



EFFECTS OF SOAKING TIME AND COLD WORK ON SENSITISATION OF AUSTENITIC STAINLESS STEELS

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Abstract: The effects of soaking and coldworks on sensitisation of austenitic stainless steels were studied. Annealed and samples coldworked to 20% and 40% were subjected to sensitisation heat treatment at 650 °C for 24 and 72 hours. Metallographic analysis carried out showed that sensitisation occurred in both annealed and coldworked samples which manifested as ditches. Soaking for 72 hours showed more ditches than 24 hours. Intergranular ditches were more prevalent in annealed and lower coldworked samples. In contrast, heavily coldworked samples were more susceptible to transgranular carbide precipitation evident by ditches on slip bands and recrystallised grains

Key words: sensitisation; soaking time; cold work; carbide; intergranular

Uticaj vremena natapanja i hladne deformacije na senzitivaciju austenitnog nerđajućeg čelika. Uticaj vremena natapanja i hladne deformacije na senzitivaciju austenitnog nerđajućeg čelika. Pripreмки koji su normalizovani i hladno deformisani na 20% i 40% su bili izloženi procesu senzitivacije na 650 °C za 24 i 72 sata. Metalografska analiza je pokazala da se senitivacija javila i kod normalizovanih i hladno deformisanih pripreмки u vidu kanala. Natapanje od 72 sata je pokazalo više kanala nego natapanje od 24 sata. Intergranularni kanali su bili više izraženi kod normalizovanih i slabije deformisanih pripreмки. Sa druge strane više deformisani pripreмки su bili podložniji transgranularnom izlučivanju karbida sa vidljivim kanalima na ravnima klizanja i rekristalizovanim zrnima.

Ključne reči: senzitivacija, vreme natapanja, hladna deformacija, karbid, intergranularno

1. INTRODUCTION

Austenitic stainless steels (ASS) remain preferred candidate materials for engineering structural application owing to their good strength and excellent corrosion resistance [1-5]. Austenitic stainless steels may be graded as high carbon (e.g. ASS 304H) and low carbon grade (e.g. ASS 304L) depending on their carbon content if it is higher than and less than 0.03wt% respectively [2]. The application requirements of these steels often determine the choice of the grade that may be considered. High carbon grade ASS type 304 (ASS 304H) remained a preferred choice for reactor cap design on account of their excellent creep resistance despite their probable risk of sensitisation [6]. The propensity of high carbon grade to sensitisation constitutes a marked difference in their applications compare to the less susceptible low carbon grade. Sensitisation is a phenomenon used to describe the localised precipitation of chromium carbide usually at the grain boundary area being a region of higher energy [1], when the material is soaked in the temperature range 500°C-850°C, thereby leading to chromium depletion adjacent to the grain boundaries and eventual loss of passivity [6, 7] (see Figure 1).

The linking of the Cr-depleted zones (Figure 1) provides a continuous path of lower corrosion resistance along the grain boundaries. It is along this path that the propagation of intergranular corrosion or SCC occurs [8]. Sensitized microstructures may also develop during slow cooling from high temperatures, heat treatment, high temperature service and welding. The higher affinity of

chromium for the carbon makes this precipitation reaction readily feasible and occurred in form of $M_{23}C_6$, though reactions with other elements like nitrogen may also occur to form chromium nitride of the form M_xN_y . Where M denotes elements including: Fe; Cr; Mo etc [2, 3].

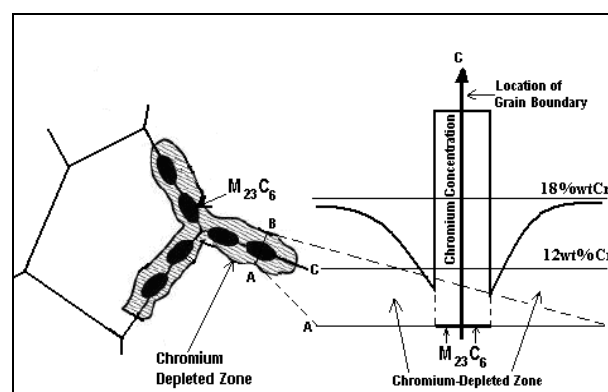


Figure 1. Schematic Illustration of Sensitization Mechanism [8]

On the other hands, cases of intragranular precipitation of carbides is not uncommon where precipitation of carbides occur within the grain matrix, usually on the dislocations structure of cold worked materials [3]. In addition, Kain et al.[9] also observed that susceptibility of ASS to sensitisation increases with cold reduction up till about 15-20% but later decreases beyond 20% cold work when carbides nucleation occurred within the grain rather than on the grain

boundary. This was attributed to rising internal energy with dislocation density [1, 9]. The above is consistent with the observation of Ahmed et al.[10] where it was found that material cold worked to 20% represented the the peak of intergranular stress development, with probable IGSCC failure mode. This is not unconnected with intergranular stress build up caused by strain mismatch, and beyond 20% cold work, the deformation becomes increasingly more uniform with less strain heterogeneity. At higher cold work levels, the slip band and dislocation line becomes probable carbide nucleation sites and Transgranular Stress Corrosion Cracking (TGSCC) mode becomes more dominant [11].

The danger of sensitization in ASS cannot be underestimated as it may lead to intragranular corrosion failure or intergranular stress corrosion cracking expecially in the pressurised areas of application including Pressurised Water Reactor (PWR) environment [1, 6, 8, 9]. Hence, the objective of this work was to highlight the capability of optical microscopy for the assesment of effects of cold work levels and soaking time on the sensitisation of austenitic stainless steels.

2. EXPERIMENTATION

2.1 Materials

The material used for this study was low carbon grade ASS, Type 304L, with the chemical composition shown in Table 1. The ASS plate (300×100×30mm) as-received was initially solution annealed at 1050°C for 30 minutes and quenched in water. Fast cooling was done to prevent probable intergranular precipitation of the chromium carbide by sensitisation process [11]. The material was subsequently heat treated at 400°C and furnace cooled to partially relieve internal stresses and remove any martensite which might have formed due to fast cooling. The material was subsequently cold worked by uniaxial rolling.

C	Cr	Mn	N
0.030	18.387	1.804	0.086
Ni	P	S	Si
8.133	0.034	0.005	0.411

Table 1. Chemical composition of as-received ASS Type 304L (wt %)

2.2 Experimental Procedures

2.2.1 Cold Rolling

Cold working could be achieved through a number of methods. However, cold rolling was used because of the ease of achieving different degrees of cold work through reduction in the sample thickness and it equally allows test samples to be manufactured from different orientations of the rolled plates. Some of the annealed materials were cold worked by multipass uniaxial rolling to 20% and 40% reductions in thickness. Each rolling pass corresponds to thickness reduction of 0.5mm and the final thickness of rolled plates reduced from 30mm to 27mm and 18mm respectively. The degree of cold work was determined using Equation 1

[12]. Schematic illustration of the rolling process is shown in Figure 2.

$$\text{Cold Work (\%)} = \frac{h_0 - h_f}{h_0} \quad (1)$$

Where h_0 and h_f are the initial and final through thickness dimensions respectively.

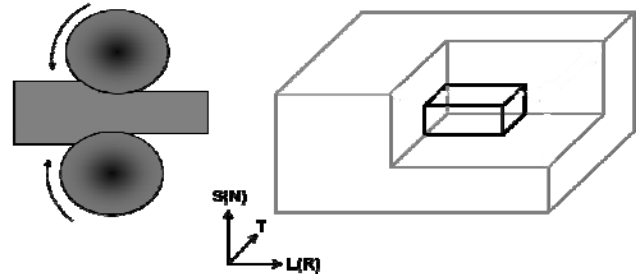


Figure 2. Schematic Diagram of Cold Rolling

2.2.2 Sensitisation Heat Treatment

Annealed and cold rolled samples with the dimensions 1cm × 1cm were sensitized. The sensitisation heat treatment was carried out in an electric heating tube furnace. Argon gas was used to achieve oxygen-free inert environment. The sample was initially heated to 700°C in 30 minutes under steady flow of argon gas to prevent high temperature oxidation. The temperature was later stabilised at 650°C with the aid of thermocouple in contact with the sample. The sample was then soaked for 24 hours and 72 hours accordingly at 650°C and then air cooled to ambient temperature.

2.2.3 Optical Metallography

The Rolling (R), Transverse (T) and Normal (N) directions of cold rolled plate correspond to the Longitudinal (L), Transverse (T) and Short-transverse (S) directions of the annealed material. The samples used for optical metallography were sectioned from the middle of the cold rolled plate. The samples Normal plane (R-T), perpendicular to the Normal direction were considered for metallography (see Fig 1.). The plane of the sample are defined by two orthogonal directions in the parenthesis.

The sample preparation was carried out following the metallographic wet grinding with silicon carbide paper in order of 320, 400, 600, 800, 1200 and 4000. The specimen was subsequently electropolished in a solution containing 8% Perchloric acid and 92% Acetic acid at 42V for 90s following the procedures of the ASTM standard E 1558-99 [13]. The electropolished sample was then electrolytically etched in a solution containing 10% Oxalic acid and 90% distilled water at current density of 1A/cm² for 60s in line with the ASTM standard A 262-01 [14]. Electrolytic etching with oxalic acid has the potential to reveal the austenite grain boundaries, the residual delta ferrite and the slip bands. The sample was then rinsed with deionised water and then in ethanol before it was dried with warm air. The etched samples were examined under the Optical microscope.

3. RESULTS AND DISCUSSION

3.1 Optical Metallography

The results of the optical metallography for the annealed samples are contained in Figure 3. The common microstructural features revealed in all the micrographs in Figure 3 are the austenite grain boundaries, the residual delta ferrite and twins within the austenite grains. The grains are fairly equiaxed. Figures 3A showed the un-sensitised optical micrograph while Figures 3B & C showed the micrographs of the annealed samples sensitised at 650°C for 24 hours and 72 hours respectively. Figure 3D was the optical micrograph of the sample sensitised for 72 hours but larger magnification for clarity. The obvious difference between annealed un-sensitised (Figure 3A) and sensitised samples (Figures 3B & C) could be seen on the austenite grain boundaries. The colour contrast also showed that sensitised samples are more darker than the un-sensitised sample and the degree of sensitisation was observed to more after the sample was sensitised for 72 hours than 24 hours

samples. Higher magnification sample (Figure 3D) showed that the grain boundaries of the sensitised samples contained ditches compared with unsensitised samples. The ditches were not found on the twin boundaries or the coincident site lattices nor was any observed within the austenite grain matrix and consistent with the Moura et al.[6]. The ditches on the sensitised austenite grain boundaries was attributed to the network of chromium carbide precipitate along grain boundaries during the sensitisation heat treatment at 650°C for prolonged time. The precipitation of noble chromium carbide along the grain boundaries resulted in the depletion of the much needed chromium adjacent to the grain boundaries [15] leaving behind a network of nobler chromium carbide precipitate and neighbouring less noble region, with chromium level below minimum required for the stainless steel to maintain its passivity. The contact between the nobler chromium carbide precipitate and the less noble neighbouring region would make the material susceptible to galvanic corrosion attack in addition to electrolytic etching in oxalic acid

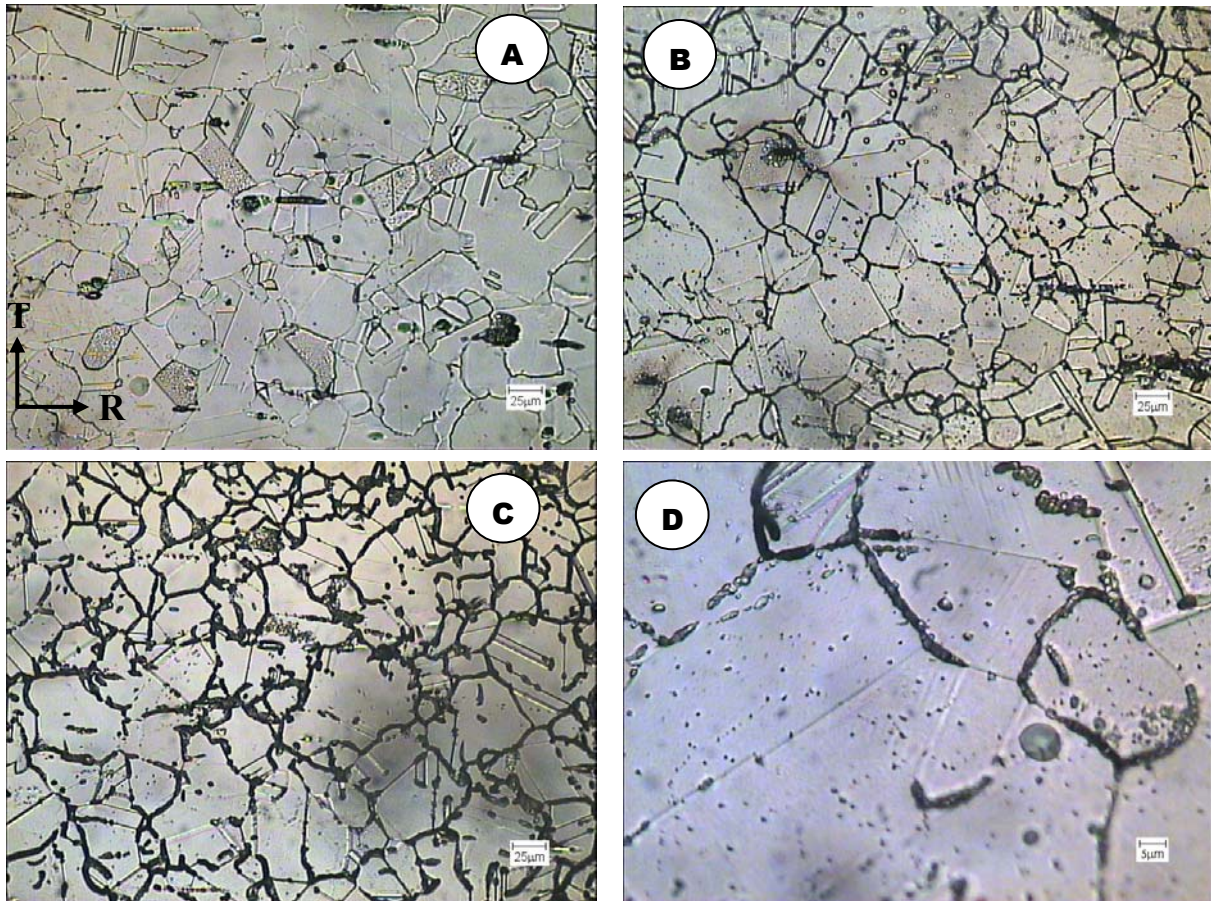


Figure 3. Normal Plane of ASS Annealed: un-sensitised (A), sensitised for 24Hr (x20) (B), sensitised for 72Hr (x20) (C), sensitised for 72Hr (x80) (D)

The result of optical microscopy of the 20% cold worked sample are contained in Figure 4. Figure 4A showed the macrograph of the un-sensitised sample, while Figures 4B & C were the optical micrographs of the cold rolled samples and sensitised at 650°C for 24 hours and 72 hours respectively. Figure 4D was the higher magnification micrograph of the sample sensitised for 72 hours. The difference between the un-sensitised

and sensitised 20% cold worked samples is consistent with those observations in annealed sample. In addition to the ditches on sensitised austenite grain boundaries, there was evidence of recrystallisation in the 20% cold worked samples sensitised for 72 hours (Figure 4C & D) compare to sample sensitised for 24 hours (Figure 4B). The newly recrystallised grain boundaries also evidence of limited ditches which suggested that the boundaries

became carbide nucleation sites but the extent of these was not very pronounced. Similar observation was

reported in the work of Alvarez et al.[16] on ASS cold rolled to 50% reduction and elsewhere [1].

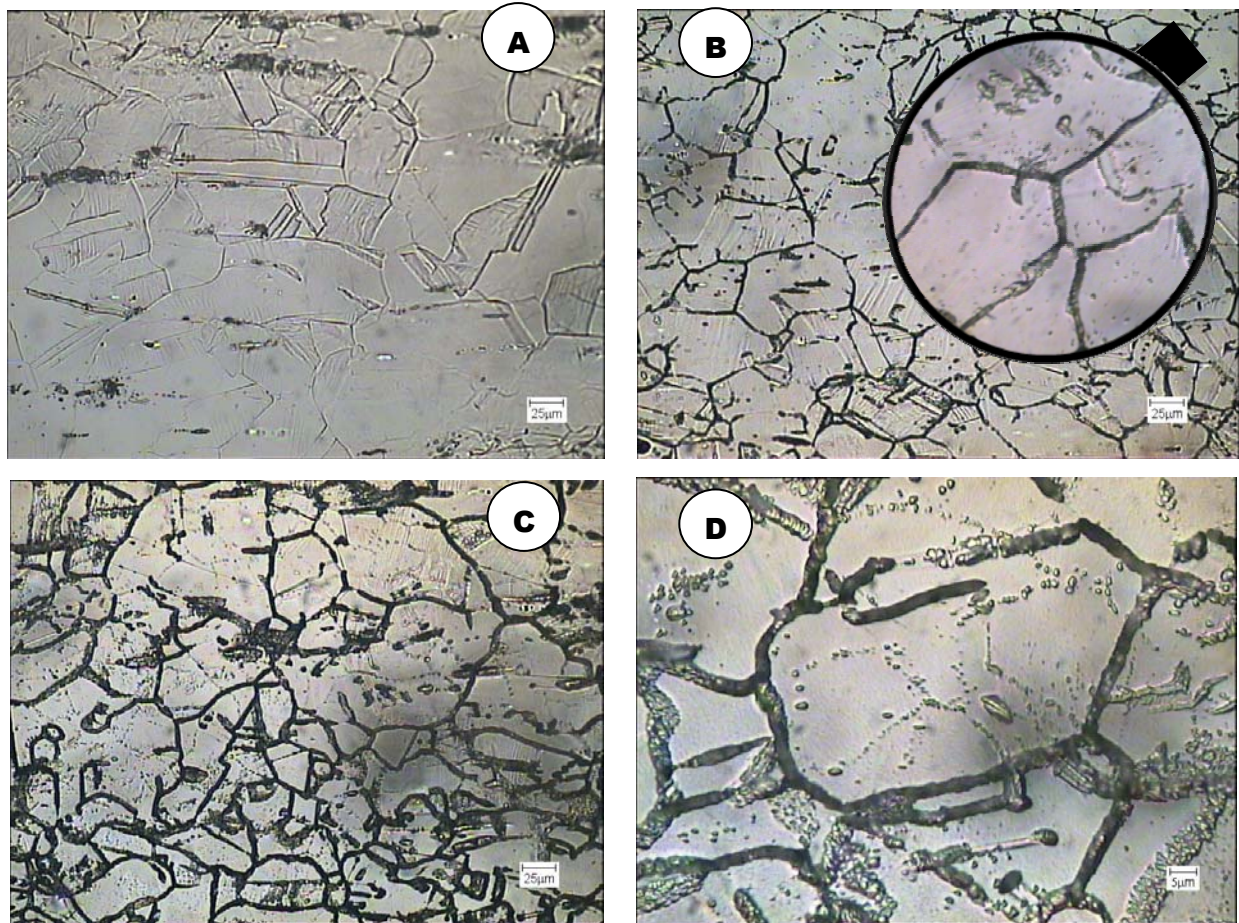


Figure 4. Normal Plane of ASS 20% Cold Rolled: un-sensitized (x20) (A), sensitized for 24Hr (x20) (B), sensitized for 24Hr (x80) (C), sensitized for 72Hr (x20) (D)

The result of optical microscopy of the 40% cold worked sample are contained in Figure 5. Figure 5A showed the macrograph of the un-sensitized sample, while Figures 5B & C were the optical micrographs of the cold rolled samples, sensitized at 650°C for 24 hours and 72 hours respectively. Figure 5D was the higher magnification micrograph of the sample sensitized for 72 hours. The difference between the un-sensitized and sensitized 40% cold worked samples is consistent with those observations in annealed and 20% cold worked samples. In addition to ditches on sensitized austenite grain boundaries, there was evidence of intragranular precipitation of chromium carbide within the austenite grains probably on deformation substructures including the slip bands. The slip bands within the 40% cold worked samples sensitized for 24 hours and 72 hours (Figure 5B & C) also appeared darker like the austenite grain boundaries due to galvanic corrosion ditches between the network of grain boundary carbides and adjacent neighbourhood.

A lot of works have been carried out on cold worked ASS which showed that cold working is accompanied with dislocation and deformation bands within the austenite grain boundaries [10, 17, 18]. It has equally been shown that heavily cold worked ASS materials subjected to sensitization heat treatment exhibit intragranular precipitation of chromium carbides rather

than on the grain boundaries [1, 5]. The implication of grain boundaries carbide precipitation has been duly studied and has been linked to the intergranular stress corrosion cracking of the ASS in range of environments [5, 7, 19]. However, others have argued that grain boundary carbide precipitation was not that all bad. It has been shown that [20] grain boundaries carbides can help improve creep resistance of the material by under pinning and preventing the grain boundary sliding. On other hands, heavily cold worked material with high dislocation density and slip bands enhances intragranular precipitation of carbides [11], which is consistent with the results in Figure 5. This helps in two ways: prevention of intergranular failure and help with desensitisation by facilitating diffusivity of chromium back to the matrix through the deformation substructures including dislocation and slip bands within close proximity [5].

The effects of soaking time was obvious from the above results in two ways: Long soaking time allowed enough time for extensive precipitation of chromium carbides on the austenite grain boundaries in the annealed and lower cold worked level samples. While long soaking time in heavily cold worked sample allowed sufficient time for intragranular precipitation of chromium carbides on the recrystallised grains within the prior austenite grains.

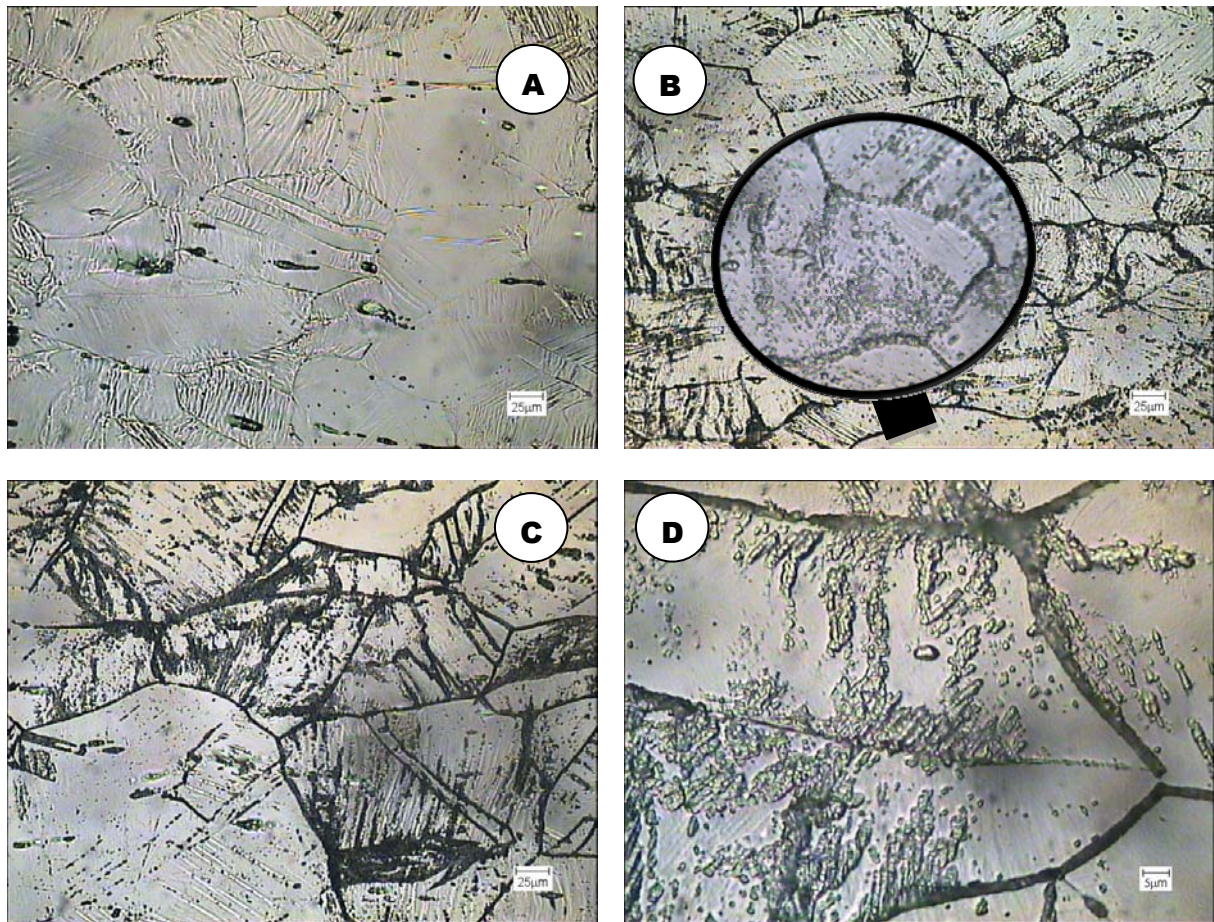


Figure 5. Normal Plane of ASS 40% Cold Rolled: unsensitized (A), sensitized for 24Hr (x20) (B), sensitized for 24Hr (x80) (C), sensitized for 72Hr (x80) (D)

The need requirement of the materials will have to determine how the grain boundaries may be engineered to meet the requirement. It has been highlighted in this work that sensitization in annealed and lower cold worked austenitic stainless steels for shorter soaking time enhances intergranular precipitation of chromium carbide which makes the materials susceptible to intergranular stress corrosion cracking. On the other hands, intergranular carbide precipitation may equally be considered good for the materials as it increases the resistance of the materials to creep damage by preventing grain boundary slidding. It has also been shown in the work, that sensitization of the heavily cold worked sample for a prolonged time enhances intragranular carbide precipitation on the recrystallised grains within the prior austenite grains. Though the material may be less susceptible to intergranular failure, however, it thus becomes vulnerable to transgranular stress corrosion cracking.

4. CONCLUSION

The following are the conclusions of study investigating effects of soaking time and cold worked levels on the sensitization of austenitic stainless steels type 304L:

1. Sensitization occurred in austenitic stainless steels both in annealed and cold rolled conditions.

2. Sensitized microstructure showed evidence of galvanic corrosion ditches on the austenite grain boundaries.
3. The severity of the galvanic corrosion ditches increases with soaking time.
4. The corrosion ditches on the grain boundaries were attributed to galvanic interaction between nobler carbide precipitates and the chromium depleted within the close proximity.
5. Intergranular precipitation of chromium carbide were more copious on the annealed and lower level of cold reduction (20% cold work), while heavily cold rolled samples (40% cold work) exhibited evidence of transgranular carbide precipitation.

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