GRAPHITISATION IN TYPE A201 CARBON STEEL IN PETRO-CHEMICAL PLANT AFTER LONG TERM SERVICE

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Graphitisation is a process of microstructural degradation whereby cementite in steels breaks down to the equilibrium components of iron and graphite. The phenomenon was first observed in 1943 and remains of major concern to both the power and petro-refinery industries because the presence of graphite may be detrimental to the properties of steel and may thus limit the remaining life of components. This paper investigates the significance of graphitisation in three petro-refinery vessels made from A201 carbon steel. A variety of mechanical testing and metallography is reported and it is concluded that the main effect of dispersed graphite nodules, in the form of random graphite and weld isotherm graphite (WIG), is to reduce the stress bearing cross-section of materials. The significance of the dispersed WIG was considerably less deleterious than the continuous eye-brow or necklace graphite, reported by other authors. Comments are made concerning the process of remaining life assessment of the vessels via replication and mechanical testing.

INTRODUCTION

Concern about the remaining life of Fluidised Catalytic Cracker Units (FCCUs) arises from the age of vessels and the possibility that operating conditions may have exceeded the original design envelope. Metallurgical evaluation and life assessment of a FCCU are used to determine the extent of materials deterioration during service and the possibility of continued safe service. Because of the large capital investment associated with FCCUs, life extension of equipment presents an attractive proposition. The main issues controlling the remaining life of vessels are safety factors, economic incentives, avoidance of unexpected failures, hazardous situations and extended plant shut-downs. Forced shut-downs for repair are expensive, the estimated cost for loss of production from an unscheduled shut-down is in excess of A$10K/hr[1].

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With time in elevated temperature service the initial pearlitic microstructure of carbon steels transforms to one or both of two stable forms, spherodised pearlite and graphite. Both processes are known to cause a degradation in mechanical properties and can limit the life of Fluidised Catalytic Cracker Units (FCCUs). The graphitisation rate increases with temperature and graphitisation occurring preferentially to spheroidisation at lower temperatures. WIG is so named because it forms chains or necklaces along isotherms which have reached the AC1 temperature during welding (figure 1).

Concern about graphitisation has existed since a major piping failure in 1943 was attributed to segregated "eye-brow" graphitisation (2,3). In refinery equipment the first case of graphitisation in carbon steel was reported in 1951 (4). Material changes from C to C-Mo to Cr-Mo steels and cautious operation and maintenance of components has reduced the level of concern and amount of related research. In response to the concern generated by early failures, graphitisation related research was conducted in the 1940's, '50s and '60s. Data collected by Wilson *et al* (5) on 554 samples of carbon steel from refinery plant is shown in figure 2. 45% of A201 samples were found to be graphitised, although there were no cases of eye-brow graphitisation. Furthermore, only 6.1% of the total (A201 and A285) had sufficient graphite to impair ductility in a bend test. It was found that the higher the service temperature the greater the susceptibility to graphitisation, severe graphitisation requires exposure to temperatures greater than 500°C. Graphitisation in specimens was classified according to the scheme of Thielsch *et al.* (6) in which the graphitisation is described as nonexistent, mild, moderate, heavy or severe (figure 3). The concern of graphitisation for vessels is illustrated by the fact that the ASM Committee (7) for refinery applications maintains that graphitised steel should be used at stress levels that are "somewhat less" than those given in the ASME Code for materials in the virgin condition. Ibarra (8) maintained that the presence of segregated or eye-brow graphite requires the vessel to be removed from further service. More recent observations by Port and Mack (9,10) of graphitisation have regenerated concern since they show the unexpected occurance of a form of non-weld related planar graphite which occurs in deformation bands resulting from plastic strain. Such graphitisation has resulted in the brittle, in-service failure of type T1 tubing at reheater headers in power generation boilers which necessitated extensive replacement of C-Mo and plain C steel tubing(11).

This paper describes work undertaken on three pressure vessels from Australian refineries where graphitisation was present and life assessment was of interest.

CASE STUDIES

Material was available from 3 refinery reactors, designated A, B and C. Samples were either removed from the vessels at (a) the location judged to experience the most onerous conditions of temperature, (b) where the greatest amount of spheroidisation and graphitisation was found by non-destructive metallographic inspection or (c) where material was made available as a result of repairs (due to erosion). Service conditions for the three vessels are summarised in table 1.

TABLE 1. Reactor Operating Conditions

Reactor	Age (yrs)	Plate (mm)	Temp. 1 (°C)	Pressure 1. (MPa)	Temp. 2 (°C)	Pressure 2. (MPa)
A	36	50	523	0.21	510	0.316
B	27	19	500	0.14	510	0.17
C	33	33	521	0.138		

All vessels were designed in accordance with ASME Boiler and Pressure Vessel Code Section VIII (1950's versions). The vessels were constructed to the relevant SAA Boiler Code of the time from rolled A201 (Grade A and B) plates which were subsequently double V butt welded longitudinally then circumferentially. In the case of reactor B, 2mm of stainless steel overlay was deposited prior to ring construction and INCOWELD capping was used to finish off the A405 cladding at DVB weld locations. The composition and microstructures of the 3 steels (table 2) are typical of grade A201 materials supplied in the 1950's with Si and Al being added as de-oxidising agents. However, Al is now known to strongly promote graphite nucleation, whilst Cr retards graphitisation because Cr acts as a sink for free carbon in ferrite (12).

TABLE 2. Chemical Composition (wt%)

Reactor	C	Si	Mn	P	S	Ni	Cr	Mo	Al	Cu	Sn
A	.13	.38	.62	.038	.033	.09	.11	.04	.038	.23	
B	.21	.31	.75	.01	.023	.05	.04	.01	.02	.08	
C	.12	.31	.54	.026	.033	.04	.06	.01	.033	.16	.021

Metallography

Cross-sections of the plates and welds were cut from the samples and were prepared metallographically. Materials had similar microstructures and were comprised of a mainly ferrite microstructure in which spheroidisation, of what was originally pearlite, was near complete and graphite nodules of up to 0.5mm diameter were present. The grain size, hardness and degree of spheroidisation as per Toft-Marsden (13), is summarised in table 3. Carbides were found almost entirely at grain boundaries and largely at grain boundary triple points. Graphite was concentrated on the planes where pearlite had previously banded and around welds. The largest graphite nodules were randomly dispersed between the band of WIG and the weld. The diameter and number of graphite nodules decreased on moving away from the weld. When viewed in section, WIG was found to be a more diffuse feature than was suggested by surface replication. No evidence of cavitation was found in any as-received material. The microstructure of material from vessel B was more complex because of the presence of stainless steel cladding. Carbon migration was observed where stainless steel was overlaid on the carbon steel. A high Ni layer between the cladding and the base metal had hardnesses up to 232Hv.

TABLE 3. Microstructural Characteristics

Sample	Hardness* (Hv20)	Grain Size+ (μm)	Toft-Marsden Spheroidisation
A	120 - 140	30	C - D
B	124 - 140	20	D - F
C	114 - 120	27 - 40	D - F

*- measured on cross section samples +:- mean linear intercept grain size

Mechanical Testing Program

Charpy testing was carried out on specimens from plate and cross weld samples with the notch in one of two orientations in order to investigate the deleterious effect of the graphite. Specimens were etched before notching was carried out to allow accurate location of the notch with respect to the microstructure. In total, 20 specimens for vessel A, 15 from B and 81 from C were tested, mainly at ambient temperature.

Specimens with the notch in the A/ST orientation generally exhibited high impact values (>100J). Energy was dissipated in delaminating the rolling structure of the plate along which bands of graphite had formed. As the primary crack advances secondary cracking (via delamination) blunts the crack. Conversely, specimens with a ST/A notch resulted in lower energy values (lowest recorded value 40J) and more brittle fracture surfaces. WIG samples with ST/A orientation failed with typical impact energies of 30J and showed graphite on the fracture surface. More detailed examination showed that the fracture surface had some ductility (evidenced by equiaxed dimples) and regions of stretching could be seen around deep dimples. Large dimples (up to 1mm diameter) occurred at graphite nodules and smaller (up to 3μm diameter) at large spheroidised carbides. Examination of the different regions of the fracture surface showed that larger dimples occurred in regions close to the notch where fracture had occurred in a more ductile manner. Where the fracture was slightly more brittle, dimpling associated with graphite nodules was shallow and particles of graphite had fractured. Specimens from steel B which contained cladding had lower impact energies because of the presence of hard, brittle cladding materials.

Tensile Testing was carried out on specimens prepared from cross-weld material with the specimen longitudinal axis both parallel and transverse to the plate rolling direction (the direction of hoop stress in the vessel).

The lowest recorded yield and tensile stresses were 198 and 373MPa respectively for transverse specimens and 211 and 373MPa for longitudinal specimens. Elongation values were generally in excess of 30%, the lowest recorded value was 29%. Room temperature yield data were similar to the original test certificate data, but UTS values have dropped by up to 20%. Cross weld specimens tested at 510°C gave yield and UTS values around 120 and 190MPa respectively, ie. well in excess of the required values set in ASME Section VIII and BS5500 code for allowable stress limits in design (70MPa).

TABLE 4. Parent Plate Tensile Test Data*

Sample	Yield Stress (MPa)	Tensile Stress (MPa)	El (%)	RA (%)
A	274	419	38	67
B	238	373	36	69
C	232	380	35	71
ASTM Spec.n	-	380	29	-

* Average of longitudinal and transverse (at least 2 tests)

Metallography on the specimens tested at both ambient and elevated temperature revealed that plastic flow had occurred around the graphite particles. Cross weld specimens failed in the HAZ because the larger graphite nodules of this region result in a smaller cross section of load bearing metal. The maximum reduction of cross sectional area was estimated as 10%.

Cyclic Tensile Testing was carried out at elevated temperatures on material from vessel B to determine whether low cycle fatigue cracks would initiate at graphite particles. Although some literature is available to describe the fatigue properties of A201 materials (14), none were found which deal with graphitised steels. A series of interrupted, stress controlled, fatigue tests (with R = 0) were carried out on both conventional test specimens and a through thickness "full size" plate specimen. No cracking was associated with graphite particles in the conventional specimens cycled at stress levels up to the yield stress. The through thickness specimen was tested at 400 and subsequently 510°C. Replication metallography was performed after 30 and 100 cycles were carried out and the test was then resumed at an elevated stress. No fatigue damage was found to be associated with graphite particles. The full size specimen was finally broken by tensile overload, the ductility differences between the various components of the vessel wall was demonstrated clearly.

Creep Testing involved both parent plate and cross-weld samples. The gauge length in XW specimens was located in the through thickness location with the most graphite because such material would be representative of material with the "worst case properties". A number of data sources were used (15,16,17,18) to determine the average properties of virgin A201 plate and weld materials to allow comparison with rupture data of the ex-service material used in the present study. The lower bound of creep rupture properties estimated from the literature together with creep data of material from the three FCCUs are presented in figure 4.

It was found that tests carried out at higher stresses and temperatures failed in a more ductile manner than other tests and because creep failure in service would occur in a low ductility manner (cavitation) less emphasis was placed on this data when performing extrapolation for life assessment. The longer duration tests were judged to be more representative of the likely failure mechanism in service (19). Generally, fracture occurred in the grain refined weld metal approximately 10 grains from and parallel to the fusion line. The reduction of area was greater in the HAZ than in the weld metal. Although cavitation was observed in HAZ regions it was not seen in the parent plate except close to the fracture surface. Recrystallisation was observed in a number of specimens at the fracture surface and at specimen shoulders. The graphite nodule size of creep specimens increased during creep rupture testing eg. in steel B from 7 to 12μm after 2366 hours at 630°C. Accelerated aging during creep/rupture testing indicated that the extent of graphitisation will increase with further service but it is unlikely that the graphite will change from its present nodular form to some sort of continuous film.

Bend Testing is the mechanical test used most commonly to evaluate the level of graphitisation in welded joints. The specimen is bent until cracking occurs and the angle at which the cracking occurs reflects quantitatively the severity of graphitisation. A number of samples were bent, including those containing WIG, using full transverse section, 3mm thick specimens. No cracking occurred in bend specimens in materials A or C and only at the cladding/base interface and within the cladding for samples of material B. A number of tests on material B were interrupted and specimens examined after bending through 30, 110 and 180°. After 30° the cladding had fractured at one location and disbonding of the cladding/interface had begun. After 110° the cladding fracture had extended whilst the A201 remained intact. Minor tearing was found to be associated with a small percentage of graphite nodules at 180°. The presence of the graphite resulted in two deformation mechanisms; if sufficient strain was transmitted across the graphite/metal interface then large nodules of graphite cracked. Conversely, if the nodule decohered from the metal, tearing of the metal matrix occurred around the particle as the interface opened up. In many instances, however, tearing was not associated with the graphite nodules but did occur in the base metal away from the nodules. In clad specimens, micro-cracking initiated at the cladding/base metal interface hard layer and propagated either along the interface or by brittle fracture into the cladding. The A201 in the region of the cracks was sufficiently ductile to undergo plastic deformation with no cracking.

DISCUSSION

Metallography

The fact that the WIG was more diffuse when viewed in cross-section allayed fears that it was a near-continuous planar feature. This is contradictory to the work of Kersner *et al.*(20) who maintain that if graphitisation is detected at the surface then it can be expected to exist throughout the material and that the observed degree of surface graphitisation is representative of the general condition of the plate. While their work supports the use of surface information gained through replication as a measure of the degree of graphitisation throughout the metal, the present findings indicate that surface replication may give an unduly high impression of the severity of WIG. Conversely, the extent of random graphitisation in the plate was worse than was suggested by surface replication. The problem of assessing graphitisation by surface replication is that graphite nodules in the plate are concentrated along layers oriented parallel to the rolling direction and thus the degree of graphitisation observed is highly dependent on the grinding depth used in the surface preparation.

However, surface replicas will be an effective indicator of the form of the graphite in the replica region, ie. will allow the investigator to distinguish the less problematic nodular graphite from graphite in the form of films. In material B, cracking at the cladding weld/base metal interface observed in bend test specimens and during final overloading of the full size cyclic tensile specimen highlights the susceptibility of this interface to cracking. The observation of shallow dissimilar metal weld cracking at the inner surface of the plate/cladding interface is evidence that crack initiation occurs where materials properties are most varied and load shedding occurs and that this location may well be critical in limiting the life of the vessel.

Mechanical Testing

The bend tests show that the ductility for high strain (slow strain rate) tests across the WIG was higher for all three materials compared to industry experience where low ductilities obtained during bend tests (bend angles < 30°) have been correlated with failure of weld joints and graphitisation (10). The extent of graphitisation revealed by metallography of the present materials (classified as mild) would have been expected to lead to cracking at a bend angle between 60 and 90°, however, none of the bend samples showed cracking (except at the stainless overlay) even on bending in excess of 90°.

The lowest impact values were recorded for WIG material notched in the ST/A direction and we conclude that the presence of graphite is therefore embrittling to the steel. However, even with the lowest recorded impact value of 30J, the material still meets the requirement of ASME Section VIII Division 1 (Table UG-84.1 1984), of a minimum value of 18J (for the strength of the virgin materials). Examination of the Charpy fracture surfaces showed that the large graphite nodules (rather than WIG) dominate rapid crack propagation.

Tensile testing showed that yield values are similar to the original test certificate data, but the UTS values have decreased by up to 20%. This indicates that, although graphitisation has occurred, the vessels will have the same resistance to plastic collapse as envisaged in the original design. However, it is likely that the remaining life of the vessels in question is limited by creep rather than tensile properties. Furthermore, cracks did not initiate at graphite particles either during static or cyclic tensile testing because metal "flowed" around particles. Metallography showed that the graphite nodules play an important role in the failure of specimens during mechanical tests such as tensile and Charpy tests. The bend test specimens showed very little tearing and tearing was no more likely near nodules than in base metal away from nodules. During tensile testing the role of the graphitisation in reducing strength was mainly in reducing the net section available for carrying load. The volume fraction of the graphite in the current materials was such that microvoid coalescence between particles does not occur during tensile tests as the metal was able to deform plastically. However, as noted in the introduction, continuous WIG is much more deleterious than random graphitisation and has resulted in dramatic service failures reported elsewhere. The main reasons for the reduction in tensile strength below the original properties was spheroidisation, the dissolution of the fine carbides that give the material its strength.

The plate material has better rupture properties than the cross weld samples, however, failure was associated with HAZ regions rather than directly with graphite nodules. The volume fraction of graphite in the current materials is low and the creep rupture times, although lower than mean A201 data are still in excess of lower bound data. Due to the reduced matrix strength (because of spheroidisation) the cavity growth process is accelerated and the graphitised material exhibits both a reduced rupture strength and rupture ductility. However the observed ductilities were usually only a few percent lower than those reported for ASTM tests on virgin A201 plate, and suggests that the presence of graphite is not significantly creep embrittling. The cross-weld specimens were found to have a significantly lower ductility relative to the plate materials because HAZ creep crack initiation and propagation occurred due to differences in weld, HAZ and plate creep ductility. In material B, cracking at the cladding weld/base metal interface observed during both the bend tests and during the final overloading of the full size cyclic tensile specimen highlights the susceptibility of the interface to cracking. The difference in the ductilities of the cladding, plate and DVB weld are evident and suggests that the operational stress state in the various components of the shell and the possibility of disbonding of the cladding should be considered in remaining life studies.

CONCLUSIONS

- Microstructural investigation of A201 carbon steel material from three refinery FCCUs indicated the original pearlitic structure had broken down to ferrite, graphite and spherodised carbides. In the HAZ graphite occurred as a band of weld isotherm graphite (WIG) that ran parallel to the weld and as randomly distributed nodules. In the parent plate graphite nodules are concentrated along layers oriented parallel to the rolling direction.
- Mechanical testing and microstructural examination of failed specimens has shown that the effect of nodular graphite is less alarming than previously indicated in the literature, however, "eyebrow" WIG was not observed in the present study and is undoubtedly more deleterious to mechanical properties than random, nodular graphitisation. The main effect of graphite nodules during mechanical testing was to reduce the load bearing section of tensile and creep specimens and to act as initiation sites for tearing during impact testing.

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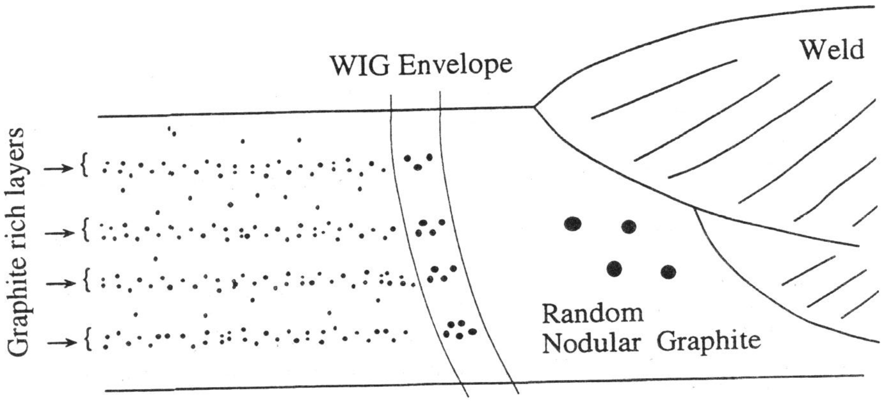

Figure 1. Schematic of graphite formation around weld site. Weld Isotherm Graphite (WIG) forms as an envelope of nodules or as a film.

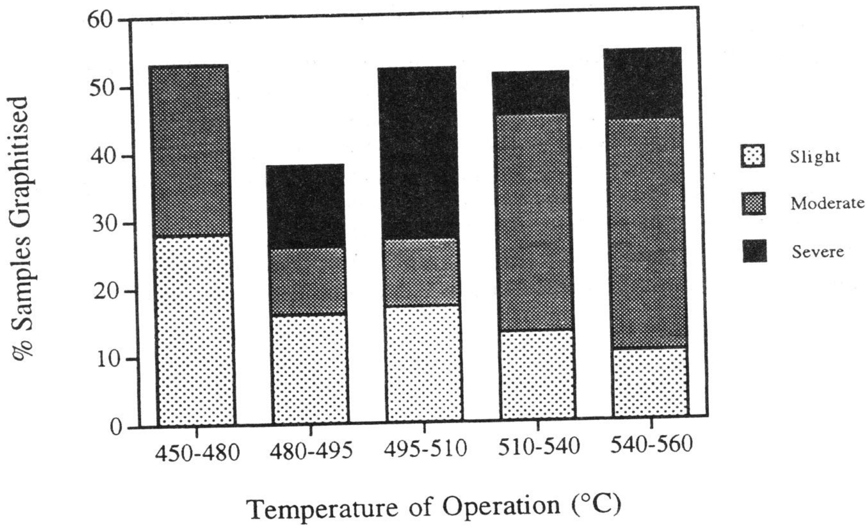

Figure 2. Welding Research Council survey of graphitisation in petro-refining equipment (Wilson et al. Ref 11)

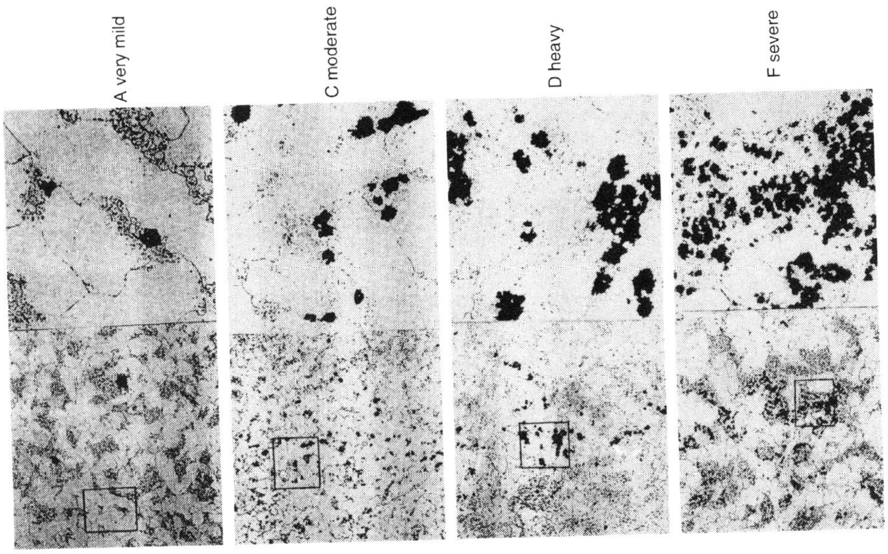

Figure 3. Examples of various degrees of graphitisation.
[after Thielsch et al. (10)]

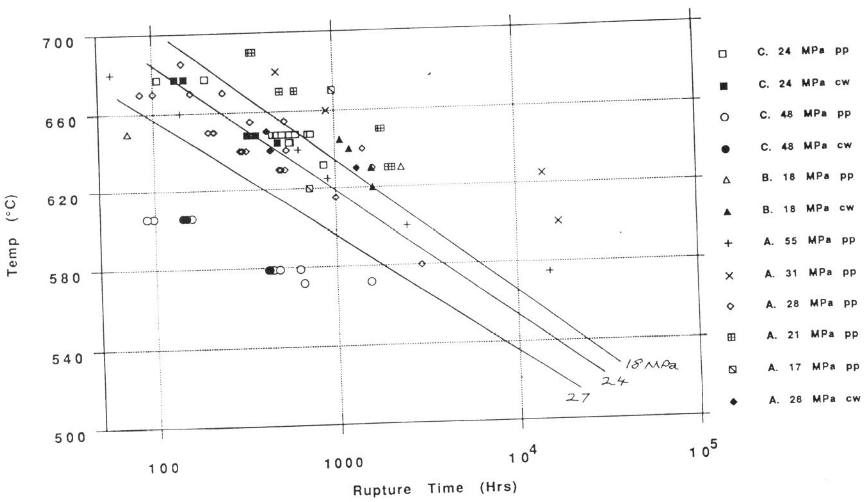

Figure 4. Collection of creep rupture data for the current three graphitised A201 steels, together with estimated lower bound limits to literature data.