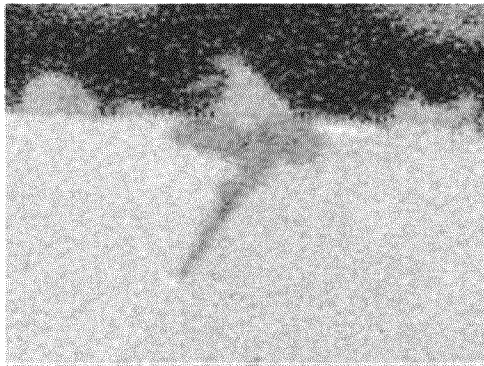
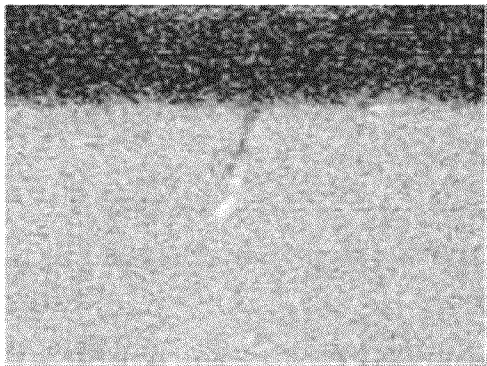
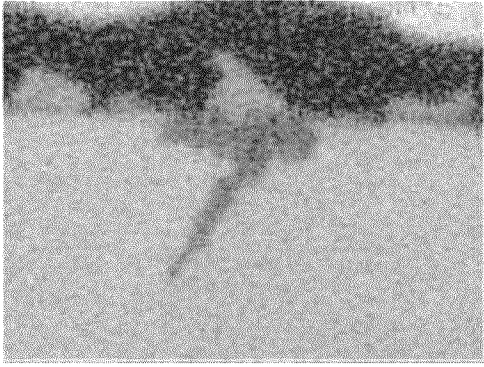
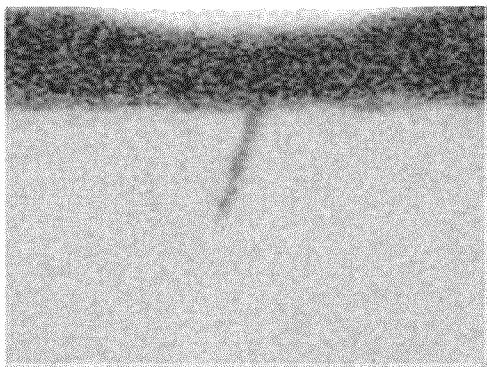
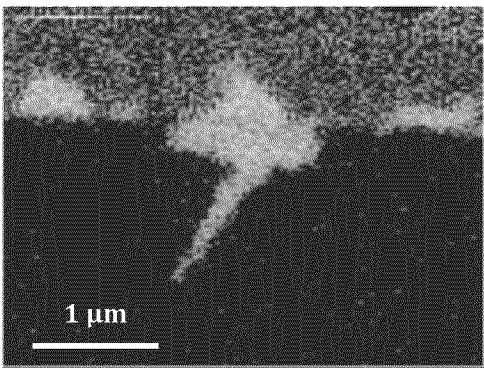
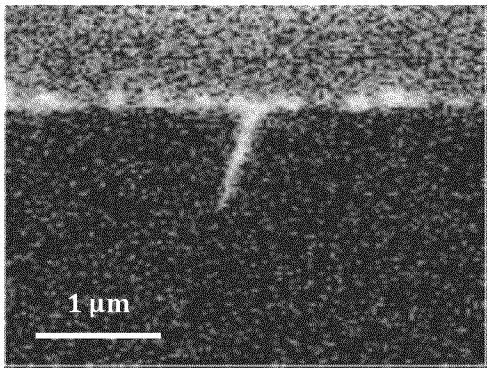
Material : 32%Ni-16%Cr		
	Test Temperature(°C)	
	320	290
Cr		
Ni		
Fe		
O		

Figure 21B

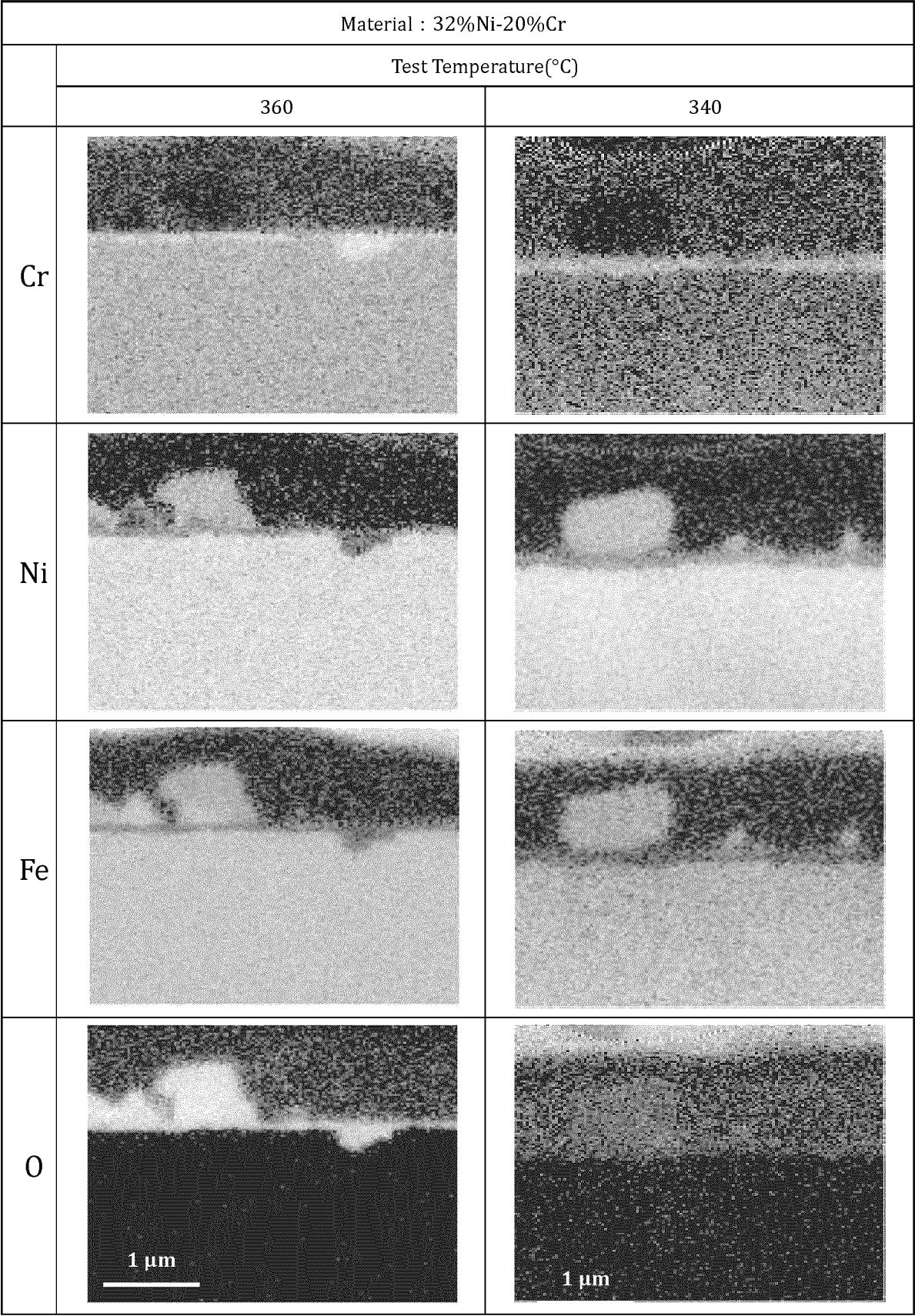


Figure 21C

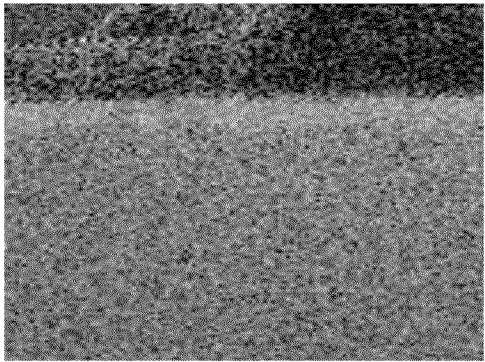
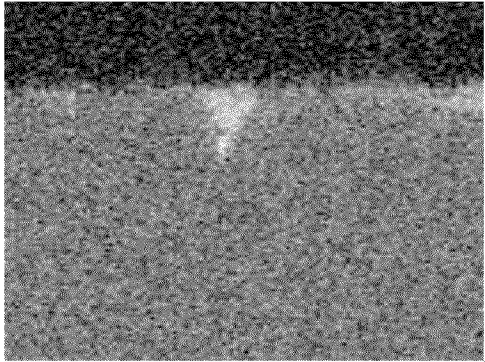
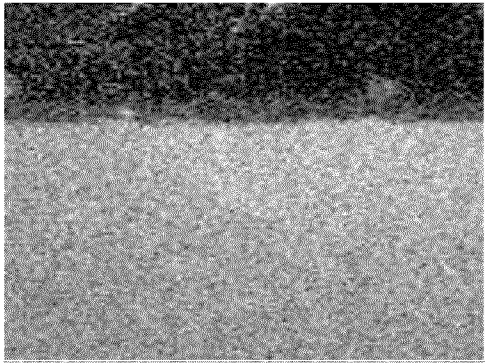
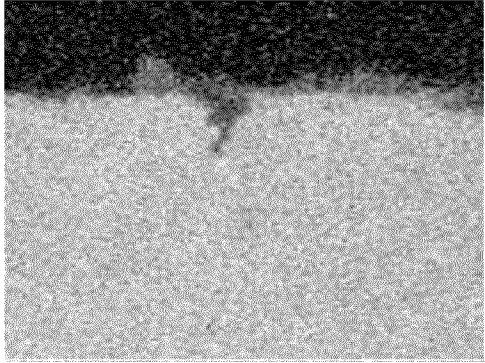
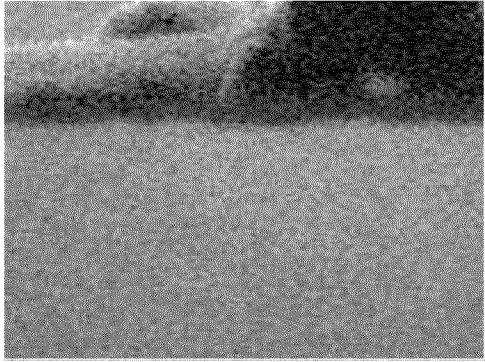
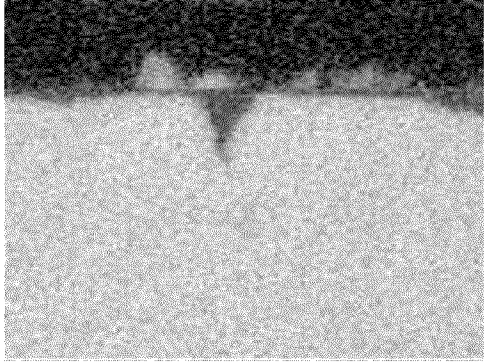
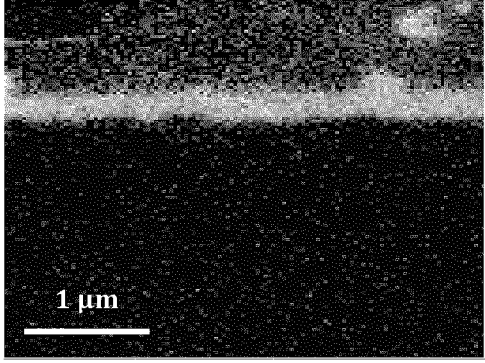
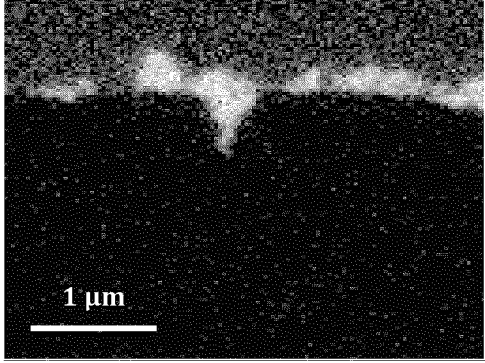
Material : 32%Ni-20%Cr		
	Test Temperature(°C)	
	320	290
Cr		
Ni		
Fe		
O		

Figure 21D
41 / 66

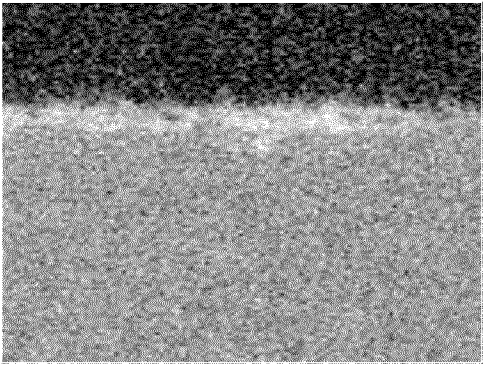
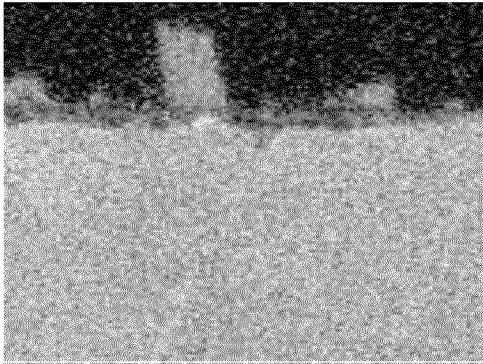
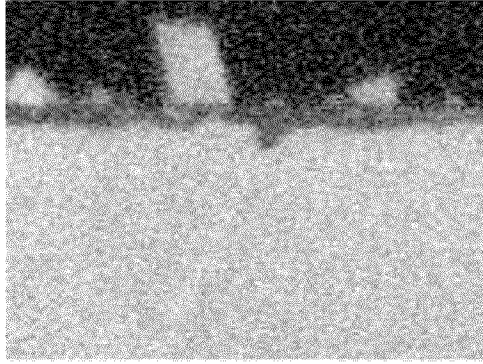
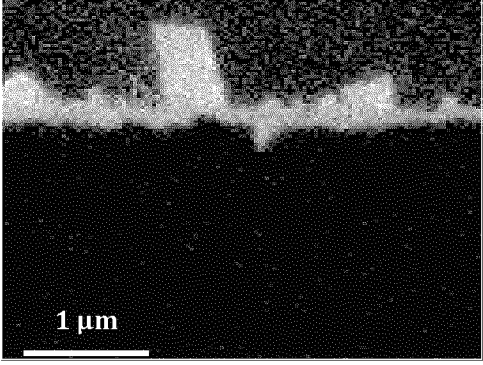
Material : 34%Ni-22%Cr		
	Test Temperature(°C)	
	360	340
Cr		—
Ni		—
Fe		—
O		—

Figure 21E

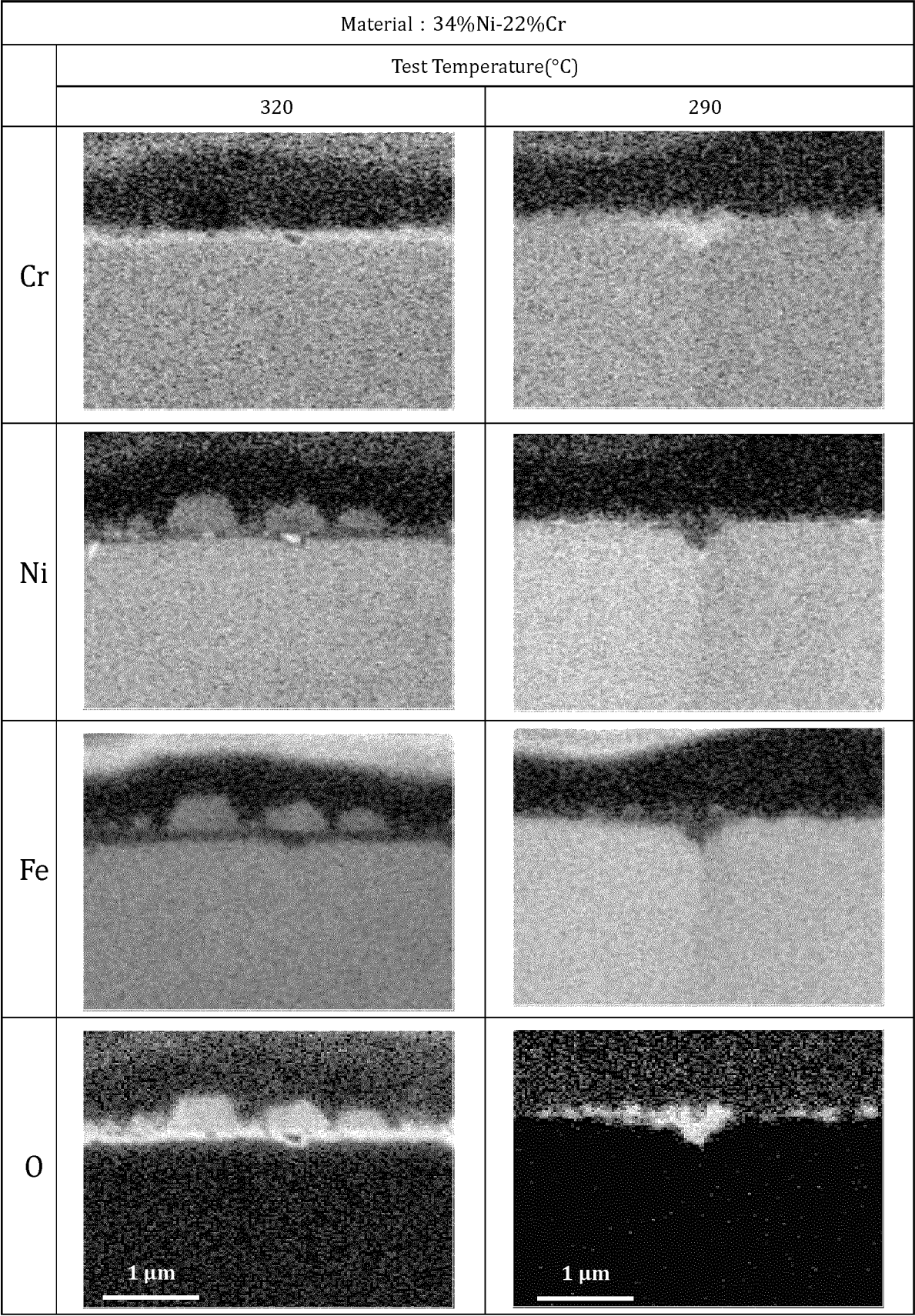


Figure 21F

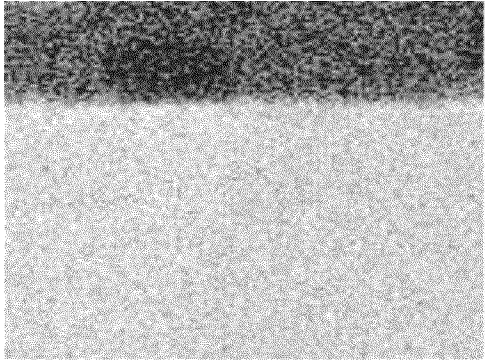
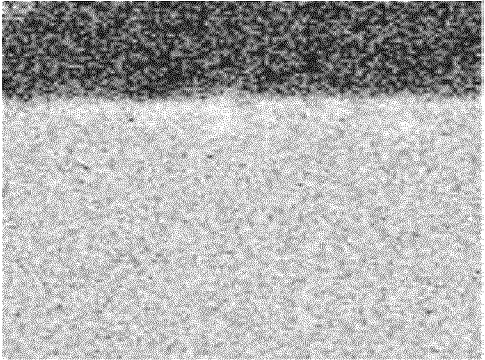
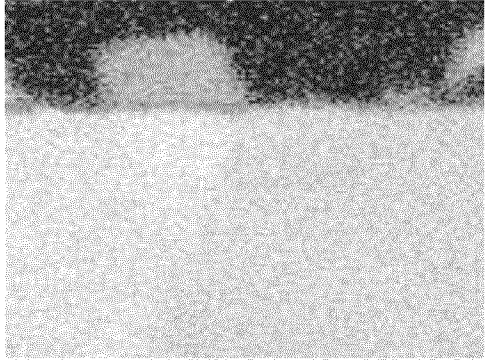
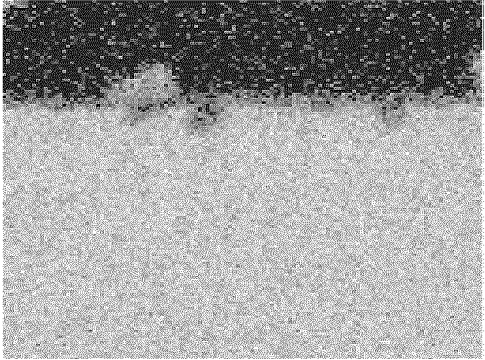
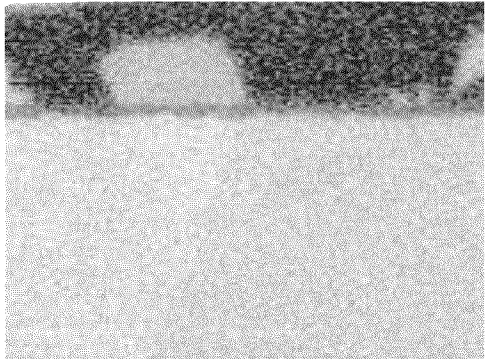
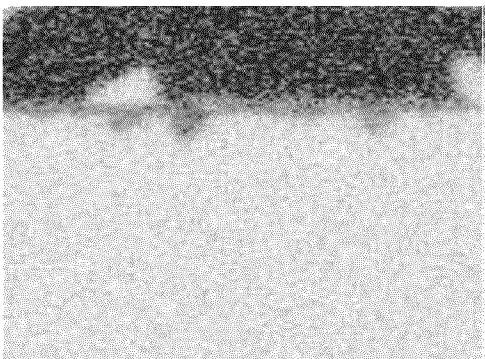
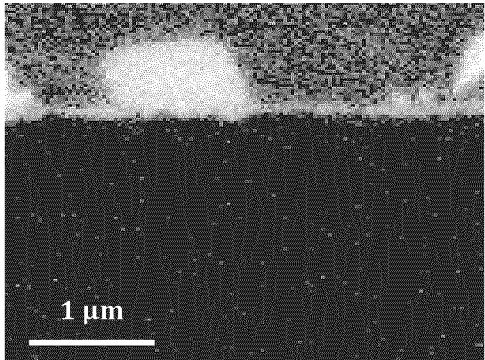
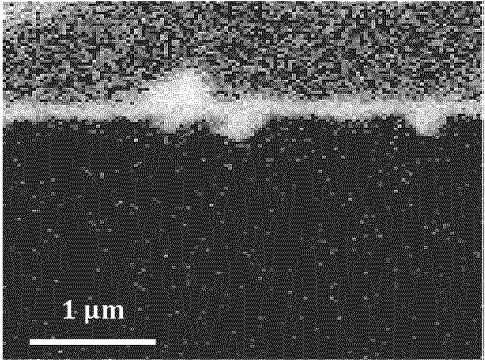
Material : 32%Ni-23%Cr		
	Test Temperature(°C)	
	360	340
Cr		
Ni		
Fe		
O		

Figure 21G
44 / 66

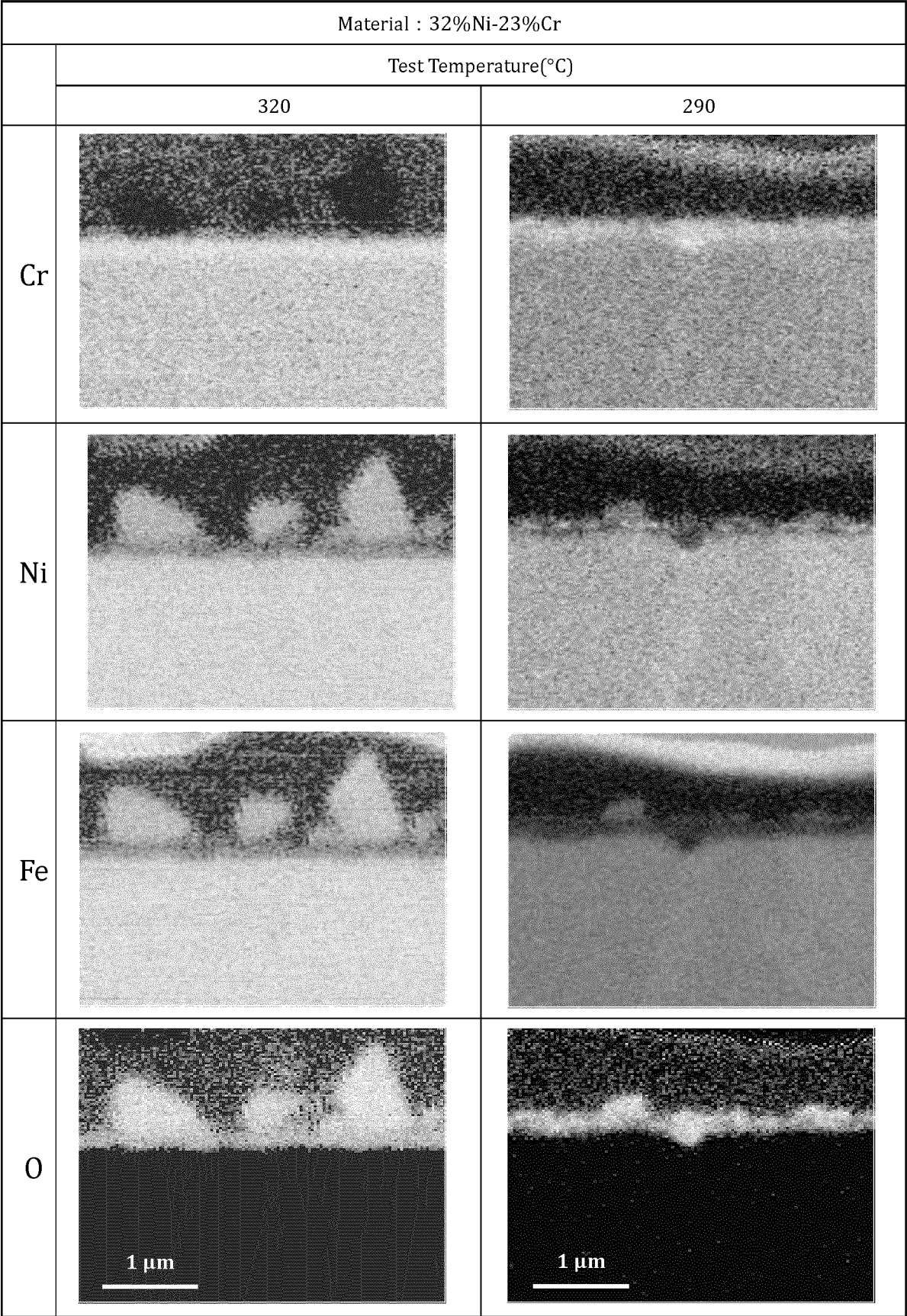


Figure 21H

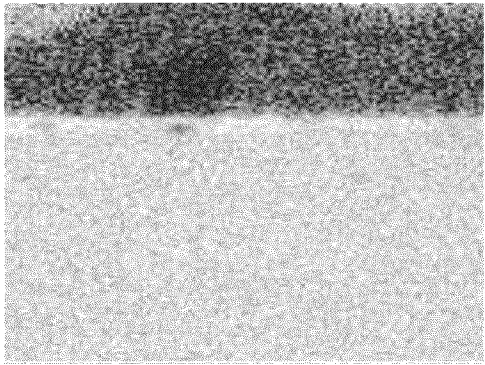
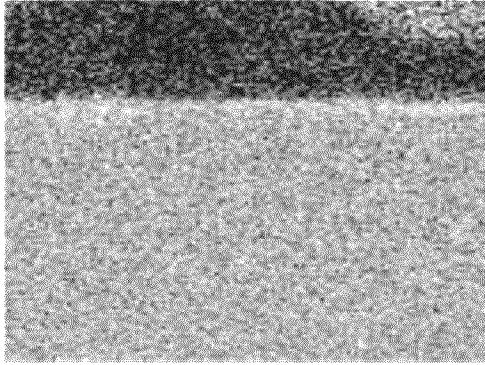
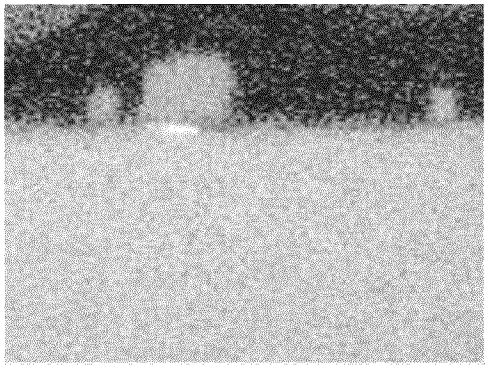
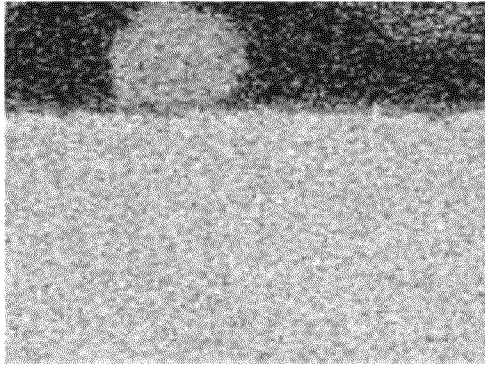
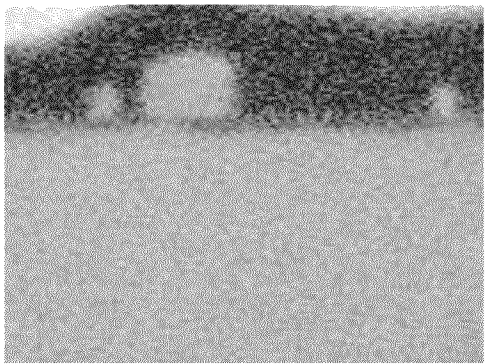
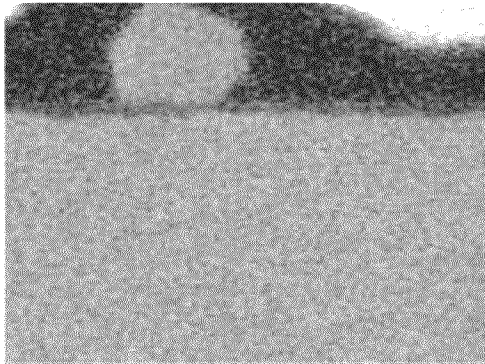
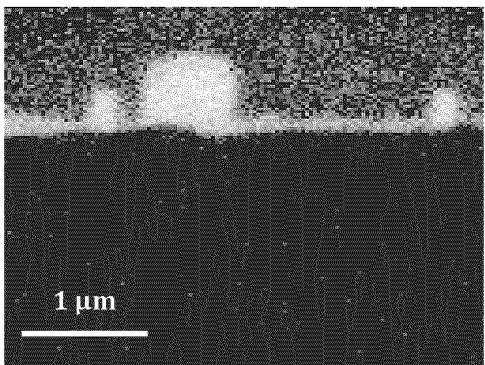
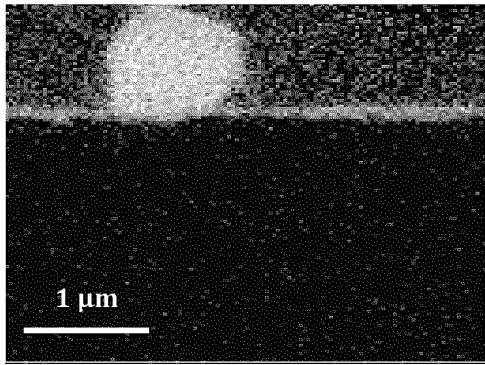
Material : 32%Ni-25%Cr		
	Test Temperature(°C)	
	360	340
Cr		
Ni		
Fe		
O		

Figure 211
46 / 66

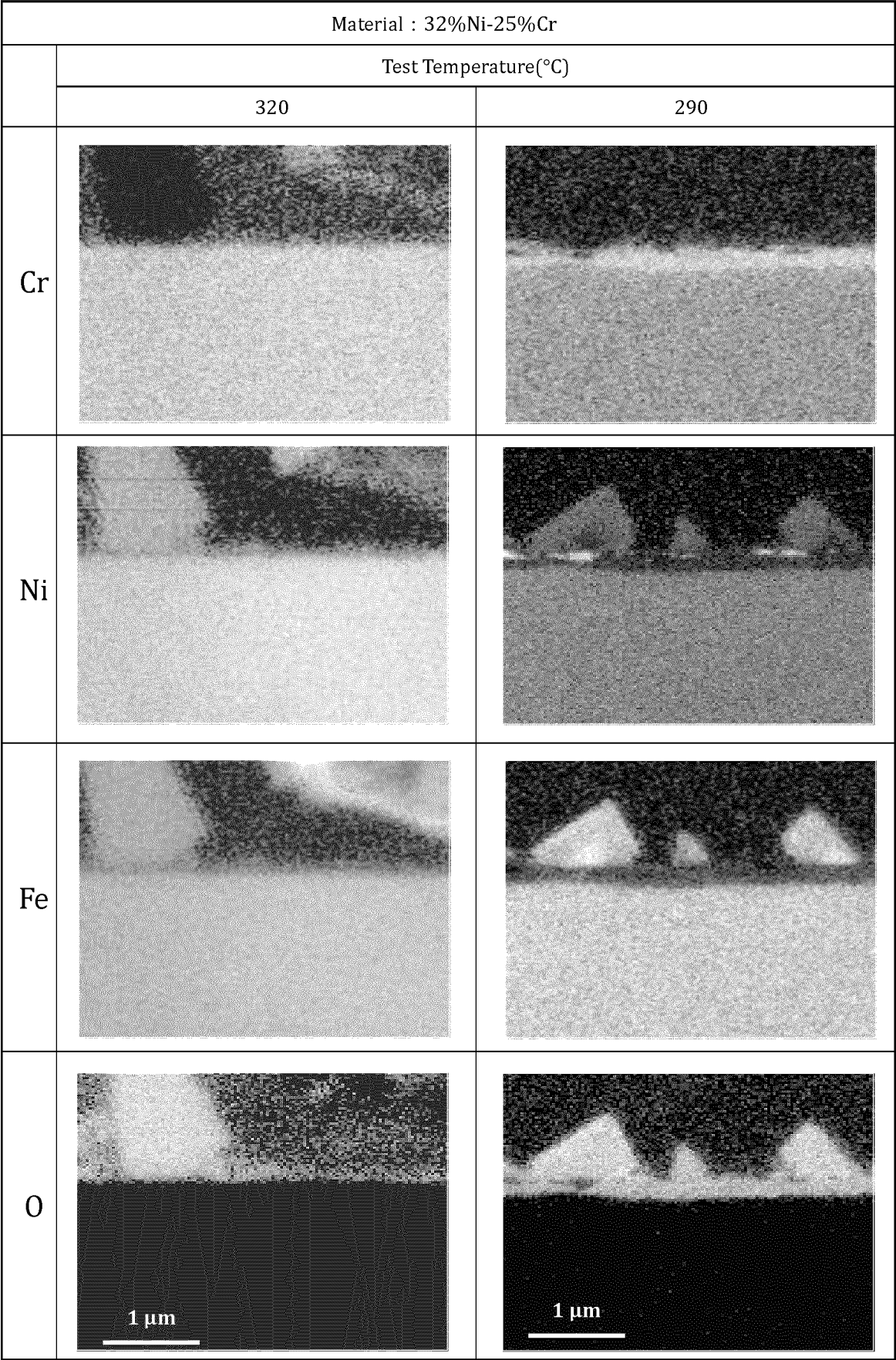
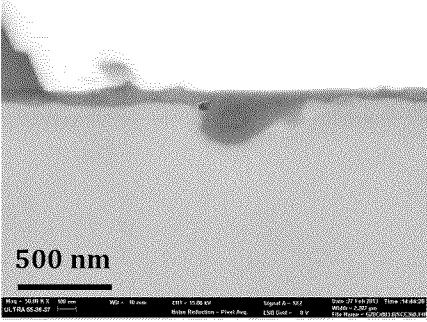
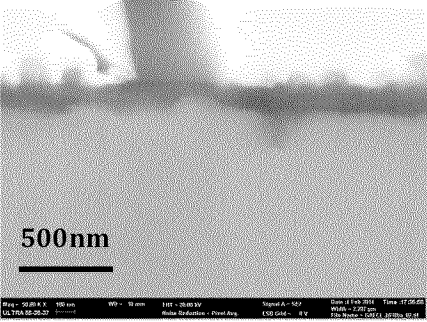
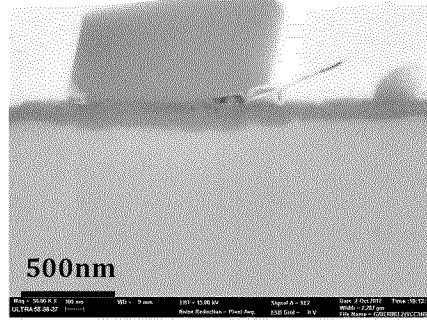
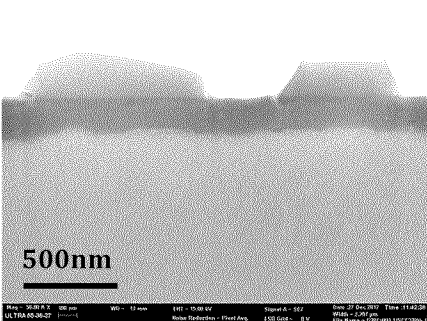
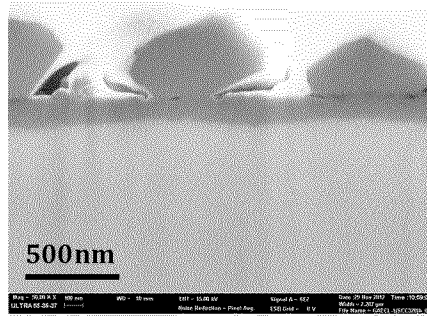
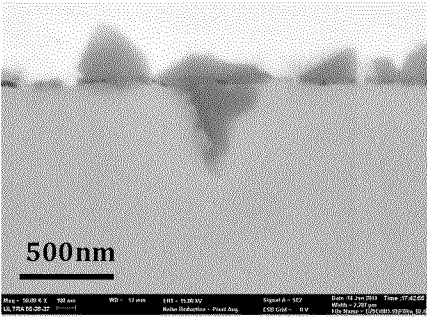
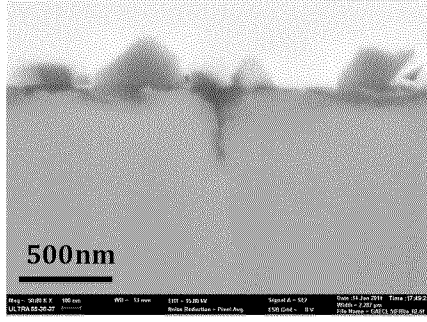


Figure 21J
47 / 66

Test Temperature (°C)	Heat treatment : 1075 °C x 1hr_W.C.	Heat treatment : 1065 °C x 10min_A.C.
	32%Ni-20%Cr	34%Ni-22%Cr
360	(5,252.6hr) 	(4,988.7hr) 
	(5,824.7hr) 	—
	(7,242.2hr) 	(5,637.5hr) 
	(4,988.8hr) 	(4,973.7hr) 

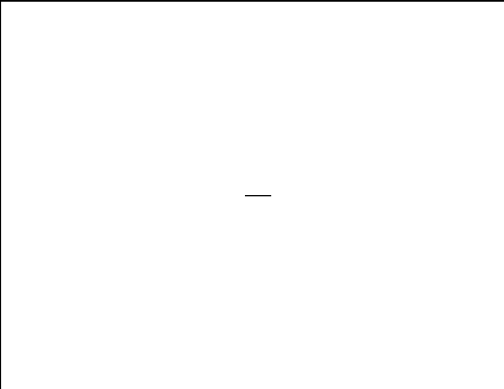
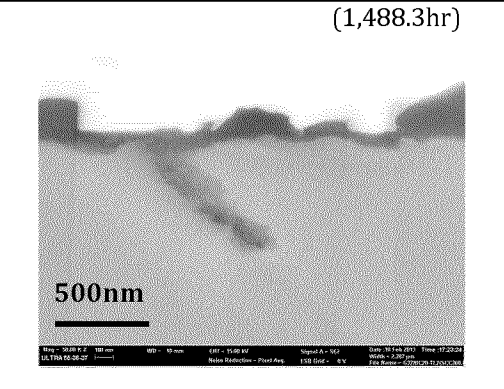
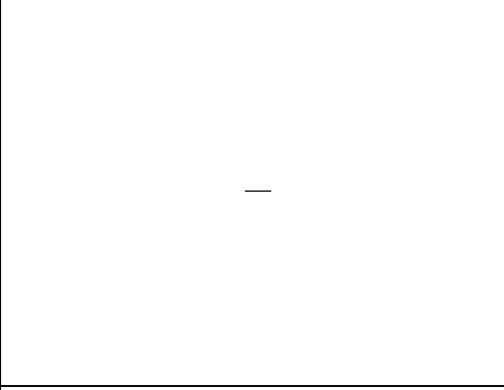
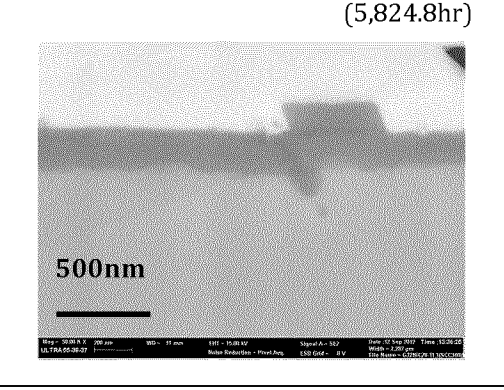
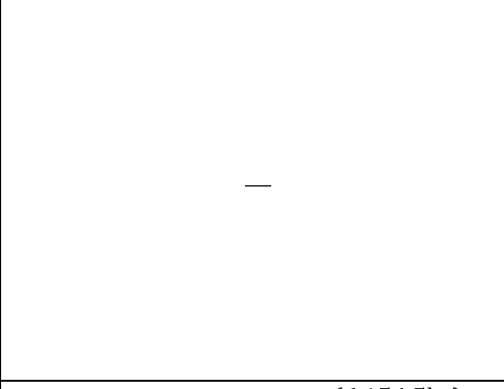
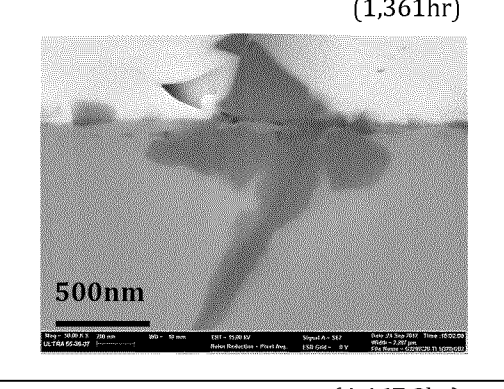
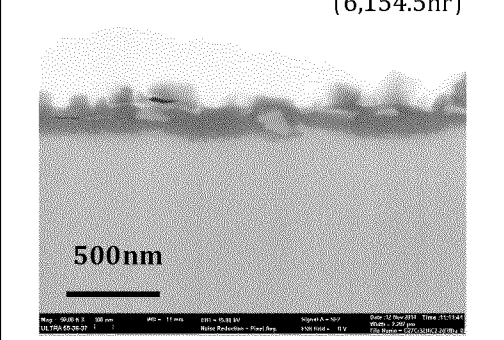
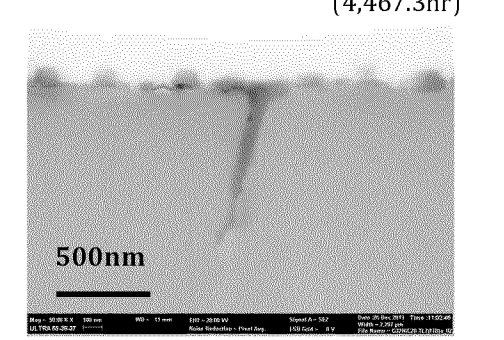
() : Test Duration

Figure 22A
48 / 66

Test Temperature (°C)	Heat treatment : 1075 °C x 1hr_W.C.	
	32%Ni-23%Cr	32%Ni-25%Cr
360	(5,252.6hr)	(5,252.6hr)
340	(5,824.7hr)	(5,252.6hr)
320	(5,637.5hr)	(6,311.8hr)
290	(4,973.7hr)	(4,973.7hr)

(): Test Duration

Figure 22B
49 / 66

Test Temperature (°C)	Heat treatment : 1075 °C x 1hr_W.C.	
	32%Ni-27%Cr	32%Ni-16%Cr
360		(1,488.3hr) 
340		(5,824.8hr) 
320		(1,361hr) 
290	(6,154.5hr) 	(4,467.3hr) 

() : Test Duration

Figure 22C

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr800-7 (12.5mm ²)	20%CW Alloy800 (TL) 25% Cr 1075°C x 1 hr W.C.	460°C Air	40	6,691.4

Depth of fatigue Pre-crack (mm)										Average depth(mm)
1.99	1.95	1.93	1.84	1.92	1.84	1.84	1.72	1.74	1.75	1.85

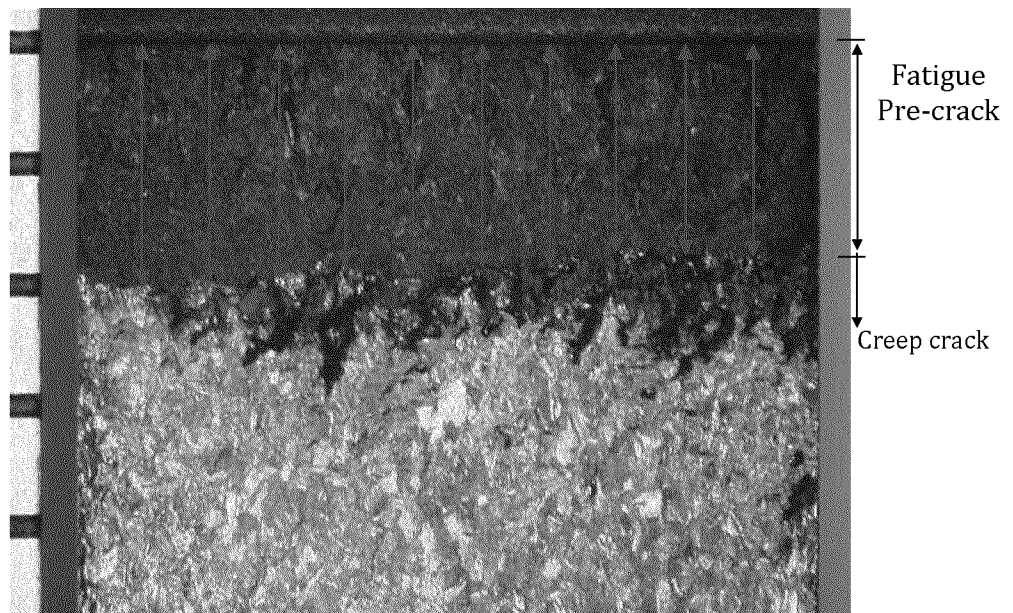
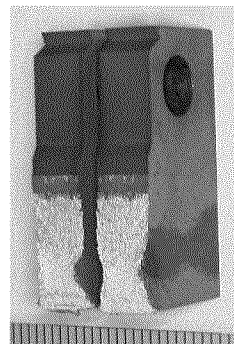
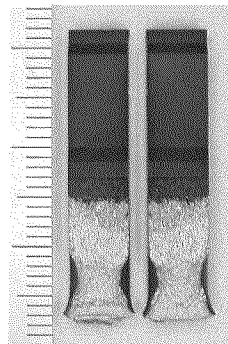


Figure 23A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr800-6 (12.5mm ²)	20%CW Alloy800 (TL) 25% Cr 1075°C x 1 hr W.C.	460°C Air	40	6,691.4

Depth of Creep crack (mm)										Average (mm)
—	0.39	0.49	0.69	0.48	0.56	0.46	0.46	0.53	0.45	0.45

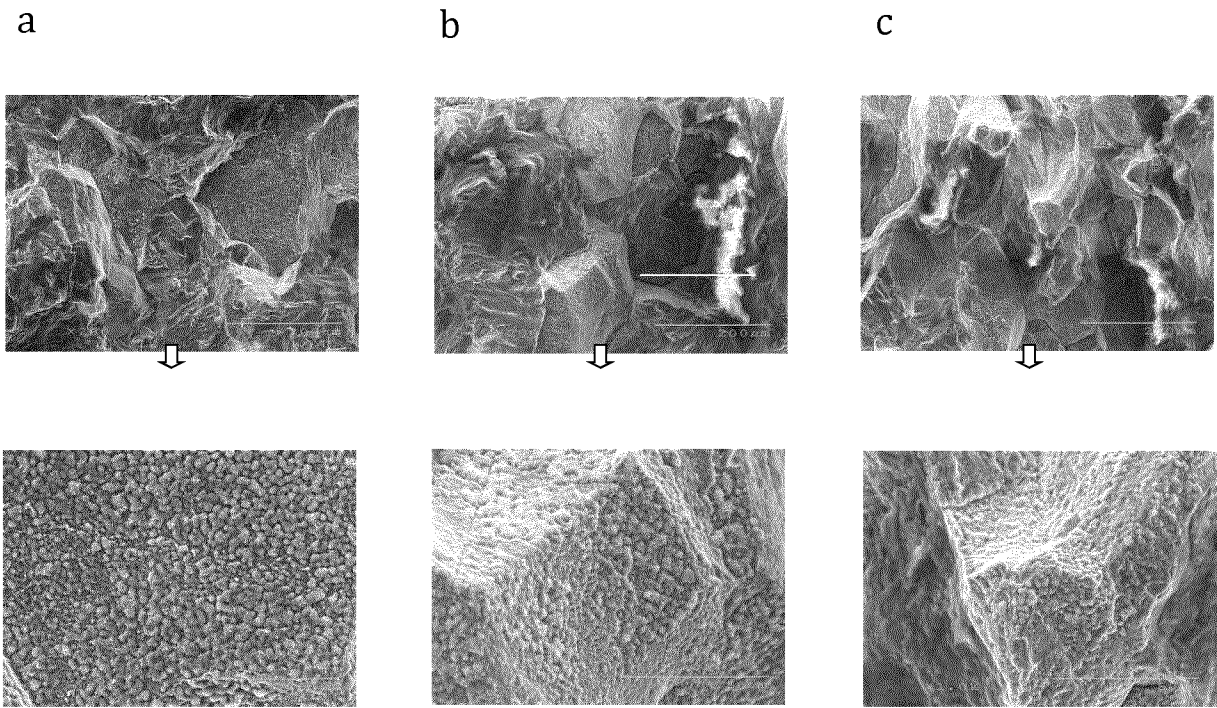
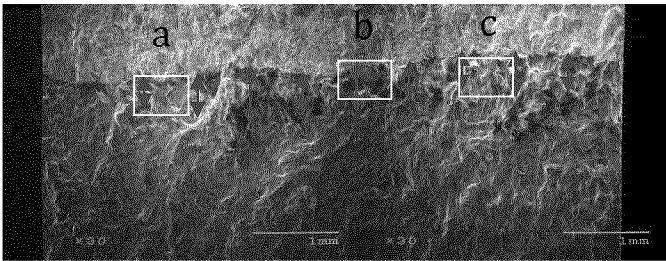


Figure 23B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr800-6 (12.5mm ⁴)	20%CW Alloy800 (TL) 25% Cr 1075°C x 1 hr W.C.	440°C Air	40	6,691.1

Depth of fatigue Pre-crack (mm)										Average depth(mm)
2.17	2.27	2.40	2.37	2.52	2.69	2.76	2.85	2.94	2.98	2.60

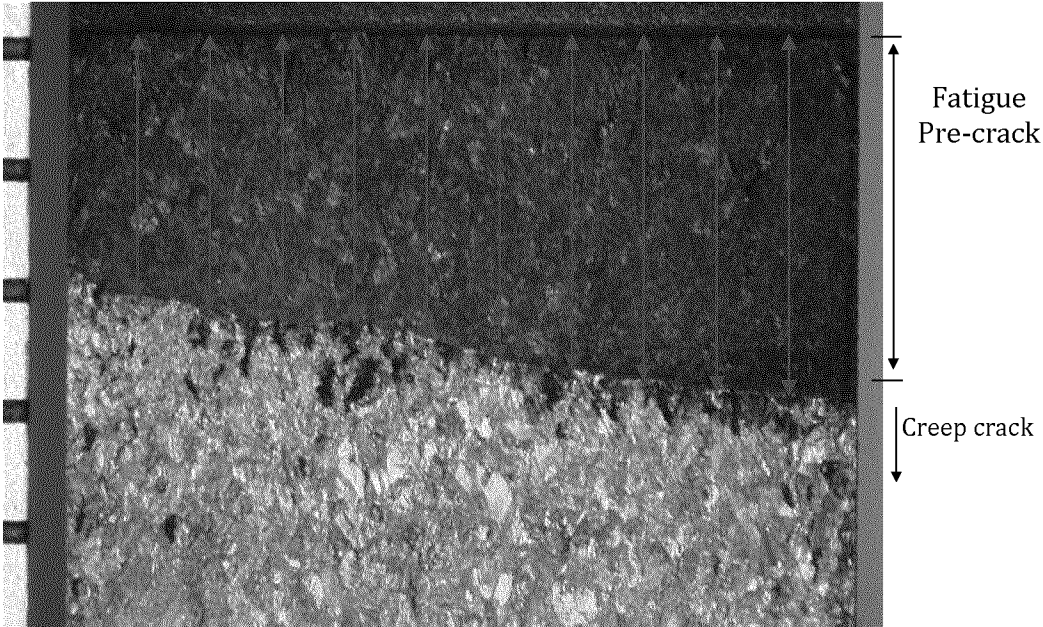
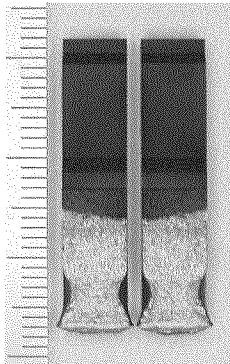
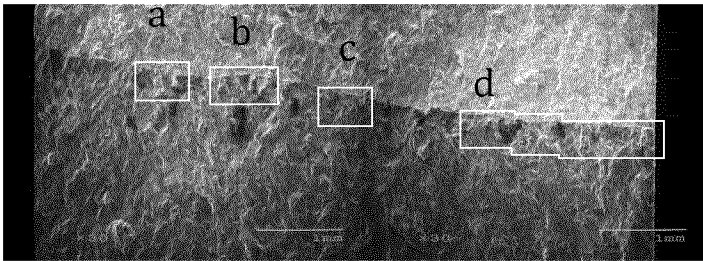


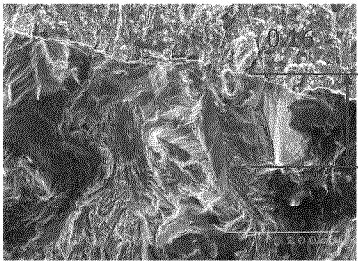
Figure 24A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr800-6 (12.5mm ³)	20%CW Alloy800 (TL) 25% Cr 1075°C x 1 hr W.C.	440°C Air	40	6,691.1

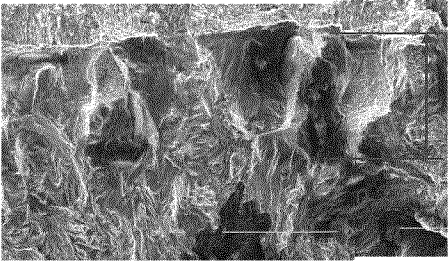
Depth of Creep crack (mm)										Average (mm)
0.16	0.22	0.12	0.34	0.38	—	—	—	—	—	—



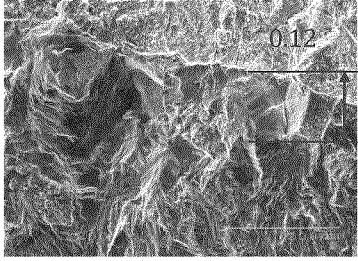
a



b



c



d

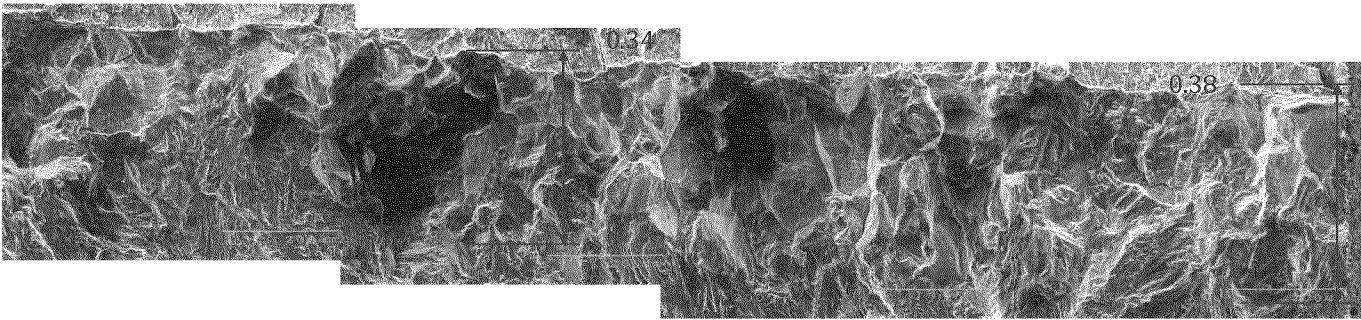


Figure 24B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr800-5 (12.5mm ³)	20%CW Alloy800 (TL) 25% Cr 1075°C x 1 hr W.C.	425°C Air	40	9,590

Depth of fatigue Pre-crack (mm)										Average depth(mm)
1.99	2.12	2.15	2.21	2.25	2.40	2.49	2.58	2.66	2.66	2.35

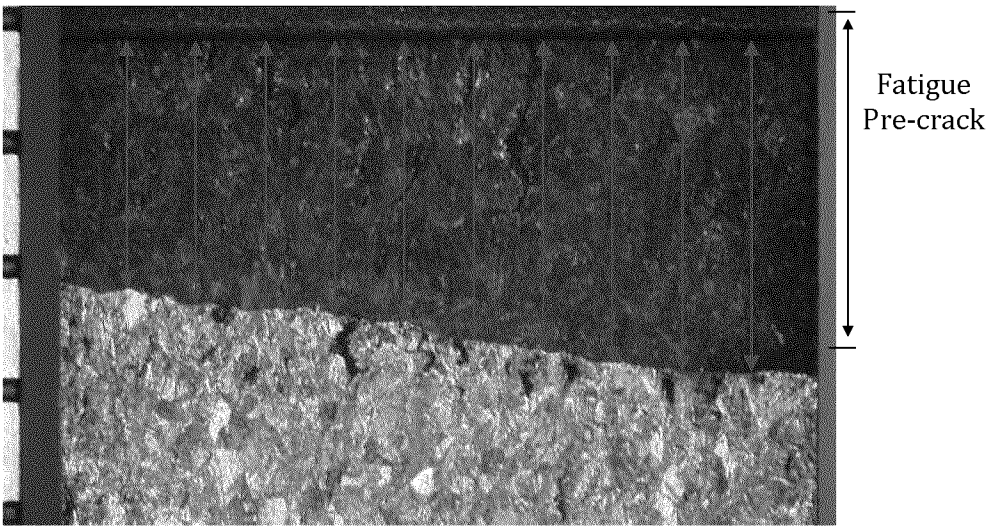
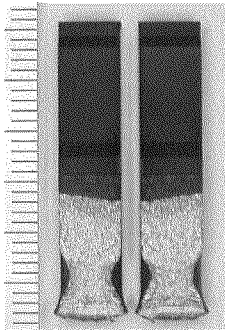


Figure 25A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
G25Cr800-5 (12.5mm ¹)	20%CW Alloy800 (TL) 25% Cr 1075°C x 1 hr W.C.	425°C Air	40	9,590

Depth of Creep crack (mm)	Average (mm)
no crack	—

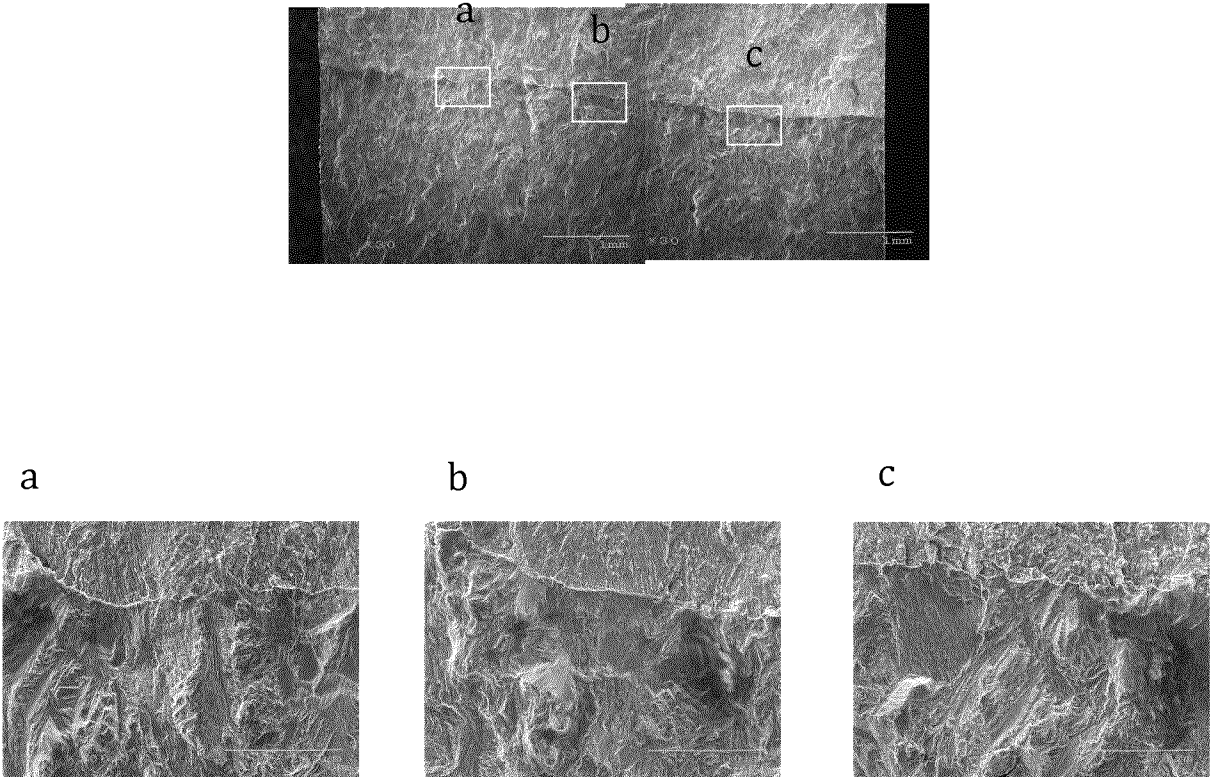


Figure 25B

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
GAECL-7 (11mm ^t)	19%CW Alloy800 (TL) 22% Cr 1065°C x 1 0min A.C.	445°C Air	40	4,030

Depth of fatigue Pre-crack (mm)										Average depth(mm)
3.15	3.25	3.32	—	—	—	—	—	—	—	3.24

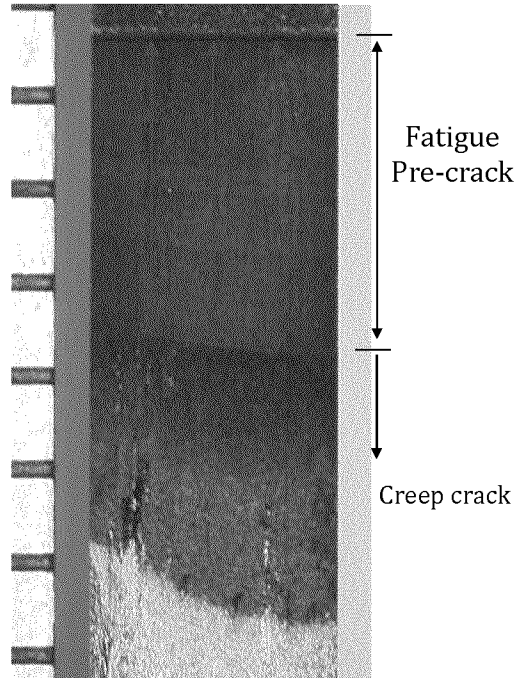
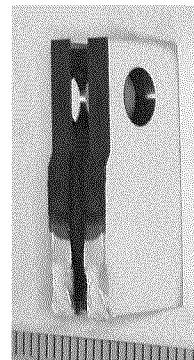
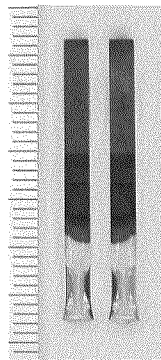


Figure 26A

TP.No & thickness	Material & heat treatment	Test Environment	K (MPa m ^{1/2})	Test Duration (hr)
GAECL-7 (11mm ^t)	19%CW Alloy800 (TL) 22% Cr 1065°C x 1 0min A.C.	445°C Air	40	4,030

Depth of Creep crack (mm)										Average (mm)
2.65	2.96	3.07	—	—	—	—	—	—	—	2.89

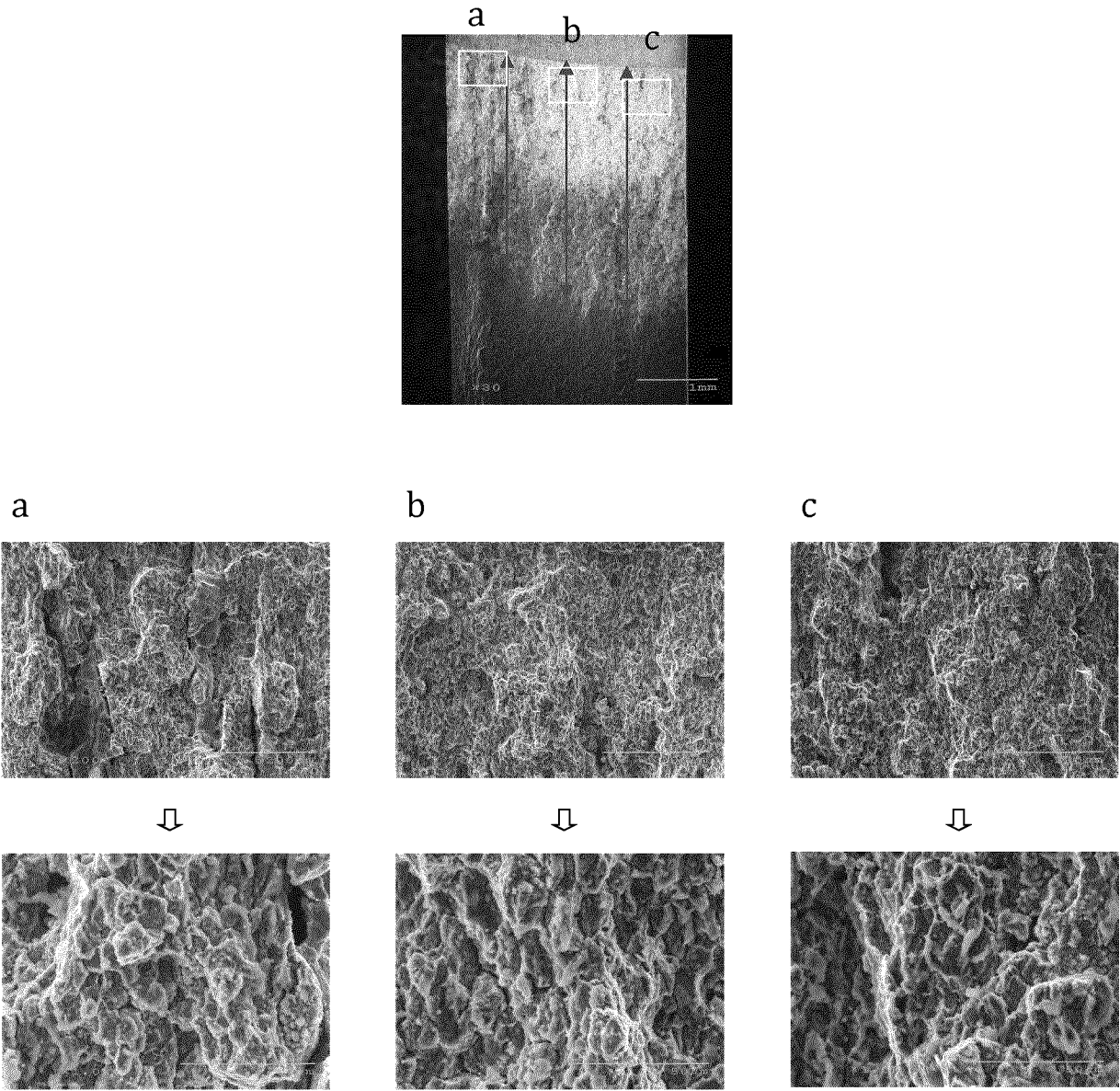


Figure 26B

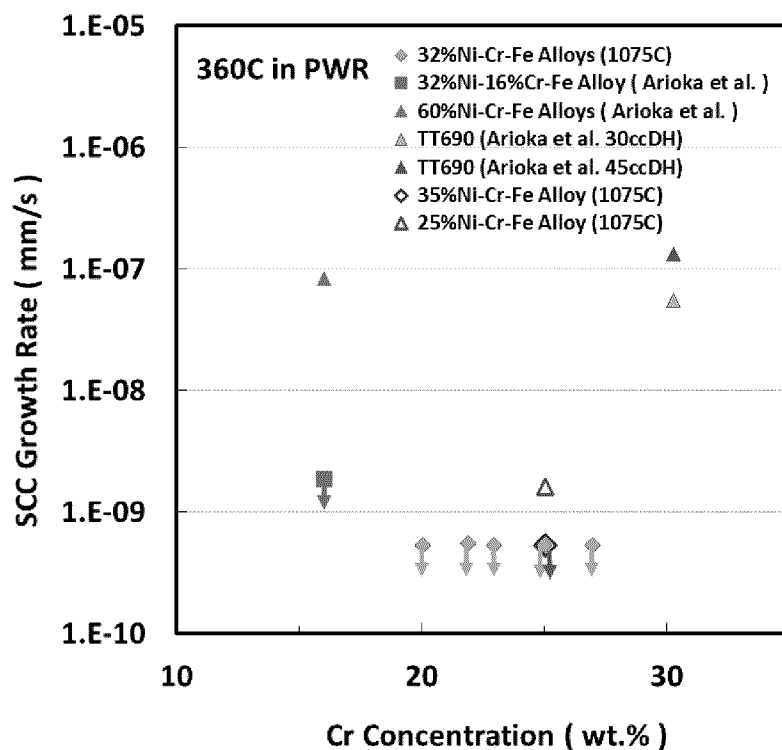


Figure 27A

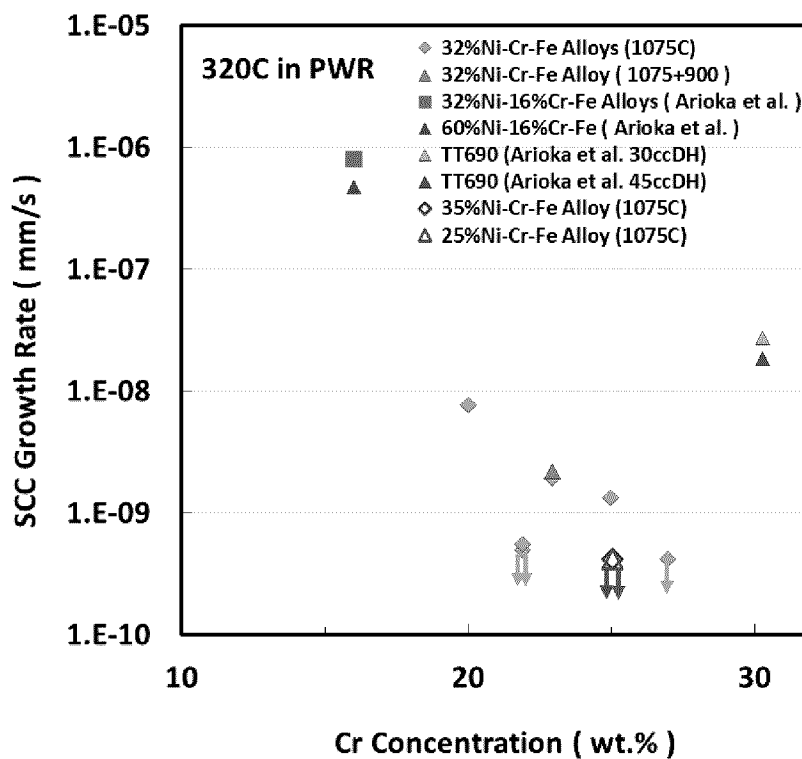


Figure 27B

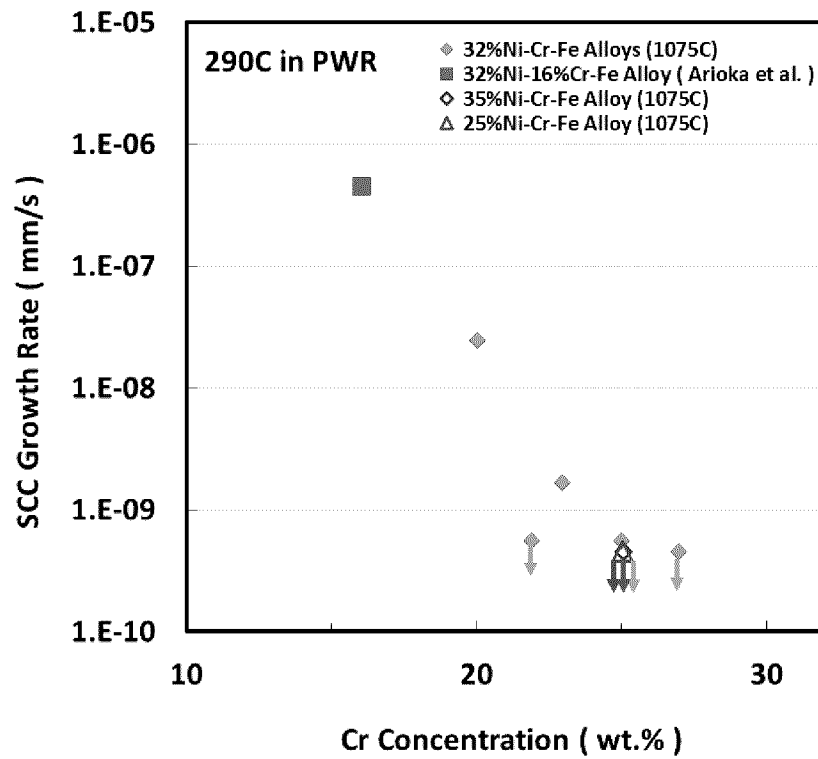


Figure 27C

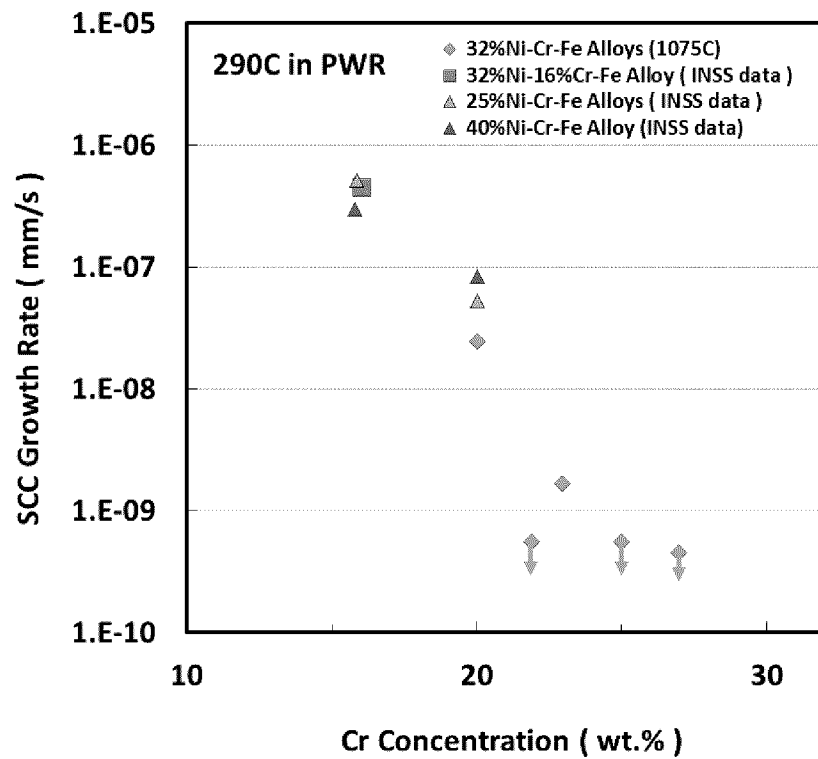


Figure 27D

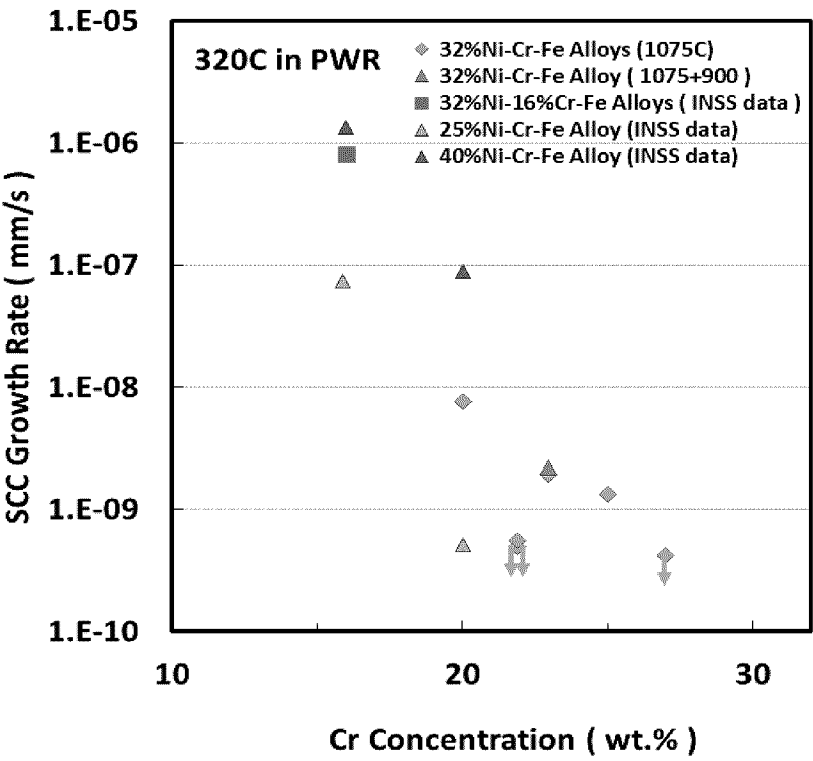


Figure 27E

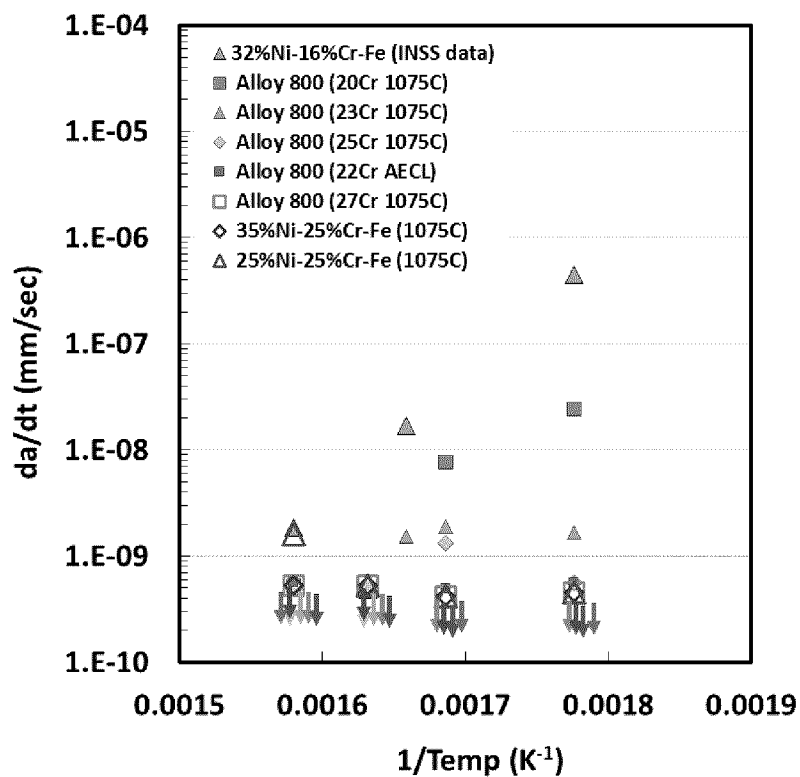


Figure 28A

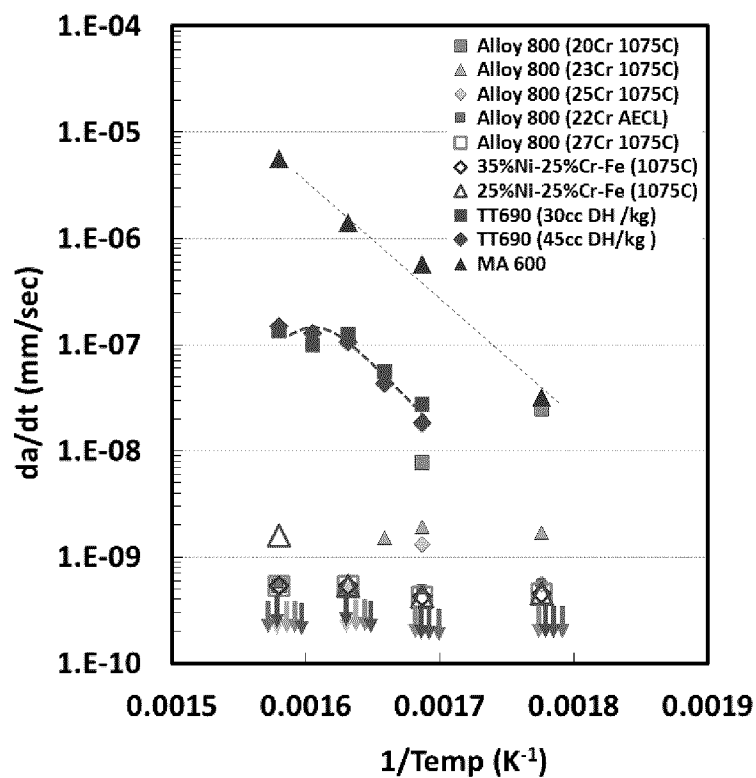
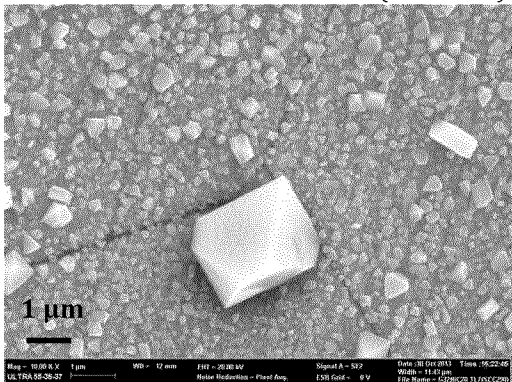
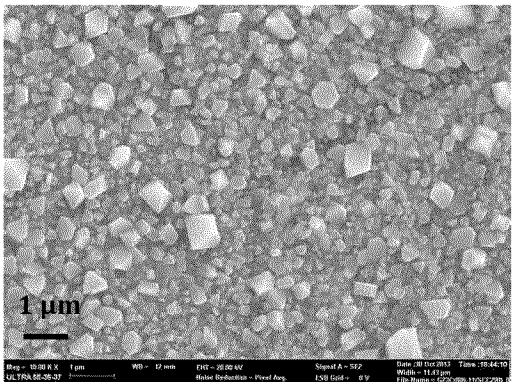
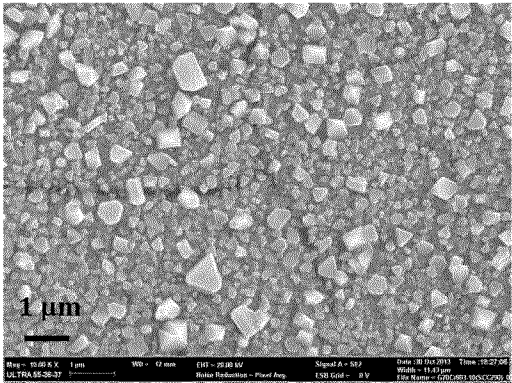
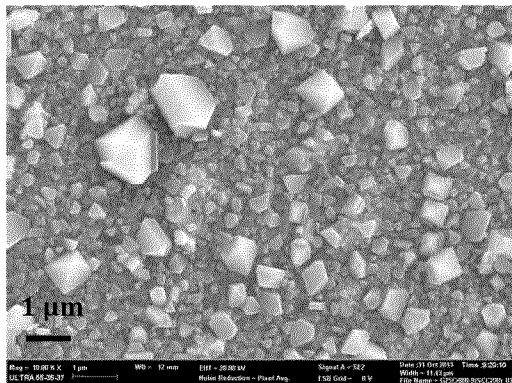
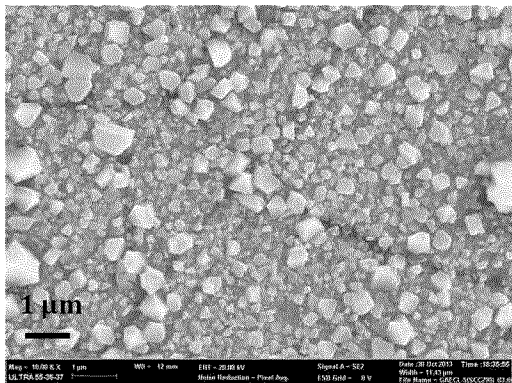
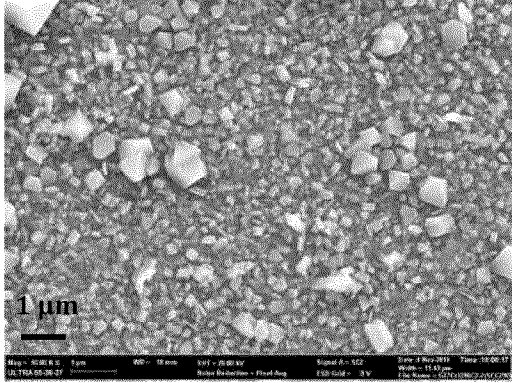
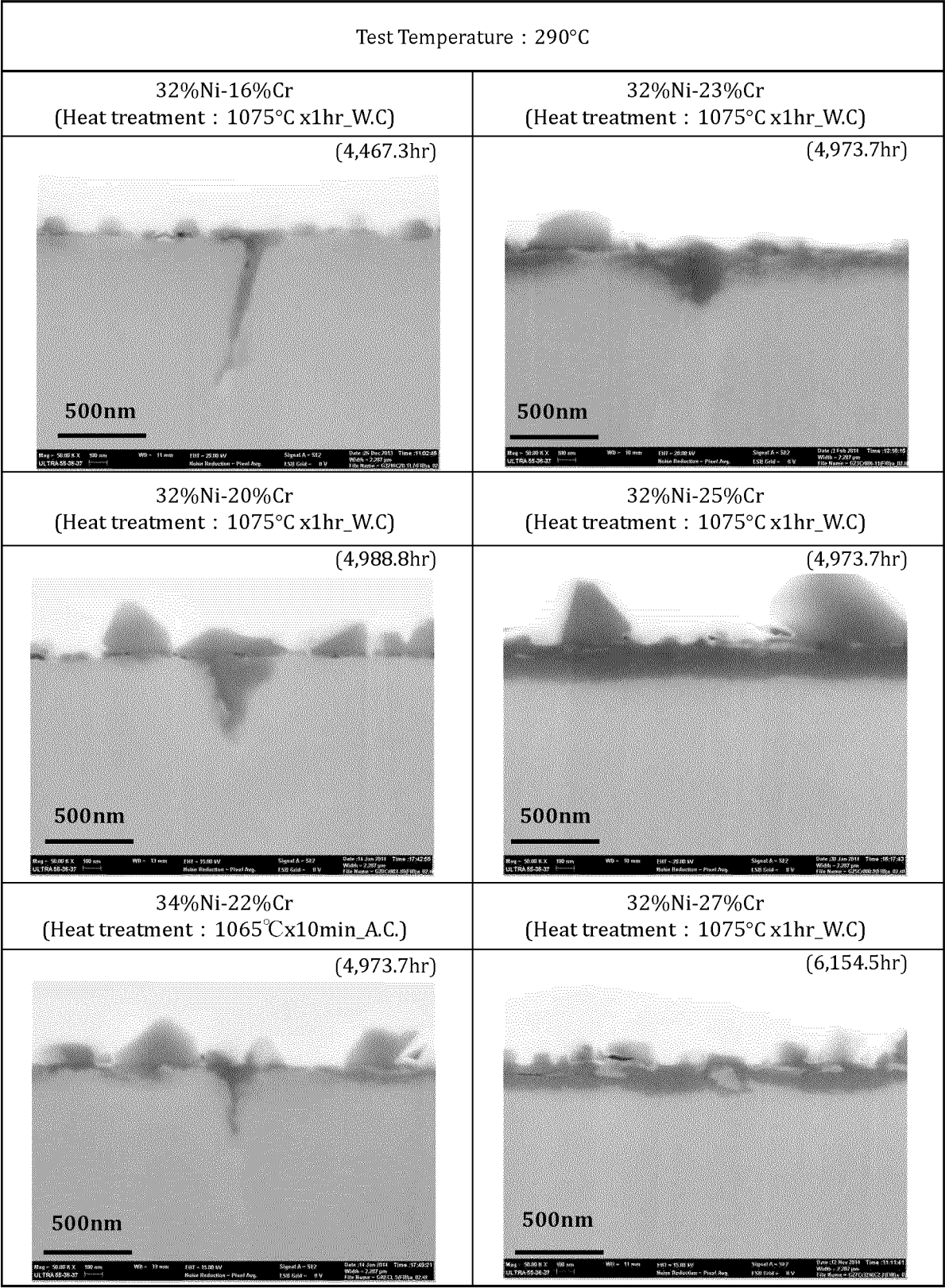


Figure 28B

Test Temperature : 290°C	
32%Ni-16%Cr (Heat treatment : 1075°C x1hr_W.C)	32%Ni-23%Cr (Heat treatment : 1075°C x1hr_W.C)
(4,467.3hr) 	(4,973.7hr) 
32%Ni-20%Cr (Heat treatment : 1075°C x1hr_W.C)	32%Ni-25%Cr (Heat treatment : 1075°C x1hr_W.C)
(4,988.8hr) 	(4,973.7hr) 
34%Ni-22%Cr (Heat treatment : 1065°Cx10min_A.C.)	32%Ni-27%Cr (Heat treatment : 1075°C x1hr_W.C)
(4,973.7hr) 	(6,154.5hr) 

(): Test Duration

Figure 29A



(): Test Duration

Figure 29B

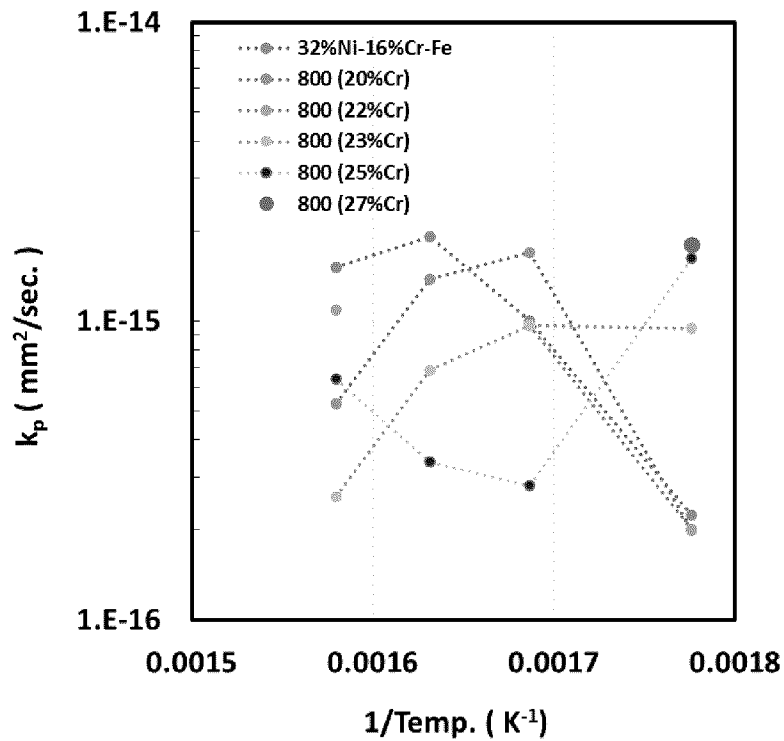


Figure 30A

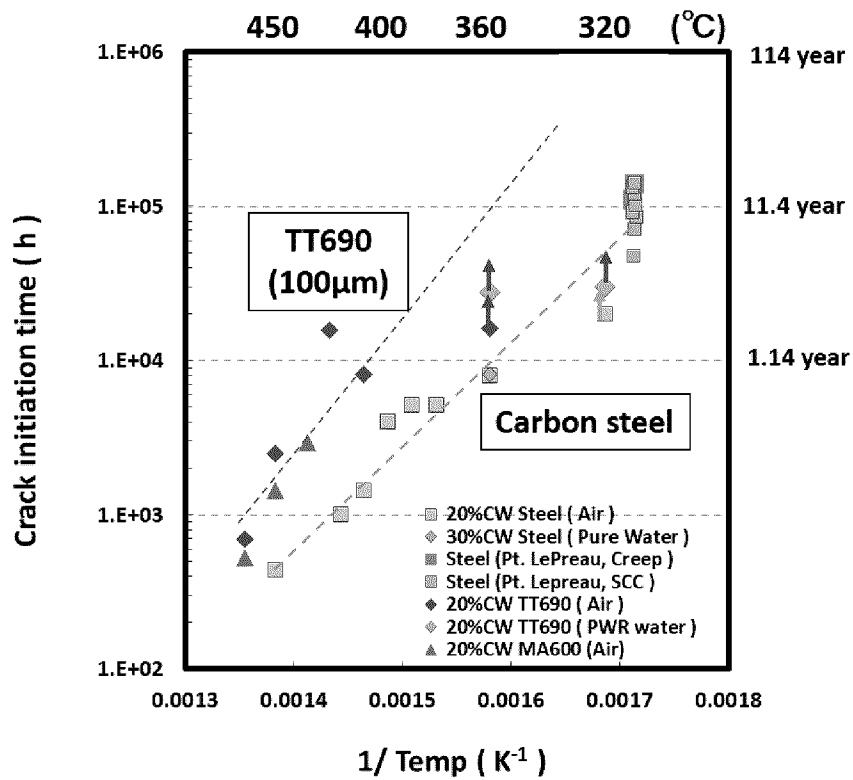


Figure 30B

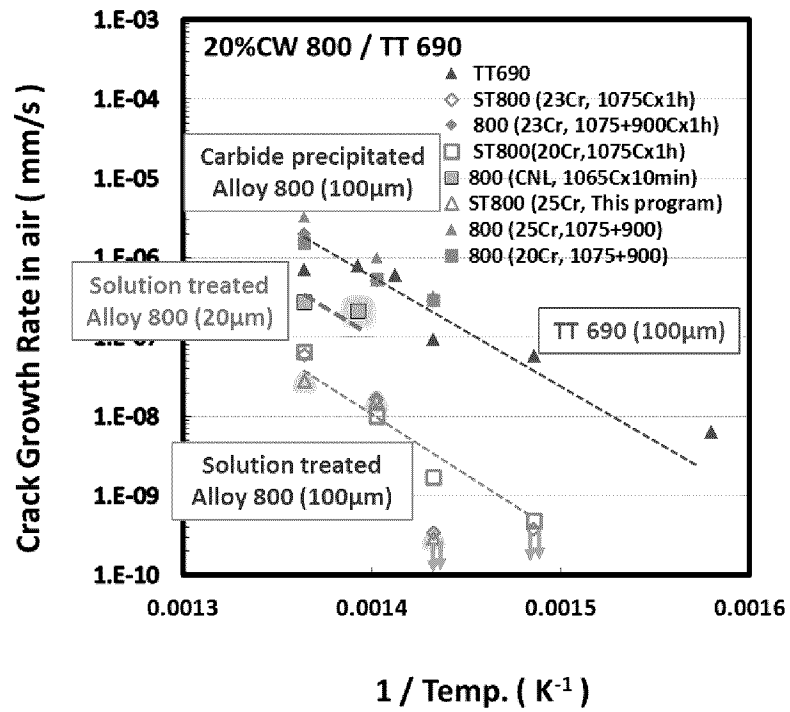


Figure 30C

$$M_t/M_0 = 1 - (8/\pi^2) \sum_{n=0}^{\infty} \left(\frac{1}{(2n+1)^2} \right) e^{-D(2n+1)^2 \pi^2 t / l^2}$$

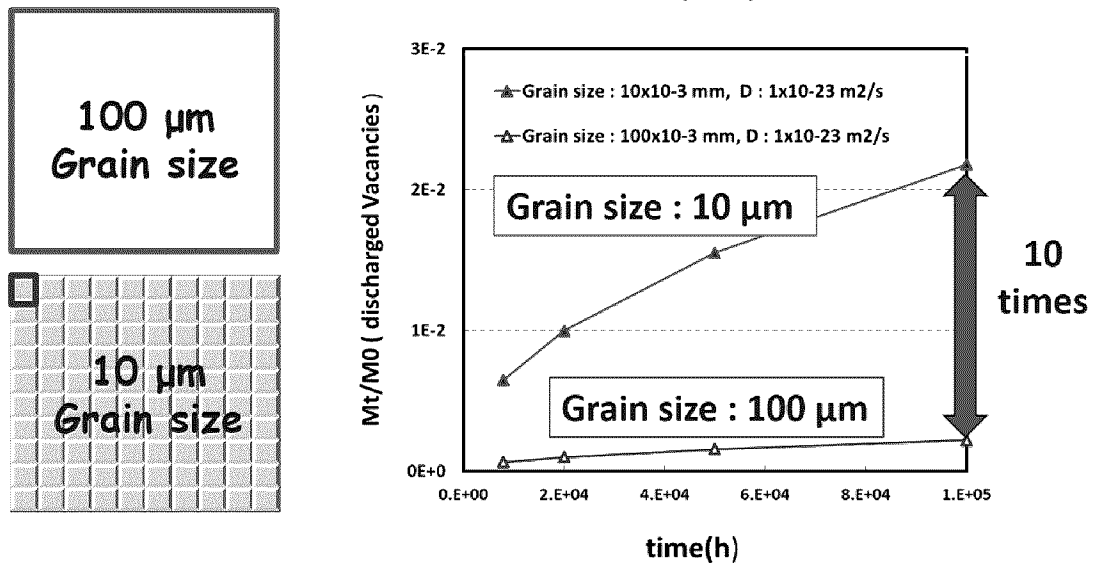


Figure 30D

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050104

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C22C 30/00** (2006.01), **C21D 1/26** (2006.01), *F22B 37/10* (2006.01), *G21C 1/08* (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 30/00 (2006.01), **C21D 1/26** (2006.01), *F22B 37/10* (2006.01), *G21C 1/08* (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Database: Questel-Orbit

Keywords: Ni, nickel, Cr, chromium, Fe, iron, Ti, titanium, Al, aluminum, nuclear, reactor, steam, tub+, pip+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP2009079240A, YONEZAWA, T. et al., 16 April 2009 (16-04-2009) ** machine translation, abstract, claims **	1-19
X	JP2003073784A, IZUMIDA, H., et al., 12 March 2003 (12-03-2003) ** machine translation, abstract, [0001], [0015] **	1-19
X	JP2005002451A, UEDA, S., 06 January 2005 (06-01-2005) ** machine translation, abstract, [0028] **	1-11, 13-19
X	WO2012121389A1, MAEGUCHI, T., et al., 13 September 2012 (13-09-2012) ** machine translation, abstract **	1-12
A	CN102181752A, DAFENG, H., et al., 14 September 2011 (14-09-2011) ** machine translation, entire document **	1-19

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
--------------------------------------	--	--------------------------	--

Date of the actual completion of the international search
11 April 2016 (11-04-2016)Date of mailing of the international search report
26 April 2016 (26-04-2016)Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 819-953-2476

Authorized officer

Anne-Marie Garand-Sheridan (819) 639-8459

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050104**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claim Nos.: 20
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 20 includes a broad statement that includes all possible means without qualification for solving the problem facing the inventor. Further, reference is made to the description and the drawings for completeness and clarity, rather than claiming the subject matter in explicit terms.

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2016/050104

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
JP2009079240A	16 April 2009 (16-04-2009)	None	
JP2003073784A	12 March 2003 (12-03-2003)	JP2003073784A JP3515770B2	12 March 2003 (12-03-2003) 05 April 2004 (05-04-2004)
JP2005002451A	06 January 2005 (06-01-2005)	None	
WO2012121389A1	13 September 2012 (13-09-2012)	WO2012121389A1 JP5675957B2	13 September 2012 (13-09-2012) 25 February 2015 (25-02-2015)
CN102181752A	14 September 2011 (14-09-2011)	None	