JOURNAL OF MATERIALS SCIENCE 24 (1989) 2833–2838

The urea nitrocarburizing of cast irons with various graphite morphologies

K. C. CHEN, M. H. HON
Department of Materials Engineering, National Cheng Kung University, Tainan, Taiwan, Republic of China

The urea nitrocarburizing of nodular and compacted graphite cast irons has been investigated. Optical microscopy, EDAX analysis and hardness measurements have shown that a thick compound layer with high contents of nitrogen and silicon is formed, and a greater hardness in the area around the graphite beneath the surface is observed. The compacted cast iron with interconnected graphite has been found to exhibit a smaller effective diffusion zone, and formed Si_3N_4 precipitates within the hardened area. The nitrided nodular cast iron exhibited a higher fatigue strength increment and a smaller elongation decrement than that of compacted cast iron. Most fracture surfaces of compacted cast iron were found to be granular whereas the nodular cast iron was characterized as transgranular cleavage.

1. Introduction

Surface hardening of ferrous components by soft-nitriding (ferritic nitrocarburizing) techniques has been successfully used to improve the wear resistance and fatigue strength [1–4]. Takase, Nakamura, Takada and Kita [5] have found that the wear resistance and fatigue strength of nodular graphite cast iron can be increased by salt-bath nitrocarburizing (Tufftride). Lee, Ikenaga, Nakamura and Okabayashi [6] also found that the resistance of gas nitrocarburized nodular cast iron to rolling wear was significantly improved by using a mixture of NH_3 and RX gas. There is no specific information available concerning the behaviour of compacted graphite cast iron after nitrocarburizing. The compacted graphite has a stubby blunt-edged flake morphology that is interconnected within the eutectic cell. In the belief that graphite morphology may influence the diffusion of nitrogen in the iron and then affect the fatigue strength and the fracture morphology, one nodular cast iron and two compacted cast irons were urea nitrocarburized and then studied extra carefully.

Urea nitrocarburizing, which uses a dissociated urea atmosphere, can eliminate the problems of the disposal of cyanide salts and are environmental hazards of the Tufftride method and confer the benefits of the more easily controlled atmosphere and shorter treatment times (for the same case depth) as compared to the mixed gas method. The urea dissociates at temperatures of between 500 and 600° C according to the reaction [7]

$$CO(NH_2)_2 \rightarrow CO + 2\dot{N} + 2H_2$$

The nascent nitrogen promotes a nitriding reaction, while the carbon monoxide provides the nascent carbon to carburize the material surface. Consequently, a compound layer of $Fe_{2-3}(C, N)$ and $Fe_4(C, N)$ is formed on the surface to bring about beneficial tribological properties. A subsurface nitrogen-rich diffusion zone, which contains nitride precipitates, is also developed which increases the fatigue strength.

2. Experimental procedures

2.1. Materials and specimen preparation

The chemical compositions of the three different cast irons are listed in Table I. They include one nodular graphite cast iron and two compacted graphite cast irons with 85% and 70% compacted graphite, respectively. The castings were normalized at 900° C for 1 h to obtain a significant amount of pearlite. Urea nitrocarburizing was carried out at 570° C for 90 min. Table II shows the specimen designations after various heat treatments.

2.2. Testing and investigation procedures

The specimens for tensile properties and hardness measurements were machined and tested according to ASTM E8 and ASTM E92, respectively. Case depths

TABLE I Chemical compositions of the cast iron specimens

Specimens	Elements					
	C (wt %)	Si (wt %)	Mn (wt %)	S (wt %)	P (wt %)	Fe (wt %)
Nodular Iron	3.55	2.45	0.35	0.01	0.02	Balance
Compacted Iron 1	3.78	2.41	0.06	0.01	0.03	Balance
Compacted Iron 2	3.45	2.68	0.11	0.01	0.03	Balance

0022–2461/89 $03.00 + .12

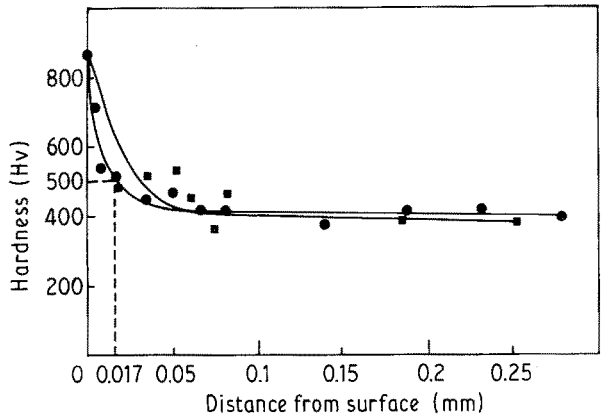


Figure 1 Hardness distribution of DNS. (■ near to a graphite, ● matrix).

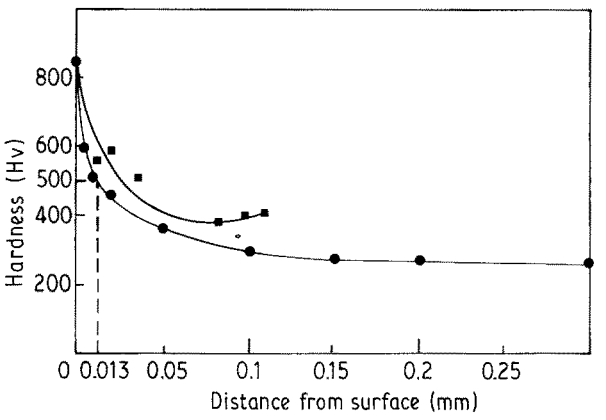


Figure 2 Hardness distribution of C2NS. (■ near to a graphite, ● matrix).

TABLE II Specimen designations of various heat treatments

Designations	Materials and heat treatments
DN	Nodular Cast Iron, Normalized.
DNS	Nodular Cast Iron, Normalized and Urea Soft-Nitrided.
C1NS	Compacted Cast Iron 1, Normalized and Urea Soft-Nitrided.
C2N	Compacted Cast Iron 2, Normalized.
C2NS	Compacted Cast Iron 2, Normalized and Urea Soft-Nitrided.

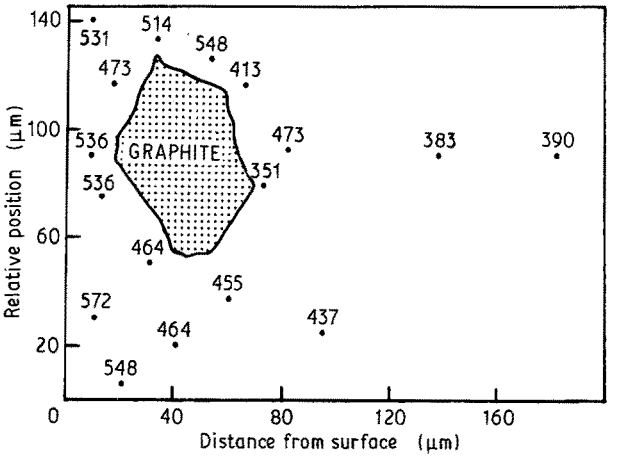


Figure 3 Microhardness profile of DNS.

were measured as the depth harder than Hv 500. The fatigue strength was determined using a rotating-beam reverse-stress testing machine. Impact testing was conducted using a 45° V-notch charpy impact testing machine.

The compound layer was investigated by optical microscopy. The etching solutions used were 4% picral and/or 5% Nital. The phases of the compound layer and diffusion zone were determined by X-ray diffraction (Fe Kα).

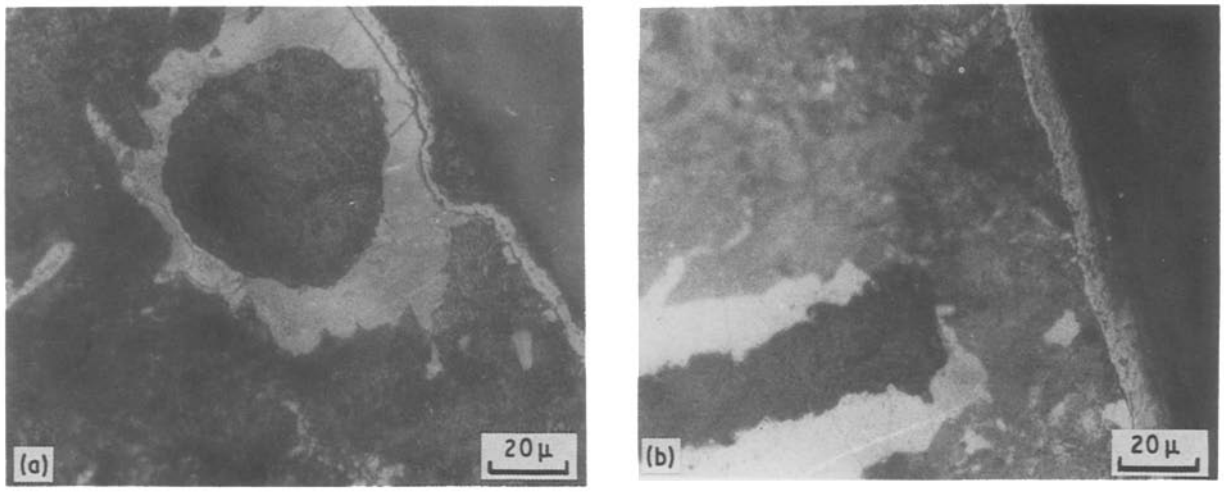
Scanning electron microscopy (SEM) was used to analyse the fracture characteristics of fatigue and impact specimens. Elemental distribution mapping. line scanning and wavelength dispersive analysis were used to determine the distribution of nitrogen, silicon and carbon within the compound layer and diffusion zone.

3. Results and discussion

The mechanical properties are tabulated in Table III. The tensile strength, hardness, fatigue strength and wear resistance have been found to increase while their elongations and impact values have been found to decrease by urea nitrocarburizing. The case depth observed on nodular cast iron (17 μm) is larger than that on compacted cast irons (14 μm for C1NS and 13 μm for C2NS). The hardness distribution between the surface and a graphite and the microhardness profile of matrix for the DNS and C2NS specimens are presented in Figs 1 and 2, respectively. The results of microhardness measurements in the area around the graphite underneath the surface of the DNS specimen are shown in Fig. 3. It is apparent that the hardnesses around the graphite are higher and the case depth is larger. All the specimens have formed a compound layer of 6 μm at their surface as measured in Fig. 4. A thicker surface compound layer is observed around the graphite. The compositional profile of the specimen DNS, which is determined by WDS analysis,

TABLE III The mechanical properties of cast iron specimens

Properties	Specimen				
	DN	DNS	C1NS	C2N	C2NS
Tensile strength (kg mm^{-2})	65.8	67.9	—	44.1	45.5
Elongation (%)	9.7	8.0	—	3.5	1.8
Impact values (kg m cm^{-2})	0.70	0.58	0.46	0.64	0.52
Wear loss (mg)	6.5	1.5	1.4	7.0	1.4
Surface hardness (Hv)	375	880	825	270	850
Case depth (μm)	—	17	14	—	13
Fatigue strength (kg mm^{-2})	23.6	31.9	—	20.0	22.1



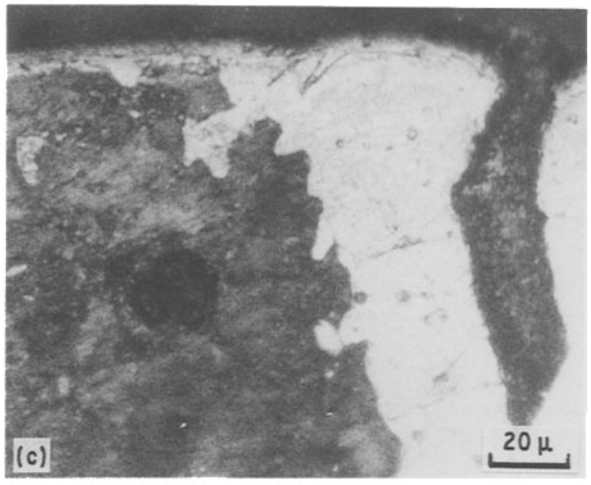
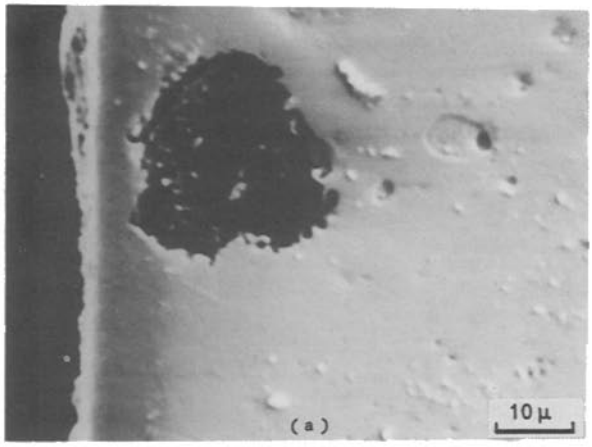
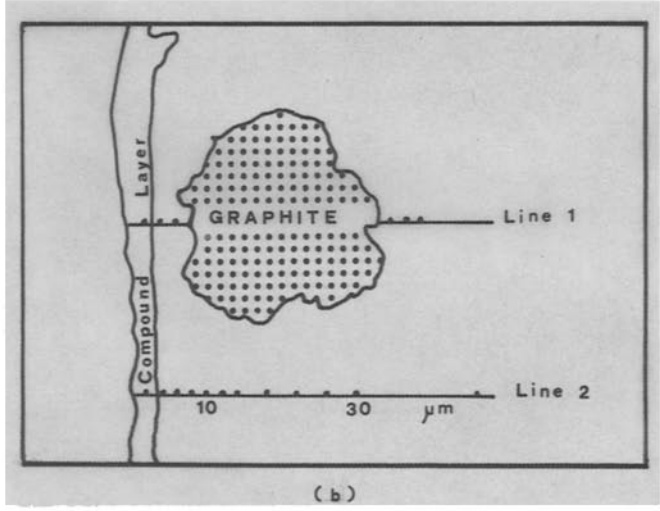
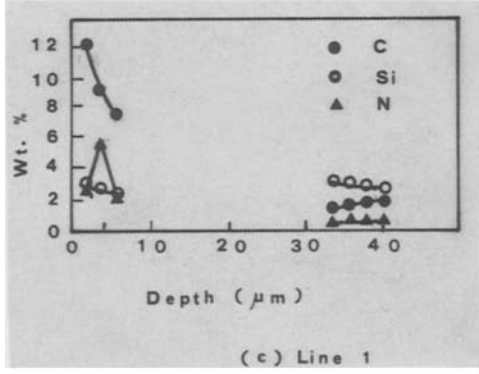


Figure 4 The optical metallography of irons. (a) DNS, (b) CINS, (c) C2NS.

is given in Fig. 5. With respect to the nitrogen content, which is relatively large near the surface and quite small behind the graphite, the diffusion of nitrogen seems to have been retarded by graphite. By defining the case depth as the sum of the compound layer and the effective diffusion zone, the compacted graphite cast iron with the interconnected graphites has exhibited a smaller effective diffusion zone (8 or 7 μm) than nodular graphite cast iron (11 μm). As a result of nitriding, a higher fatigue strength increment (38%) for the nodular cast iron than for the compacted cast iron (20%). It is postulated that the Si_3N_4 precipitated







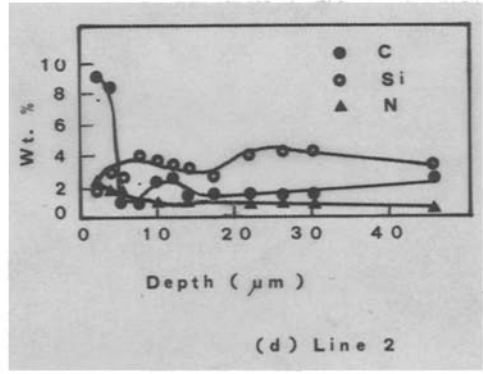


Figure 5 WDS analyses of DNS. (a) SEM metallography. (b) The measuring positions of WDS analysis. (c) The elemental distributions along Line 1. (d) The elemental distributions along Line 2.

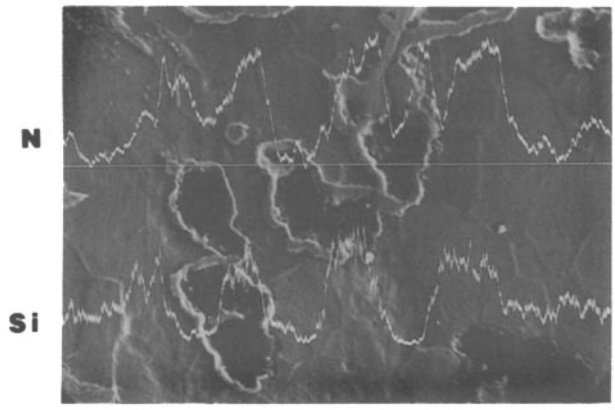


Figure 6 Nitrogen and silicon line scanning in the diffusion zone of the C2NS.

in a nitrogen-rich diffusion zone is probably responsible for the fatigue strength improvement. The larger the effective diffusion zone, the more the fatigue strength is increased.

Line scans of nitrogen and silicon in the diffusion zone of a C2NS impact specimen, which has had 7 μm carefully polished off the surface opposite the notch, are given in Fig. 6. It is found that both elements are enriched near the interface of the matrix and graphite. Fig. 7 shows that the region around the graphite has higher nitrogen and silicon contents and lower carbon content in DNS specimens. The Si_3N_4 precipitates were identified in the salt-bath nitrocarburized nodular graphite cast irons by using transmission electron microscopy techniques [5, 8]. It seems reasonable to suggest that Si_3N_4 precipitates are also present in the matrix–graphite interface, thus embrittling the ferrite matrix and the grain boundaries. This leads to the intergranular fracture characteristics of compacted graphite cast irons as is shown in Figs 8 and 10. On the other hand, from Fig. 9, it can be seen that the fracture surfaces of nodular graphite cast iron exhibit mostly transgranular cleavage or quasi-cleavages although some intergranular fractures at the notch edges of impact specimens were also observed. This explains the larger elongation decrements and lower impact values of urea nitrocarburized compacted graphite cast iron as is indicated in Table III. Previous investigations of fracture in both compacted [9] and nodular [10–12] graphite cast irons have indicated that crack initiation occurred in the ferrite–graphite interface, and that crack propagation appears to be in a brittle cleavage mode, i.e. transgranular in ferrite and interlamellar in pearlite. The mode of fracture

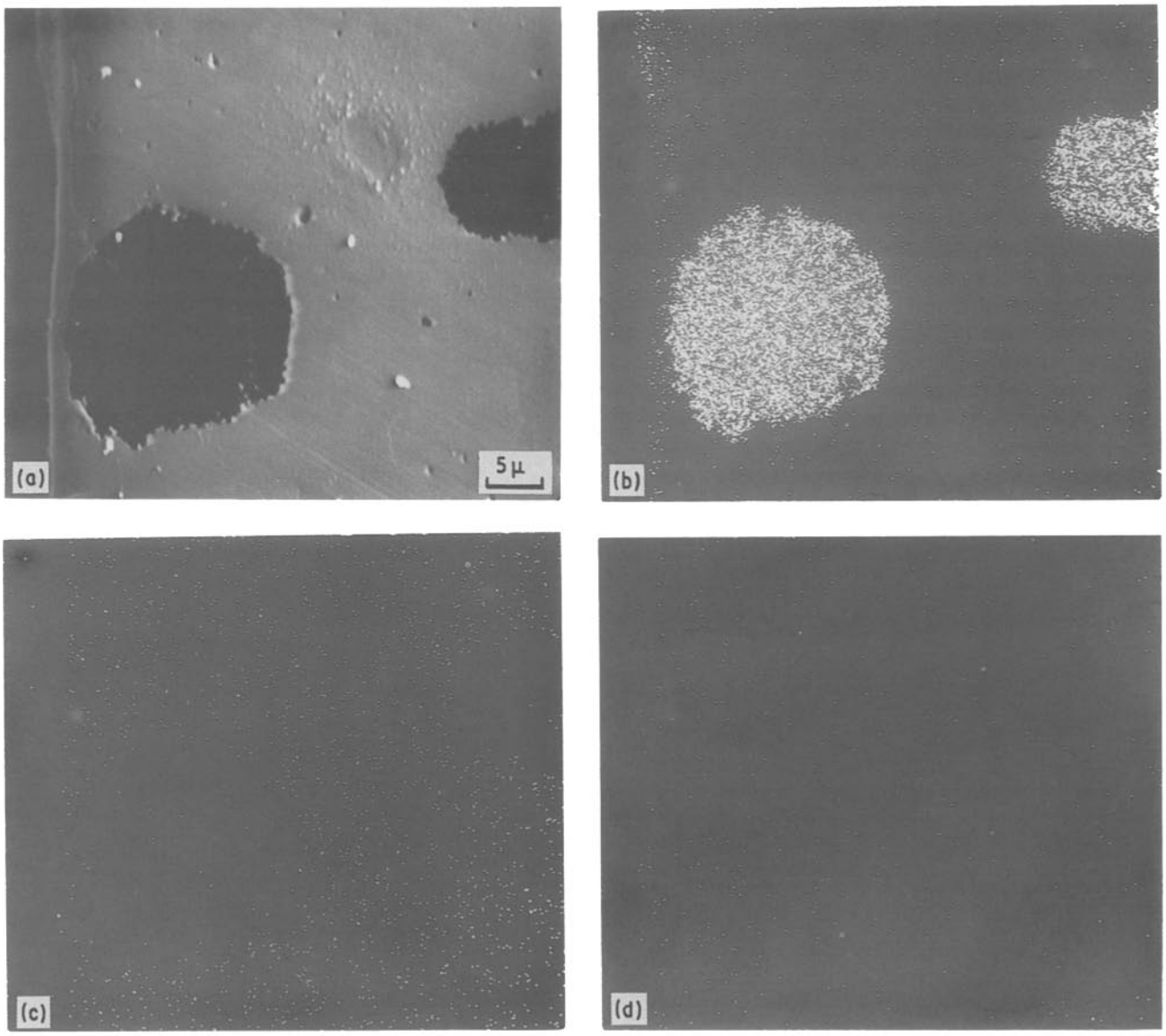


Figure 7 Mapping of DNS. (a) SEM metallography, (b) carbon, (c) silicon, (d) nitrogen.

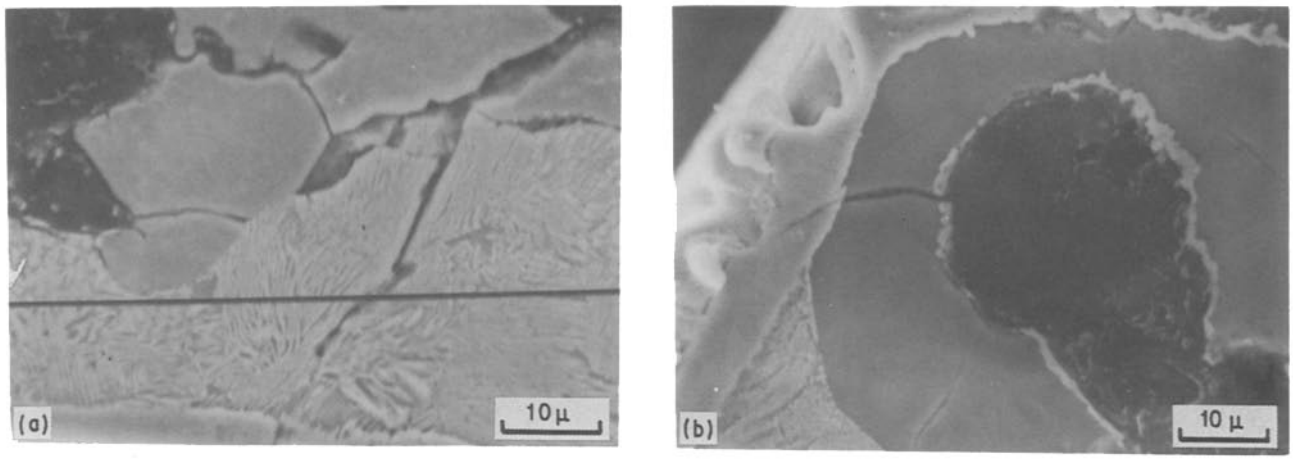


Figure 8 SEM metallography of C2NS. (a) Cracks in the ferritic matrix and pearlitic lamellae. (b) Cracks in the ferritic shell.

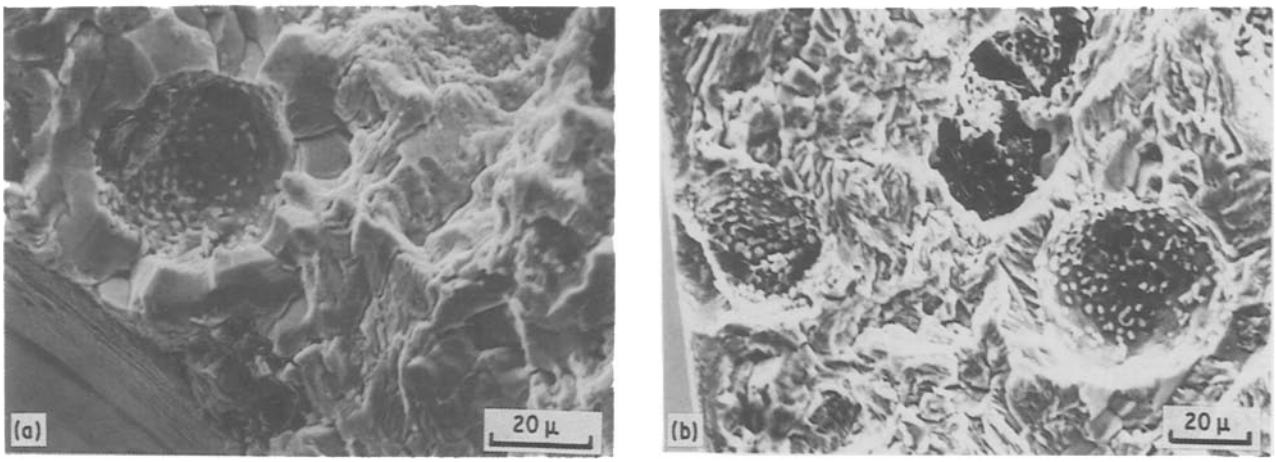


Figure 9 Fractography of DNS. (a) Impact specimen, (b) Fatigue specimen.

appeared to be independent of strain rate and notch sensitivity. In the present study, after urea nitrocarburizing, the fracture of compacted graphite cast irons have been found that the cracks propagate along the grain boundaries of the ferritic shell and the cleavage planes of the fine pearlite lamellae as shown in Fig. 8. This intergranular feature in the ferritic matrix is attributed to the embrittlement due to Si_3N_4 precipitates in the grain boundaries of ferritic shells. The similarity of impact and fatigue fracture surface indicated that the fracture is unaffected by strain rate. The nodular graphite cast iron with only some intergranular fractures in the ferritic shell of the impact specimen is notch sensitive. From the X-ray diffraction analyses of Figs 11 and 12, it can be seen that both the ε and γ' carbonitrides are present in the compound layer of DNS and C2NS specimens. From Table III, the wear losses are 6.5 and 7.0 mg before urea nitrocarburizing and 1.5 and 1.4 mg after nitriding. The wear resistance improvement is due to the formation of a hard compound layer on the specimen surface. The wear characteristics are not affected by the graphite morphology.

4. Conclusions

The conclusions are as follows.

(1) The tensile strength, fatigue strength, hardness and wear resistance of cast irons are increased while

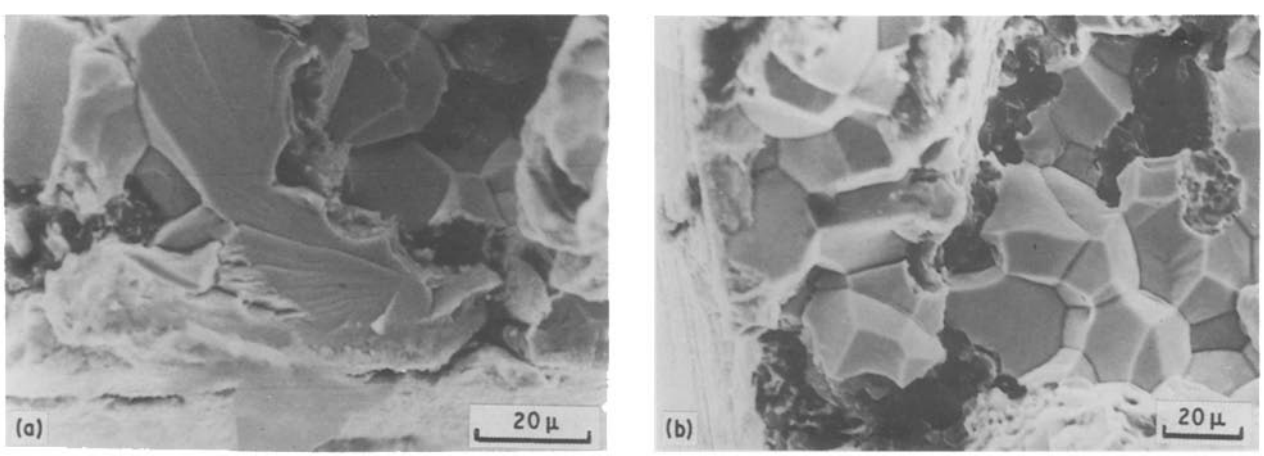


Figure 10 Fractography of C2NS. (a) Impact specimen, (b) Fatigue specimen.

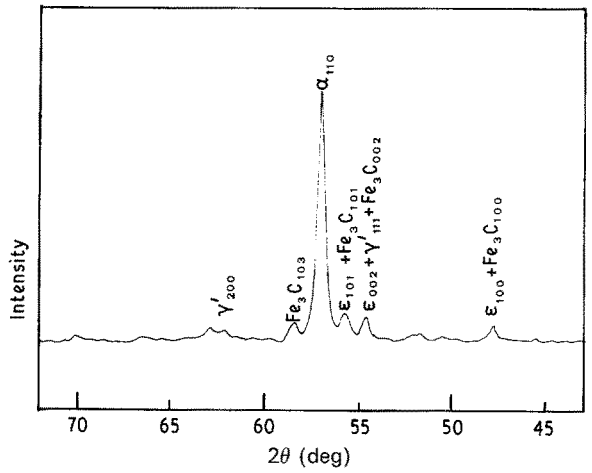


Figure 11 X-ray diffraction curve of DNS.

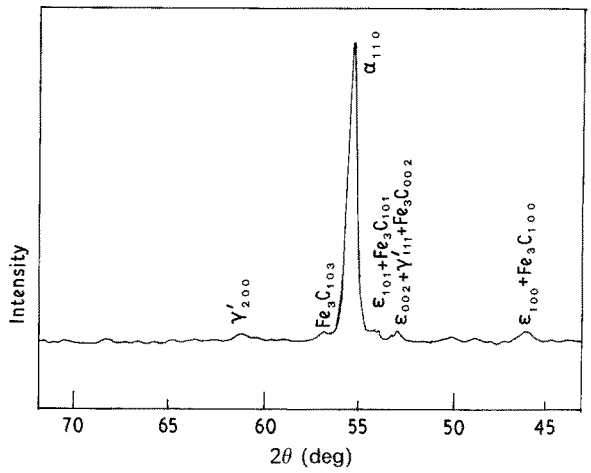


Figure 12 X-ray diffraction curve of C2NS.

their elongation and impact values are decreased by urea nitrocarburizing.

(2) Compacted graphite cast iron with interconnected graphite exhibits a smaller effective diffusion zone and thus a smaller fatigue strength increment.

(3) After urea nitrocarburizing, the intergranular fracture characteristics of compacted graphite cast irons in contrast with the mostly transgranular cleavage or quasi-cleavage fractures of nodular graphite cast irons have been found. This explains the larger elongation decrement and lower impact value of urea nitrocarburized compacted graphite cast irons.

(4) The improvement in wear resistance is attributed to the formation of ε and γ' carbonitrides in the compound layer of the surface of urea nitrocarburized cast irons. The wear losses have not been affected by the graphite morphology.

Acknowledgement

The authors would like to thank the National Science Council of Republic of China for the financial support of this research under contract number NSC74-0405-E006-17R.

References

1. T. BELL, *Heat Treatment of Metals* **2** (1975) 39.
2. C. DAWES and D. F. TRANTER, *ibid.* **3** (1985) 70.
3. K. BENNETT, Q. WEIR and J. WILLIAMSON, *ibid.* **4** (1981) 79.
4. H. TSUJII, M. YAKUSHIJI, Y. KONDO and M. IKENAGA, *Netsu Shori, Jpn* **26** (1986) 201.
5. T. TAKASE, Y. NAKAMURA, Y. TAKADA and K. KITA, *Imono, Jpn* **48** (1976) 419.
6. J. N. LEE, A. IKENAGA, M. NAGAMURA and K. OKABAYASHI, *ibid.* **55** (1983) 17.
7. L. KIKUCHI and C. ASAKA, *Netsu Shori, Jpn* **14** (1974) 23.
8. T. SASAKI and T. YAMADA, *ibid.* **18** (1978) 9.
9. A. F. HIEBER, *AFS Trans.* **31** (1978) 143–154.
10. J. O. T. ADEWARA and C. R. LOPER, Jr, *ibid.* (1976) 513.
11. *Idem, ibid.* (1976) 527.
12. L. ELDOKY and R. C. VOIGT, *ibid.* (1985) 365.

Received 8 February
and accepted 11 October 1988