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475°C Embrittlement in Stainless Steels

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Abstract : *The effect of 475°C embrittlement on the mechanical properties of duplex stainless steels (DSS) was investigated. Specimens of compact tension specimens (CT) were heat treated at 475°C for different times and pulled to failure in air. Hardness was measured and fracture surface was studied for each specimens using optical and scanning electron microscopy. Depends on treatment time results showed that specimen hardness , fracture mode , cracking bath , fracture toughness and the crack length were affected by the treatment at 475°C. An increase in specimens hardness was clearly measured with increasing treatment time at 475°C. The ferrite phase fractured in a brittle manner with more tendency to cleave with increasing treatment time. No intergranular failure was observed for all tested specimens. The austenite phase fractured in a ductile manner, plastic deformation, and showed no effect of heating at 475°C on this phase fracture mechanism.*

Keywords : Hardness, 457°C embrittlement , cleavage , brittle fracture

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1. Introduction :

Duplex stainless steels are widely employed in industry for apparatus working with sea water , petroleum, chemical plants and in nuclear power plants. This is due to their excellent corrosion resistance associated with superior mechanical properties. Duplex stainless steels commonly have a balanced ferrite , α, to austenite , γ, content known as 50α /50γ microstructure obtained by controlled chemical analysis and well-balanced heat treatment [1] . Zeron 100 is a typical super duplex stainless steel which is characterized by its high content of molybdenum and nitrogen having a pitting resistance equivalent number (PREN) guaranteed to be greater than [2] . The microstructure of worked duplex stainless steels is usually typified by elongated colonies of grains of one phase in a matrix of the predominant phase producing a microstructure This is, however, not the only structure which can be developed. It is possible to age harden the alloy by the precipitation of an additional phase or phases . It is usual for duplex stainless steels to be delivered in the annealed two-phase condition, solution treatment usually being performed in the range 1050-1100 ºC . Regarding duplex stainless steels strength enhancement it has been suggested that four effects can be operative simultaneously [3] . These are:

- Solution hardening of austenite due to enrichment of carbon and nitrogen arising from element partitioning
- Grain refinement because of the mixed structure.
- Strengthening effect of ferrite grains.
- Dislocations generated during thermal cycling due to the different coefficient of expansion at the two phases.

1.1 Embrittlement at 475ºC:

Ferritic and duplex stainless steels have higher hardness and lower ductility after heating in the range of ~ 300-550°C [4] . This phenomenon has been observed in DSS after only 15 minutes of aging at 475°C [5]. Embrittlement of duplex stainless steels at 475°C is accompanied by an increase in both the ferrite hardness and the ductile to brittle transition temperature[6] . Overall, the fracture toughness is reduced by the development of this phenomenon 35. The hardening can be caused by several transformations [7] . The formation of α` phase by spinodal decomposition or by conventional nucleation and growth.The precipitation of intermetallic phases, nitrides or carbides.The precipitation of copper or tungsten rich phases.

1.2 Mechanism of 475°C embrittlement:

Depending on the temperature and chemical composition, the 475°C embrittlement takes place either by spinodal decomposition of the ferrite phase into two phases (i.e. α and α′) or by nucleation and growth of the ferrite phase i.e. α′ [8] . The two phases α and α′ are rich in iron and chromium respectively [9]. Spinodal decomposition is a process by which chromium rich and chromium depleted regions are formed by a process which does not involve the development of a nuclei which have the ferrite α′ composition but rather the gradual build up of chromium rich regions, until α′ is eventually formed [10] . As shown in Fig.(1.1), chromium rich regions form and the chromium concentration in these regions increases slowly with time. Nucleation and growth of chromium rich ferrite phase i.e α′ is another mechanism by which 475°C embrittlement takes place . It is believed that 475°C embrittlement takes place within Fe-Cr alloys due to the presence of a miscibility gap in this system [11,12] as illustrated in Fig. (1.2). In the region where the nucleation and growth mechanism takes place i.e $\partial 2f/\partial c2 > 0$, the resultant activation energy restricts decomposition to nuclei of a critical size and a composition very near the equilibrium values. In the spinodal region i.e $\partial 2f/\partial c2 < 0$ no activation energy for growth exists and the decomposition is governed by diffusion alone [13]. The rate of 475°C Embrittlement was reported to be increased by higher chromium and molybdenum and decreased by higher nickel [13]. The development of 475ºC embrittlement was suggested to be accompanied by an increase in the ductile to brittle fracture transition temperature [14 , 7] and a reduction in corrosion resistance 46, probably due to chromium depletion of the matrix. Spinodal decomposition is reversible by reheating to a region of 600°C, whereupon the α′dissolves [15] .

1.3 Effect of 475°C embrittlement on DSS :

In ferritic and duplex stainless steels, age hardening at a temperature between 270-520°C causes an increase in the ferrite hardness and the brittle to ductile temperature [16] . As shown in Fig.(1.3) the ferrite hardness in a Fe26Cr5Ni duplex stainless steels increased with aging time and temperature. The ferrite hardness was suggested [17] to increase largely due to the mismatch in moduli and lattice parameters between the components of the decomposed ferrite. Marrow [18] reported an increase in the friction stress from 190 MPa to 260 MPa for yielding in ferritic stainless steels age-hardened for 136h. The mobility of dislocation was lowered by precipitation of chromium –rich particles on those dislocations in order to minimize the total free energy of the system. This caused an increase in hardness and decrease in impact toughness of the chromium- iron alloys as shown in Fig.(1.4) . This is in agreement with the work of Jacobsson et al. [19] who noticed an increase in the friction stress with time for 18Cr-2Mo ferritic stainless steels age-hardened at 475°C. The dislocation distribution, which was homogeneous in the unaged state, became localized and planar . Whereas, in the unaged condition, the room temperature fracture appearance is normal dimple rupture, aging causes it to become mixed with an increasing proportion of brittle fracture surfaces [7] .

1.4 Fracture in stainless steels aged at 475°C :

It is documented [20 , 21] that for duplex or ferritic stainless steels aged at 475°C, fracture took place by cleavage of the ferrite phase and that twinning was more predominant than slip as a crack nucleation mechanism. For Zeron 100 duplex stainless steels age-hardened at 475°C and tested at different temperatures , Marrow and Harries [22] reported the fracture surface to change from a ductile to brittle mode based on the testing temperature or specimen hardness. Alloy composition i.e alloying elements , ferrite content, grains orientation , grain shape , ageing temperature and ageing time are the main parameters controlling the fracture mechanism of DSS. The fracture of DSS can be classified into two main types , ferrite cleavage and austenite ductile tearing. The amount of cleaved ferrite and ductile austenite two areas depends on those parameters mentioned later. Erauzkin and Irisarri [23] reported a decrease in the fracture toughness (CTOD) value to 0.2mm for stable crack initiation in 22Cr-5.6Ni duplex stainless steels after being aged at 475°C for 24h. Iurgoyen et al. [24] studied the influence of aging at 475°C on the fracture resistance of a duplex stainless steel. They suggested a change in the deformation behavior between the annealed specimens and the age-hardened ones. In the annealed condition, the ferrite and austenite two phases deform plastically in the same time leading to large voids in the ferrite fracture surface. In the specimens age-hardened at 475°C, the austenite phase deforms plastically while the ferrite phase still in the elastic regime. Internal stresses are produced in both phases in the later case due to a discontinuity in the plastic strain at the interphase. Ferrite cleavage and austenite rupture are observed in the fracture surface.

2. Material and Experimental Method :

The as-received material was in the form of extruded bars solution heat treated at 1100°C for 105min and water quenched. The as-received material chemical composition is shown in table.(1.1) . Specimens from the as-received material were cut perpendicular to the bar axis and were mounted in plastic resin. The mounted specimens were ground on SiC papers and polished. In order to reveal the as-received microstructure, specimens were electro-chemically etched in 10% oxalic acid solution, 10g oxalic acid in 100ml distilled water, for 30-40 second with $\approx$ 10-15V. Two phases were present , the ferrite phase and austenite phase. The as-received material microstructure was observed to be free of sigma phase. A hardness of 258Hv was measured for the as-received material. A total of 24 specimens were machined as straight notch compact-tension (CT) specimens. In order to investigate the effect of 475°C brittleness and fracture mechanism the following aging times 2h, 5h, 13h, 24h, 49h, 72h, 166h, and 118h (three specimens at each heating time). That was in addition order to obtain different levels of hardness. Finally, specimens were allowed to air-cool to room temperature. An emery paper with a suitable roughness was used in order to remove surface oxide for the purposes of hardness measurement .The hardness measurement was carried out with Vickers pyramid indentation with 30Kg on the basis of ASTM-E92-82. The hardness was calculated according to the following equation;

$$H_V = \frac{1.85437P}{0.001^2 d_1 d_2} \qquad (1)$$

Where:

P the load used for hardness measurement (kg).

d_1 and d_2 the indentation diagonals lengths (μm).

At least five points for each specimen were taken and the average value was considered. Finally , the specimens were pulled to failure using Instron tensile machine for fracture surface investigation. Selected portions of the fracture surface was then attached to a (SEM) specimen support, electrically connected to each other by G3961 type silver conductive adhesive. Fracture analysis was carried out using Philips XL30FEG type scanning electron microscopy (SEM). The specimen was tilted to an angle of 40^{o} in order to obtain the optimum contrast between the specimen different topographical areas. Fracture analysis was carried out with 20KV voltage concentrating on the cracking mechanism, cleavage and ductile manner. Cracking mechanisms were studied for those grains either as ferrite or austenite grains identified according to fracture surface features.

3. Results and Discussion :

In general, hardness of the specimens was increased by the treatment at 475°C. As shown in Fig.(1.5) , specimens hardness was increased with increasing the ageing time. The increase in hardness can be expressed by the following equation ;

$$H_V = 17.071 \ln t + 258.42 \tag{2}$$

Where (t) is the specimen ageing time in hours.

The specimen yield stress (expressed as the 0.5% proof stress) increased with the specimen hardness as follows ;

$$\sigma_{ys} = 1.279 H_V + 471.76 \tag{3}$$

In general , annealing of steels is well known to cause a reduction in hardness and some other mechanical properties , yield strength , due to grain growth process . The grain growth process takes place under a driving force of reduction of total free energy of the system i.e. Gibbs free energy. Heat treatment cause grains to grow to larger size by rearrangement of their boundaries to less sides. The later action will reduce the energy associates those disappeared sides of the grain. This is not the case in duplex stainless steels where the microstructure consists of ferrite grains in a matrix of austenite phase . The two phases are different in mechanical and physical properties i.e. crystallography and mechanical behavior. In turn , each phase is expected to retard the other phase grains to grow due to difference in crystal structure . On the top of that and due to the chemical composition of duplex stainless steels , the presence of some carbide formers and nitride formers such as chromium and molybdenum, plays a strong effect on " pining " of the grain boundary migration leading to an increase in specimens hardness. Accordingly , strength is grain size dependent. The grain size in a DSS is usually smaller than that of ferritic and austenitic stainless steel of corresponding chemical composition. This is explained by mutual hindering of growth of the ferrite and austenite grains. If the effect of grain size is compensated then the strength of DSS is controlled by the stronger ferritic phase . The heat treatment of duplex stainless steels at 475°C causes the chromium-rich particles to precipitate at the ferrite grains but not at the austenite phase leading to opposition of deformation of the ferrite either by twining or by slip bands formation. Specimens aged for longer times , 166h, showed higher hardness compared those aged for shorter times i.e. 5h and 24h. The increase observed in hardness is believed to be caused by the decomposition of the ferrite phase into chromium-rich ferrite α' and iron-rich ferrite α took place at 475°C. Depending on the temperature of aging and the chemical composition of alloys, the nature of this decomposition is either spinodal decomposition or nucleation and growth. Spinodal decomposition refers to a reaction where two phases of the same crystal lattice type, but different compositions and properties, form due to the existence of a miscibility gap in the alloy system by means of uphill diffusion without nucleation. Thermodynamically this is possible at concentration between the points where the second derivative of free energy with composition equals zero. If term is negative in quantity the decomposition kinetics will be controlled by spinodal mechanism rather than by nucleation and growth. If this term is positive the kinetics is nucleation and growth of chromium-rich ferrite, α' i.e. spinodal decomposition is not encouraged. As the decomposition of ferrite is diffusion process in nature , its rate will be affected by the ageing time. Based on that and as shown in Fig. (1.5) , specimens aged for shorter periods , 2h, 4h and 24 h showed less hardness change than those aged for longer ageing time. The difference in mechanical properties between the two components α' and α gives rise to factors such as load sharing between the two phases i.e. due to a difference in elastic and plastic response difference. The observed increase in hardness with ageing time increase indicates more decomposition took place i.e. more chromium – rich particles precipitated within the ferrite phase. It is well known that for duplex stainless steels , the embrittlement process takes place only within the ferrite phase. This may be attributed to a difficulty in the deformation process of ferrite phase i.e. twining . Such a difficulty takes place when dislocations mobility is blocked or reduced. The Cr-rich precipitates, α′, cause DSS to be embrittled by lowering the mobility of dislocation and by creating microvoid near them in the ferrite matrix. Dislocations are favorite sites for α′ precipitation due to their stress field which will be minimized by such precipitation. Consequently , The loner ageing time at 475° the more "pining' to dislocations on the slip planes the high hardness is observed. This mechanism of ferrite embrittlement is supported by the poor slip system of this phase. The applied force , when specimen pulled to failure, with a difficulty in ferrite phase deformation will cause this phase to cleave rather than plastically deformed. Consequently , The longer ageing time at 475°

the more cleavage of ferrite . During aging treatment at 475° C the degradation in mechanical properties directly depends on the state of the ferrite phase. This includes volume fraction, distribution in the matrix, grain size and grain shape of the phase . In the present work, fracture surface investigation was carried put using scanning electron microscopy , SEM , for deep insight into the fracture process of duplex stainless steels. The fracture surface observed was typically consisted of cleaved ferrite and austenite grains which failed in a ductile manner as shown in Fig.(1.6). The friction stress on the slip plane, opposing dislocation movement, increases with ageing time. This encourages twinning and ferrite cleavage . The fracture surface observed by SEM for specimens aged for 13h, Fig.(1.7), indicated the same cracking mode but with more tendency for ductile failure. This can be attributed to specimen higher ductility due to less ageing time. Dislocation mobility is enhanced by reduction in the friction stress. Chromium-rich areas play a strong effect in increasing the friction stress on the slip plane leading to plastic deformation yield stress greater than cleavage stress. This argument may attribute the preferred mode of cleavage formation for specimens aged for long times rather than dimples formation noticed for small ageing times.

4. Conclusions:

- Duplex stainless steels undergoes hardness increase when heat treated at 475° C.

- Brittleness of DSS takes place in the ferrite phase.

- The austenite phase is believed not to be susceptible to embrittlement due to age hardening at 475° C.

- The embrittlement of 475° C takes place due to either spinodal decomposition of the rich- chromium ferrite or nucleation and growth of chromium-rich ferrite particles .

- The cracking mode of duplex stainless steels age-hardened at 475 is by ferrite cleavage and austenite ductile tearing.

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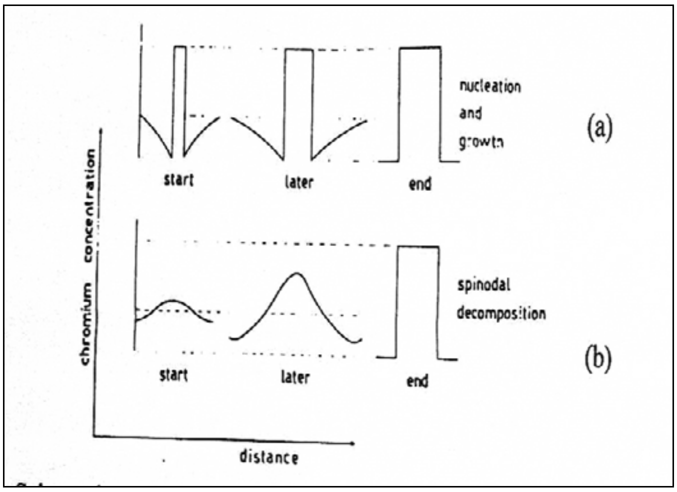

Fig.(1) Chromium rich regions development illustrating the difference between the nucleation and growth (a) spinodal mechanism (b) (17).

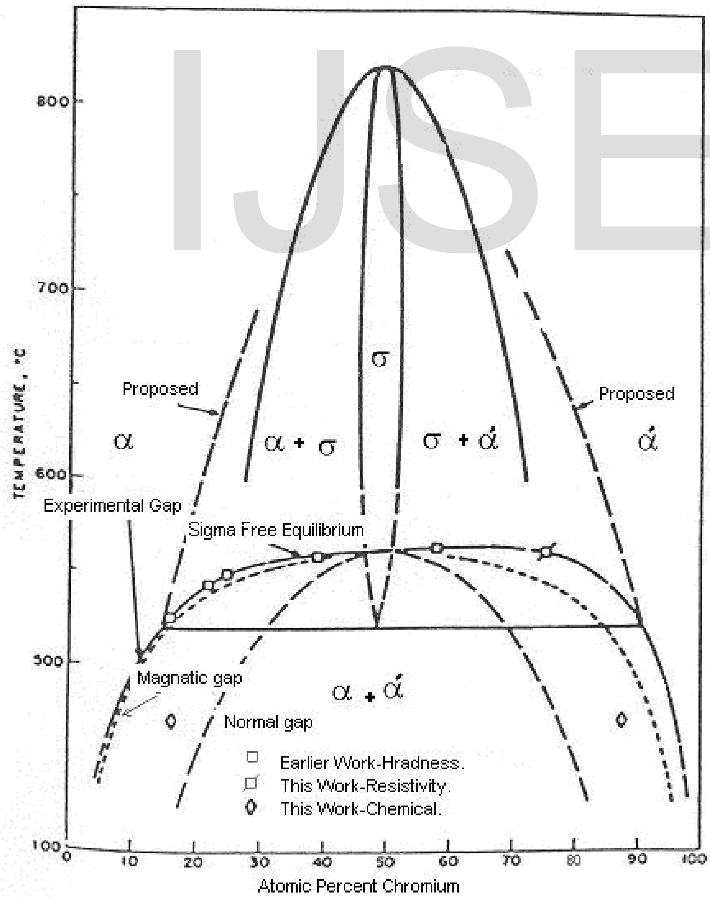

Fig.(1.2) The miscibility gap in the Fe-Cr phase diagram.(25)

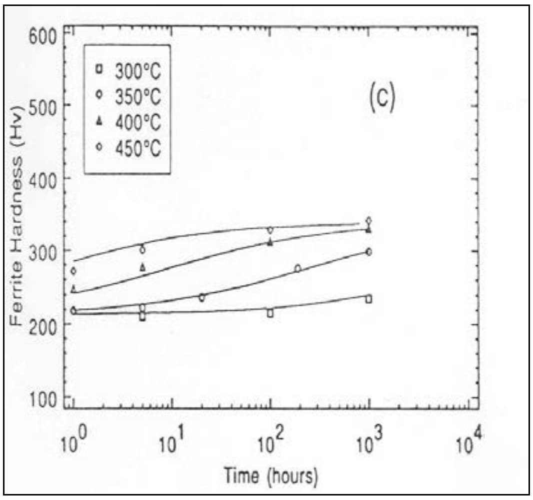

Fig.(1.3) Ferrite hardness in a Fe26Cr5Ni duplex stainless steels vs. aging time .(26)

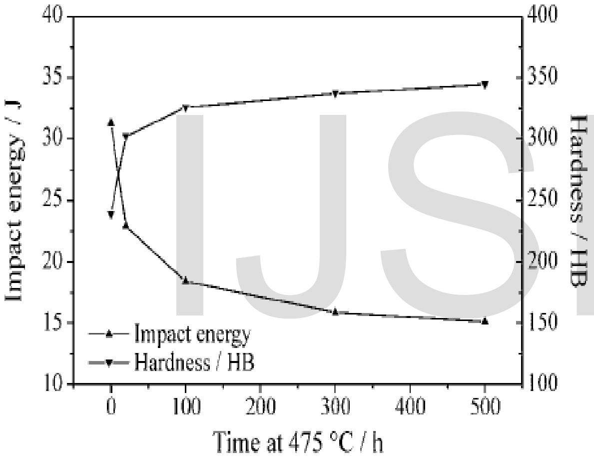

Fig. (1.4) Effect of 475°C on hardness and impact energy of UNS S31803 duplex stainless steels. (27)

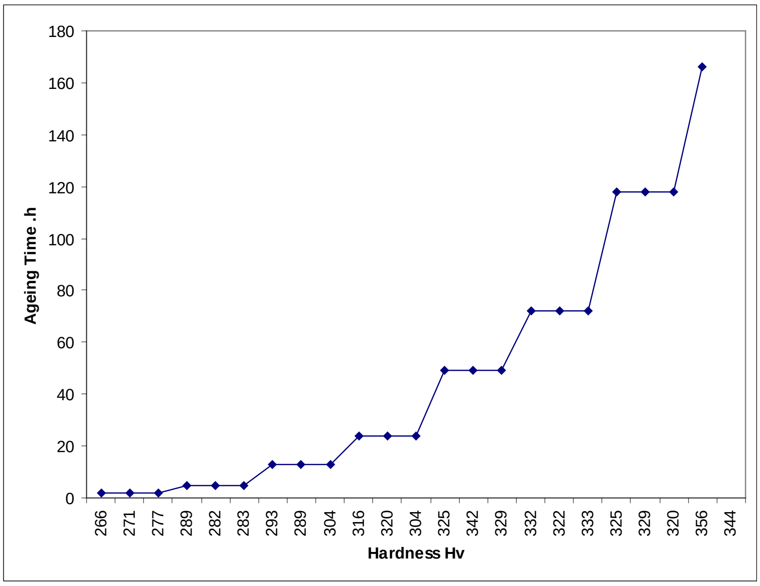

Fig.(1.5) Effect of aging time at 475°C on hardness of specimens .

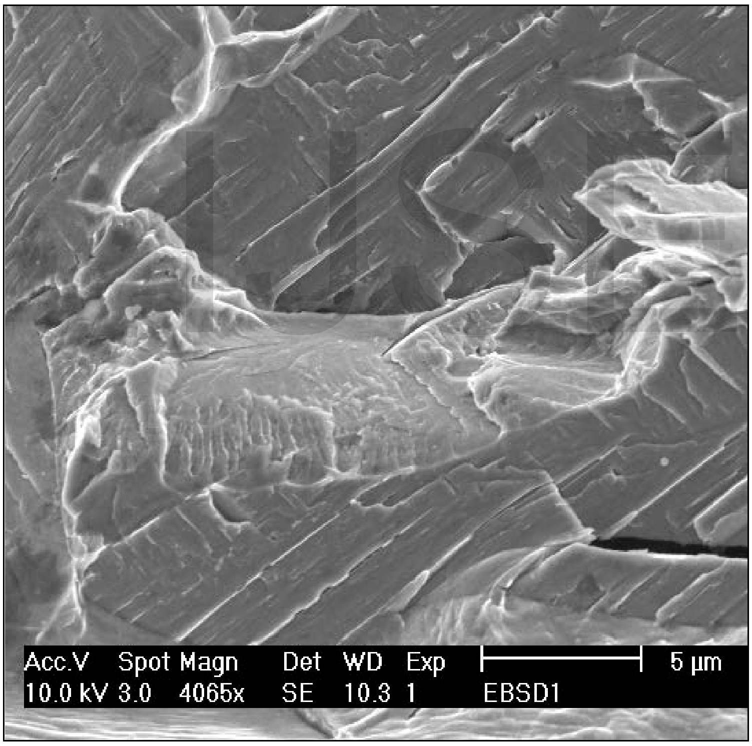

Fig.(1.6) Fracture surface of specimen aged for 100h at 475ºC .

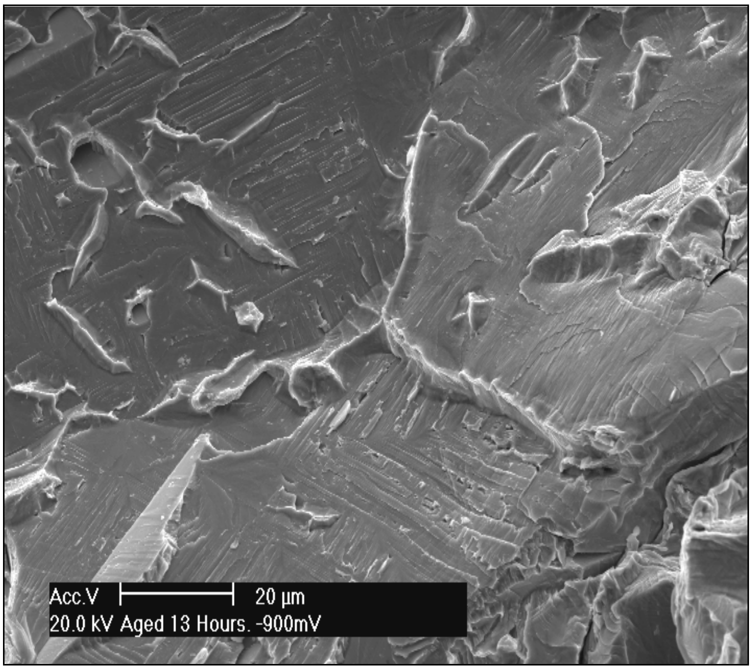

Fig.(1.7) Fracture surface of specimen aged for 13h at 475ºC .

Table. 1.1 : The chemical composition of the as-received material .

Element	Wt%
C	0.02
Si	0.22
Mn	0.58
P	0.021
S	0.001
Cr	25.12
Mo	3.55
Ni	6.90
W	0.54
Cu	0.59
Fe	Bal