The Effect of Sensitizing Temperatures for Stress Corrosion Cracking of Austenitic Stainless Steel in Magnesium Chloride Solution

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Abstract — *The change of the mechanism for Stress Corrosion Cracking (SCC) on 304 austenitic stainless steel was investigated in 42 wt% magnesium chloride solution at 106 ^{0}C by using a constant load method. The solution-annealed specimens were applied under constant load of 30.5 Kg/mm^2 and 40 Kg/mm^2. The non-solution annealed specimens were applied under constant load of 20 Kg/mm^2 and 25 Kg/mm^2. All experiments were carried out under an open circuit condition. The most of fracture mode on non-annealed type 304 at various sensitizing temperature (600^{0}C, 700^{0}C, 800^{0}C) is intergranular. All fracture mode in annealed type 304 at various sensitizing temperature is trangranular. The deformation can be easy to move by growing grains in annealed type 304 so that it can be predicted by decreasing Vickers hardness value. In non-annealed type 304, the deformation can be sustained because of the small size of grains. The role of α martensite mechanism in non-annealed type 304 significantly contribute to the forming of fracture in $MgCl_2$ solution at 106^{0}C especially in grain boundaries. In annealed type 304, mechanism of fracture can be related to deformation through slip plane in grains.*

Keywords — *Stress Corrosion Cracking, sensitizing temperature, Type 304 stainless steel, and fracture.*

I. Introduction

Generally, austenitic stainless steels are susceptible for stress corrosion cracking (SCC). The SCC of them (type 316 and type 304) was extensively investigated as functions of applied stress (σ), sensitizing temperature, sensitizing time, applied potential and environmental factors (inhibitor, sensitizing time, pH, anion concentration, anion species and test temperature) by using a constant load method [1]. The change in the mechanism for SCC on AISI 304 austenitic stainless steel was investigated in 42 wt% boiling saturated magnesium chloride solution by using a constant load method. Three parameters (time to failure; t_f steady-state elongation rate ; i_{ss} and transition time at which a linear increase in elongation to deviate; t_{ss}) obtained from the corrosion elongation curve showed three regions ; stress – dominated, stress corrosion cracking dominated and corrosion – dominated regions [2]. Type 304 stainless steel is prone to microstructural changes when exposed to sensitization temperatures due to heat treatment. Precipitation of chromium carbide takes place along the grain boundary regions in the temperature range of 480^{0}C to 815^{0}C. These results in chromium depletion near the grain boundary, and the resultant grain –boundary region is susceptible to intergranular corrosion (IGC) [3]. The extent of which depends upon the degree of sensitization. The Cr depletion zone, while the Cr carbide would serve as an barrier of dislocation movement [4]. Nishimura demonstrated that the most severe SCC susceptibility took place at a sensitizing temperature of ~931 K (660^{0}C) in hydrochloric acid solution [5]. Deformation of metastable austenite phase involves the formation of strain –induced $\varepsilon \rightarrow$ α'-martensite [6]. Austenitic stainless steel can undergo phase transformation due to applied stress or hydrogen charging.

The objectives of this present work are: (1) to investigate the effect of sensitizing temperature on the susceptibility of type 304 stainless steels to stress corrosion cracking, (2) to evaluate t_f and i_{ss} for type AISI stainless steels in 42 wt% magnesium chloride solutions at temperature of 380K, and (3) to determine the cracking mechanism for austenitic stainless steels in 42 wt% boiling magnesium chloride solutions at temperature of 380K.

II. Methodology

The chemical compositions of type 304 stainless steel) are shown in Table 1. As shown in Fig. 1, the geometry for SCC experiments is as follows: the gauge length is 25.6 mm, the width 5 mm and the thickness 1 mm [7]. The specimens were solution-annealed at 1373 K (1100^{0}C) for 1 hour under an argon atmosphere and quench in the water. The other specimens were conducted solution annealing process. Both of specimens (with or without solutions annealing process) were annealed with various sensitizing temperatures (600^0C, 700^0C, 800^0C). Prior to main experiments, the specimens (with and without solutions annealing process) were polished to 1000 grit emery paper, degreased with acetone in a ultrasonic cleaner apparatus and washed with distilled water. After that, the specimens were set into SCC cell.

TABLE I
CHEMICAL COMPOSITIONS OF THE TYPE 304 AUSTENITIC STAINLESS STEEL

C	Si	Mn	P	S	Ni	Cr	Mo
0.042	0.713	1.13	0.0297	0.008	7,92	18.309	--

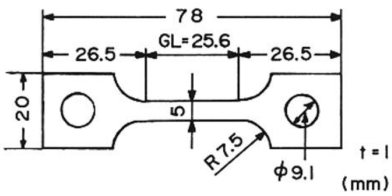

Fig 1: Geometry of SCC specimen (dimensions in mm)[1].

SCC test were conducted in 42wt % magnesium chloride solution at 379K (106^0C). The solution - annealed specimens were carried out under constant load of 30.5 Kg/mm^2 and 40 kg/mm^2. The non-solution annealed specimens were applied under constant load of 20 kg/mm^2 and 25 kg/mm^2. All experiments were done under an open circuit condition.

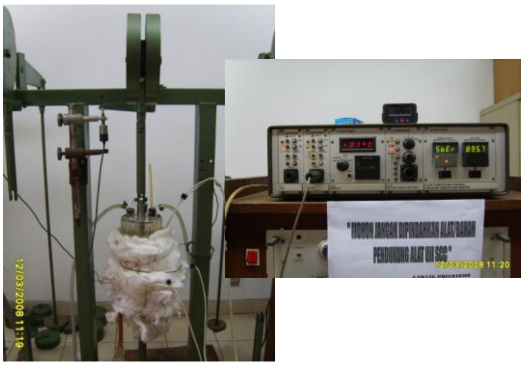

Fig 2: a lever-type constant load apparatus

As Shown in Fig 2. A lever-type constant load apparatus (lever ratio 1:10) was applied with a water cooling system on the top of a testing cell to avoid evaporation of the solution during the experiments. The specimen was insulated from rod and grip by alumina fibres. Elongation of the specimens under a constant load was measured by an inductive linear transducer with an accuracy of ±0.01 mm. The other supporting tests are Vickers hardness and oxalic acid etch test for classification of etch structures of austenitic stainless steel according to ASTM A262-02a.

III. RESULTS AND DISCUSSION

A. Dependence of sensitizing temperatures and hardness property

Table 2 shows the Vickers hardness of type 304 at various sensitizing temperatures. Generally, Vickers hardness values of the type 304 without solution annealing process are higher than without solution annealing. Fig 3 shows the behaviour of Vickers hardness at various sensitizing temperatures. The type 304 without sensitizing process that has the highest hardness values of 232.27 Hv. This material undergoes the decreasing of hardness value when heated from 600^0C to 800^0C. The same behaviour is happen on the type 304 with sensitizing process.

TABLE 2
VICKERS HARDNESS OF TYPE 304 AT VARIOUS SENSITIZING TEMPERATURES

Sensitizing temperature (celcius)	Vickers Hardness (Hv)	
	Solution annealing	Without Solution annealing
600	219.33	209.3
700	152.06	199.1
800	162.72	205.33

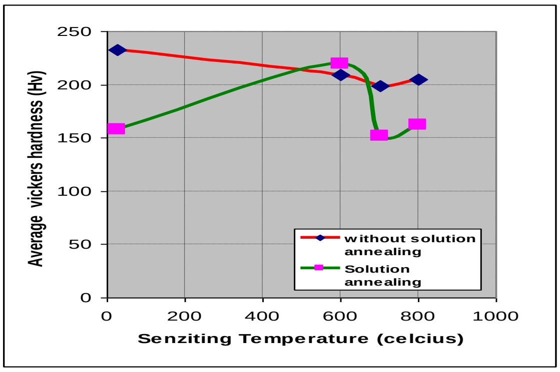

Fig 3: Curve of relationship between Vickers hardness and sensitizing temperatures

Both solution or without solution annealing process undergo a decadent hardness drastically at 700^0C after that increase at 800^0C. The lowest hardness value is 152.06 Hv on type 304 with solution annealing process. Susceptibility to intergranular attack associated with the precipitation of chromium carbides is readily detected in oxalic acid of electrolytic etches. Metallographic etching based on ASTM A-262 was conducted. Photomicrographs were obtained by using optical microscope. The microstructures that acquired were classified into three types: Ditch structure with one or more grains surrounded fully, step structure without ditches at grain boundaries and dual structure with several ditches at grain boundaries.

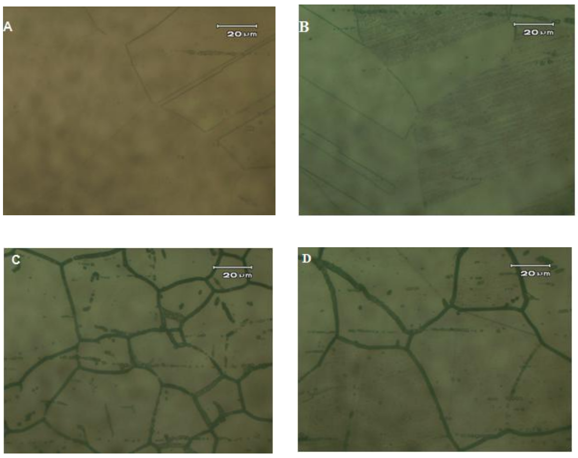

Fig 4: microstructure appearances for type 304 steel after solution annealing 1373K (a) no annealing for sensitizing condition (b) annealing for sensitization at 600^{0}C, (c) annealing for sensitization at 700^{0}C, (d) annealing for sensitization at 800^{0}C

Fig. 4 shows the kind of microstructures that depends on the influence of sensitizing temperature. Full ditch structures appear that surround grains at 700^{0}C and 800^{0}C. The grain growth process takes place from the temperature of 700^{0}C to 800^{0}C. The average of grain size increases from 60 micron to 80 micron. This phenomenon can be related by grain growth. The grain growth takes place after completing the recrystallization process. When associating the Vickers hardness of annealed 304, α'-martensite phase does not exist both grains and grain boundaries.

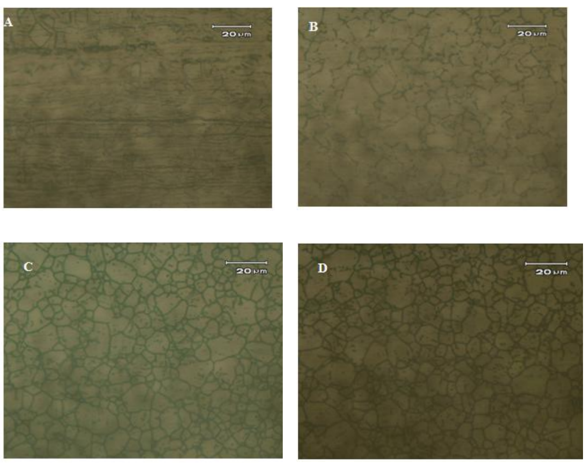

Fig 5: microstructure appearances for cold working type 304 steel (a) no annealing for sensitizing condition (b) no annealing for sensitization at 600^{0}C, (c) no annealing for sensitization at 700^{0}C, (d) no annealing for sensitization at 800^{0}C.

Fig. 5 shows the difference of microstructures among the kinds of annealing temperature. The transformation of γ (austenite) become the phase combination between γ - α'martensite that was appeared. The formation of strain-induced alpha'-martensite significantly affects the mechanical behaviour austenitic stainless steels by enhancing work hardening [6]. This statement can be associated with the difference of Vickers hardness value between non-annealed 304 and annealed 304. For overall reason, the number of Vickers hardness of non-annealed 304 is higher than annealed 304. These can be preliminary indicated that non-annealed 304 is susceptible for cracking.

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Recommended font sizes are shown in Table 1.

B. A parameter for predicting time to failure from Corrosion Elongation curve

1) Non-annealed type 304

Fig.6 shows the corrosion elongation curves for non-annealed type 304 steel at 106^{0}C under a constant applied stress condition (L=30.5 kg/mm^2) in magnesium chloride solution at various annealing temperatures. From these curves, the three parameters were obtained for the each specimen: the time to failure (t_f), the steady-state elongation rate (I_{ss}) for the straight part of corrosion elongation curve and ratio of transition time to time to failure (t_{ss}/t_f). These parameters are shown in Table 3.

TABLE 3
THE VARIATION OF SENSITIZING TEMPERATURES, FAILURE TIME, AND ELONGATION RATE AT LOAD OF 30.5 KG/MM^2 ON NON-ANNEALED TYPE 304

No	Sensitizing temperatures (^{0}C)	I_{ss} (mm/s)	t_{ss} (s)	t_f (s)
1	600	3,00E-08	60428	86400
2	700	2,00E-06	18674	25450
3	800	7,00E-07	51388	55880

The lowest and the highest failure time at 700^{0}C and at 600^{o}C are 25450 seconds and 86400, respectively. The fastest steady-state elongation rate at 700^0C is 2×10^{-6} mm/s. The slowest elongation rate at 600^0C is 3×10^{-8} mm/s. The lowest failure time at 700^0C can be identified as the critical cracking time if this is compared with mechanical property especially hardness value.

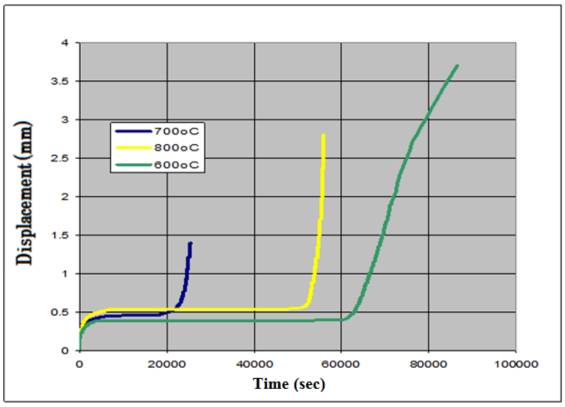


Fig 6: Corrosion elongation curves for type 304 steel at 106^0C under a constant applied stress condition (L= 30,5 Kg/mm^2) in $MgCl_2$ solutions.

On the basis of result, the increase of applied load from 30, 5 Kg/mm^2 to 40 Kg/mm^2 significantly can reduce time to failure at various sensitizing temperatures that are shown in Table 4.

TABLE 4
THE VARIATION OF SENSITIZING TEMPERATURES, FAILURE TIME, AND ELONGATION RATE AT LOAD OF 40 KG/MM^2 ON NON-ANNEALED TYPE 304

Sensitizing temperature (^oC)	t_f (s)	I_{ss} (mm/s)	T_{ss} (s)
600	31387	3,00E-07	30564
700	8348	4,00E-05	5990
800	45484	2,00E-07	42198

Fig 7 shows the differences among t_f, i_{ss}, and t_{ss}. The highest steady-state elongation rate at 700^0C is 4.10^{-5} mm/s but the lowest one at 2.10^{-7} mm/s. The fastest time to failure at 700^0C is 5990 seconds, on the contrary, the slowest one at 42198 seconds.

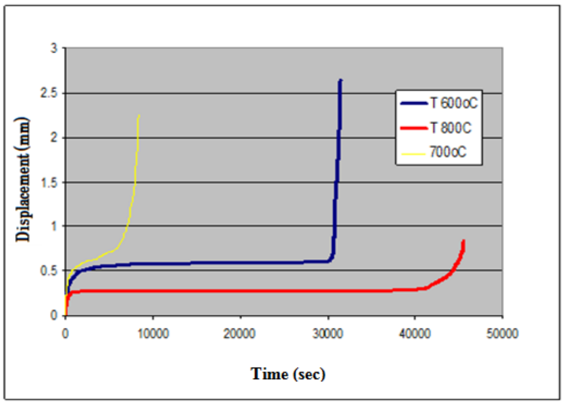


Fig 7: Corrosion elongation curves for type 304 steel at 106^0C under a constant applied stress condition (L= 40 kg/mm^2) in $MgCl_2$ solutions.

Both 30, 5 kg/mm^2 and 40 kg/mm^2 almost have the same tendency at 700^0C related to time to failure. These loads could contribute to decrease t_f. Nishimura and co-workers demonstrated that the most severe SCC susceptibility took place at a sensitizing temperature of 931 K (660^0C) in hydrochloric acid solution [5] as well as our present work.

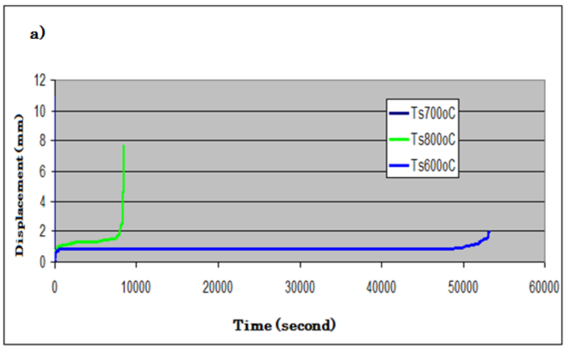
2) *Annealed type 304*

The commercial types 304 commonly have undergone work hardening. The transformation sequence during work hardening has been found to be γ (austenite)-ε-α'martensite. In order to change to be full austenite phase, the heat treatment was conducted at 1373 K to minimize α'martensite phase as the one of initial cracking site. The Table 5 shows how three parameters can influence the mechanical property of annealed type 304 under a constant load at 25 kg/mm^2 in 42 wt% $MgCl_2$ solution.

TABLE 5
THE VARIATION OF SENSITIZING TEMPERATURES, FAILURE TIME, AND ELONGATION RATE AT LOAD OF 25 KG/MM^2 ON ANNEALED TYPE 304

Sensitizing temperature (^oC)	t_f (s)	I_{ss} (mm/s)	T_{ss} (s)
600	53128	2,00E-06	48326
700	3	4,80E+00	-
800	8459	5,00E-05	4763

Fig 8(a) and (b) shows corrosion elongation curves for the prediction of time to failure. The highest elongation rate at 700^0C is 4.8 mm/s whereas the lowest one at 600^0C is 5.10^{-5} mm/s. The shortest time to failure at 700^0C is 3 seconds; on the contrary, the longest one at 600^0C is 53128 seconds.



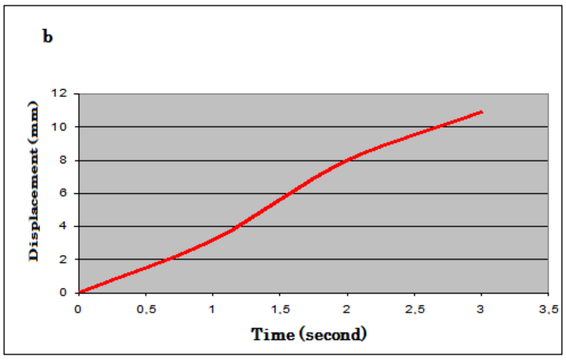


Fig 8 (a)&(b): Corrosion elongation curves for annealed type 304 steel at 106^{0}C under a constant applied stress condition (L= 25 Kg/mm^2) in $MgCl_2$ solutions.

The critical sensitizing temperature of annealed type 304 is the same behaviour as non-annealed type 304 at 700^{0}C (973 K). Both of them have a tendency to decrease mechanical property and to be susceptible for cracking. The Table 6 shows the relationship among three parameters in order to predict the behaviour of annealed type 304 at 20 kg/mm^2

TABLE 6
THE VARIATION OF SENSITIZING TEMPERATURES, FAILURE TIME, AND ELONGATION RATE AT LOAD OF 20 KG/MM^2 ON ANNEALED TYPE 304

Sensitizing temperature (^{o}C)	t_f (s)	I_{ss} (mm/s)	T_{ss} (s)
600	45103	9,00E-07	39005
700	5	2,25E+00	0
800	42006	4,00E-07	36625

Fig 9(a) and (b) show corrosion elongation curves which explain three the prediction of time to failure. The highest elongation rate at 700^{0}C is 2.25 mm/s but the lowest elongation rate at 600^{0}C is 4.10^{-5} mm/s. The shortest time to failure at 700^{0}C is 5 seconds; on the contrary, the longest time to failure at 600^{0}C is 45103 seconds.

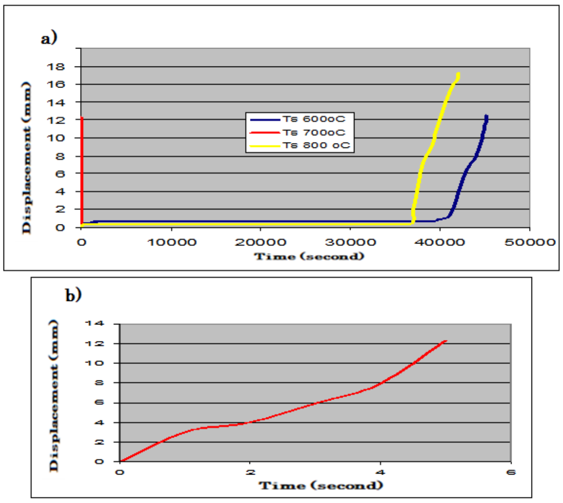


Fig 9 (a) and (b): Corrosion elongation curves for annealed type 304 steel at 106^{0}C under a constant applied stress condition (L= 20 Kg/ mm^2) in $MgCl_2$ solutions.

Although a constant load was increased from 20 kg/mm^2 to 25 kg/mm^2, the behavior of time to failure value at 700^{0}C is the same. At 700^{0}C, the reason why time to failure values at annealed type 304 are faster than non-annealed one is the existence of α' martensite and chromium carbide.

3) *Fracture Morphology*

The surfaces of fracture morphology for the austenitic stainless steels in magnesium chloride solution at 106^{0}C were observed. Fig. 10 and 11 show the fracture appearances of type non-annealed 304. They showed that the cracking mode for non-annealed type 304 were transgranular and intergranular.

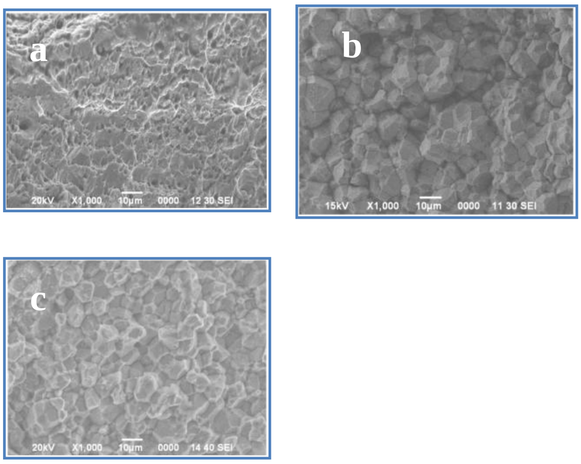


Fig 10: The fracture surface on type 304 at L = 30,5 Kg/mm^2 (a) Transgranular cracking for non-annealed type 304 at T = 600^{0}C,(b) intergranular cracking for non-annealed type 304 at T = 700^{0}C, and (c) intergranular for non-annealed type 304 at T = 800^{0}C.

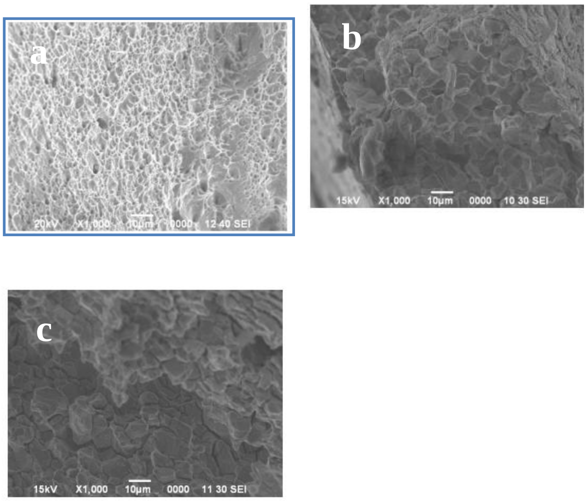


Fig 11: The fracture surface on type 304 at L = 40 Kg/mm^2 (a) Transgranular cracking for non-annealed type 304 at T = 600^{0}C,(b) intergranular cracking for non-annealed type 304 at T = 700^{0}C, and (c) intergranular for non-annealed type 304 at T = 800^{0}C.

At 600^{0}C (873 K) non-annealed type 304 appears transgranular crack. This cracking direction tears along grains. Many voids were distributed on the fracture surface appearance. These voids were an initial void coalescence to make dimples. At 700^{0}C and 800^{0}C both of them have the same cracking mode. The shape of fracture mode is intergranular crack. This fracture mode can be explained by the existence of carbide chromium approach and α' martensite in grain boundaries. The existence of carbide chromium can create the weakness region in grain boundaries. The concentration of chromium near grain boundaries is lower than its concentration in grains. The theory of dissolution in depleted chromium zone can be associated by appearing many voids in near grain boundaries. The appearance of α' martensite significantly could be considering to create these kinds of fracture. Nishimura and co-workers showed that for metastable austenitic steels like type 304, the strain induced martensite along the grain boundaries will enhance the hydrogen permeation [5]. Martensite structure has a very high diffusity coefficient and very small hydrogen content compared to those of austenite steel. This behaviour can be explained by the material's high content chromium like type 304 that is a natural inhabitant of martensite transformation. This reason can be reference why type 304 is susceptible to Stress Corrosion Cracking (SCC)

The fracture surface appearance for the austenitic stainless steels in magnesium chloride solution at 106^{0}C was investigated in a constant load (20 kg/mm^2, 25 kg/mm^2). Fig. 12 and 13 show the fracture surface appearances of type non-annealed 304. They showed that the cracking mode for annealed type 304 was transgranular at various sensitizing temperatures. This type of fracture occurs through or across a crystal or grain. The approach of mechanism of trangranular fracture can be related to void coalescence once the void forms, the connecting material continues to deform by slip, allowing the voids to expand until they begin to connect. This fracture mechanism develops a fracture topography consisting of cups an each fracture surface. A such surface is called dimple.

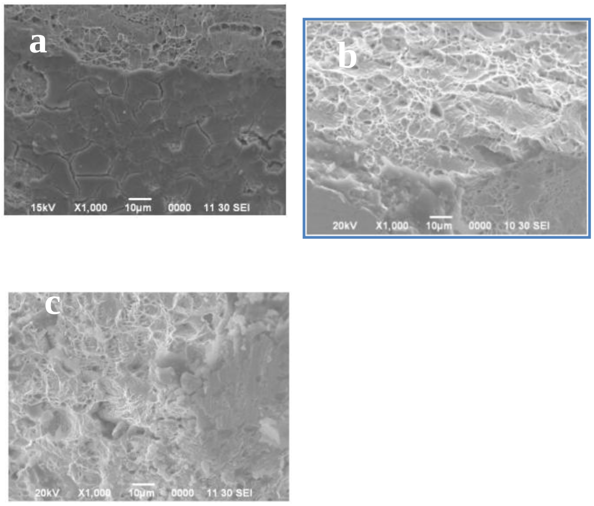


Fig 12: The fracture surface on type 304 at L = 25 Kg/mm^2 (a) Transgranular cracking for annealed type 304 at T = 600^{0}C,(b) intergranular cracking for annealed type 304 at T = 700^{0}C, and (c) transgranular for annealed type 304 at T = 800^{0}C.

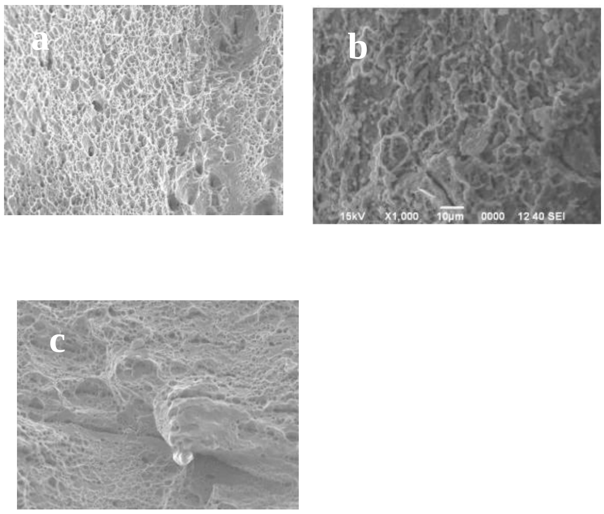


Fig 13: The fracture surface on type 304 at L = 20 Kg/mm^2 (a) Transgranular cracking for annealed type 304 at T = 600^{0}C,(b) intergranular cracking for annealed type 304 at T = 700^{0}C, and (c) transgranular for annealed type 304 at T = 800^{0}C.

The type of dimple in all fracture surfaces at various sensitizing temperatures and a constant load (L = 20 Kg/mm^2 & 25 Kg/mm^2) is equiaxed dimple. In tension, equiaxed dimples are formed on both fracture surfaces. The size of grains on annealed type 304 is bigger than non-annealed one. This main reason can be associated to hardness value. Over 25 Kg/mm^2 a constant load test was failed to hold annealed type 304 from rapid fracture because of above its yield stress. The deformation of materials will be easy to move if the size of their grains is large. The existence of void in grains makes material suffer to contribute the deformation by moving through slip plane.

IV. Conclusion

The following conclusions can be drawn from this work:

1. Using a constant load method, the effect of sensitizing temperature on stress corrosion cracking of austenitic stainless steels can be evaluated. The most of fracture shape in non-annealed type 304 at various sensitizing temperature is intergranular. All fracture shape in annealed type 304 at various sensitizing temperature is trangranular.
2. The role of α martensite mechanism in non-annealed type 304 significantly contribute to suffer fracture in $MgCl_2$ solution at 106^0C especially in grain boundaries. In annealed type 304, mechanism of fracture can be associated by deformation through slip plane in grains.
3. The deformation can be easy to move by growing grains in annealed type 304 so that it can be predicted by decreasing Vickers hardness value. In non-annealed type 304, the deformation can be sustained because of the small size of grains.
4. The role of carbide metal forming can be considered to suffer the fracture of material.
5. At 700^0C, the reason why time to failure (t_f) at annealed type 304 are faster than non-annealed is the existence of α' martensite and chromium carbide

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