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Influence of chemical composition and microstructure on thermal conductivity of alloyed pearlitic flake graphite cast irons

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Thermal conductivity is one of the most important properties of flake graphite cast iron, that decides the transient temperature and thermal stress distribution in the components which are subjected to elevated temperature applications. Such applications include cylinder heads, brake-drums, exhaust manifolds, ingot moulds, hot mill rolls and dies. Thermal conductivity values are experimentally measured in 23 flake graphite cast irons having an identical base iron composition. The irons selected can be classified into two groups: one with high carbon (3.93%) content and another with medium carbon (3.00%) content. The irons are alloyed with commonly used alloying elements such as molybdenum, chromium, vanadium, nickel, tin, antimony, copper and aluminium. Thermal conductivity values are determined up to the temperature range 40 to 500° C and values up to 40 to 700° C are presented by extrapolation. The present work has provided information regarding thermal conductivitiy of flake graphite cast irons which are used for thermal fatigue applications (where the temperature of the component usually reaches a maximum of 700° C). It is concluded that an increased amount of graphite carbon, an increased amount of type A graphite and an increased fineness of graphite increase thermal conductivity. Further, molybdenum increases thermal conductivity appreciably while nickel and copper increase it moderately. Aluminium and silicon considerably reduce thermal conductivity while chromium, vanadium, tin and antimony reduce it moderately.

1. Introduction

Thermal fatigue failure of flake graphite cast irons is caused by cyclic stresses set up in the component due to the constraint on thermal expansion and contraction during thermal cycling. The thermal stresses caused by thermal strains are determined by the temperature gradient in the component, which in turn depends on thermal conductivity of iron.

Thermal conductivity of flake graphite iron is influenced by chemical composition, microstructure and temperature. The values of thermal conductivity of various micro-constituents in grey cast iron, such as graphite, ferrite, pearlite, cementite, etc., differ substantially from each other. For a given matrix, the thermal conductivity of flake graphite cast iron primarily depends on graphite morphology and temperature.

The present study gives experimental data on the thermal conductivity of 23 flake graphite irons. All the irons have the same levels of sulphur, manganese, phosphorus, dissolved gases and trace elements. Eleven irons are designed with different alloy combinations but having identical carbon content (3.93%). The same alloy combinations were also made with a reduced carbon level (3.00%). One iron with a high silicon content (3.73%) is also included in the study.

Thermal conductivity values for all irons are experimentally measured up to the temperature range 40 to 500° C covering practically all of the cases of elevatated temperature industrial applications.

2. Thermal conductivity of grey cast iron

Thermal conductivity of metallic elements is closely connected with its electrical conductivity. The behaviour of thermal conductivity in metallic elements can be predicted by the Wieldmann–Franz–Lorenz (WFL) law [1]. However, in the case of alloys, thermal conductivity cannot be predicted simply on the basis of the electronic component, as is possible with metals. The lattice component also plays an important role in the case of alloys because the mean free path over which the electrons are accelerated depends on imperfections in the lattice such as impurities, interstitial atoms and other defects [1]. The alloy additions are known to have the effect of reducing thermal conductivity in this way.

Thermal conductivity values for the main structural constituents of cast iron at room temperature are given in Table I [2]. It could be seen from the values reported in the table that high carbon iron should have a higher thermal conductivity than a low carbon iron and that the presence of free cementite would lower the thermal conductivity. These observations are found valid in practice but are subject to interferences

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TABLE I Thermal conductivity of main structural constituents of cast iron [2]

Iron	Structural constituent	Thermal conductivity ($W m^{-1} {}^{\circ}C^{-1}$)		
		0–100° C	500° C	1000° C
1	Graphite along *c*-axis	84	–	–
2	Graphite along basal plane	293–419	84–126	42–63
3	Ferrite	71–80	42	29
4	Pearlite	50	44	–
5	Cementite	7	–	–

both by alloying constituents and the physical form adopted by the graphite. Papers published by Donaldson and Sohnchen (cited in [2]) and work carried out at BCIRA show that, of the alloying constituents in the matrix, silicon is the most significant one and lowers thermal conductivity apreciably because it forms a solid solution with iron. Aluminium also behaves in the same way.

A limited amount of work [3] has been reported to determine the effects of varying chemical composition on thermal conductivity of cast iron. In general, according to Angus [2] manganese, nickel and phosphorus slightly decrease thermal conductivity; molybdenum increases it; while there is little influence on thermal conductivity by additions such as chromium, vanadium and copper. The large values of thermal conductivity reported by Donaldson (cited in [2]) and Bertodo (cited in [3]) are less useful in determining the influence of chemical composition on thermal conductivity of cast irons. This is because Donaldson made no attempt to define the microstructure in his iron alloys and Bertodo did not indicate the temperature at which the values were determined.

Thermal conductivity of grey cast iron decreases with increasing temperature and hence should be determined as the mean conductivity between various temperature ranges with not too large a difference. The thermal conductivity of all pure metals decreases linearly with temperature [4]; this is also true for many alloys. The thermal conductivity of grey cast irons over a wide range of composition falls by 1.5 to 1.9 $W m^{-1} {}^{\circ} C^{-1}$ for each 100° C rise between 100 and 450° C [2]. It is reported that the thermal conductivity of grey cast iron varies linearly with temperature [5] in the temperature range 100 to 700° C. TPRC data [6] also present a linear relationship between thermal conductivity and temperature.

Table II gives some reported values of thermal conductivity of grey cast irons along with their chemical composition.

3. Scope of the present work

A review of the literature on thermal conductivity of flake graphite cast irons indicates that the information is insufficient and incomplete. With the data available, it is not possible to understand the influence of chemical composition and microstructure of an iron on thermal conductivity.

The present work was undertaken to generate sufficient data on thermal conductivity of different alloy

TABLE II Some reported values of thermal conductivity of grey cast irons

Investigator	Chemical composition (%)				Thermal conductivity ($W m^{-1} {}^{\circ} C^{-1}$)	
	C total	C graphitic	Si	Alloy content		
				Temperature range:	95° C	425° C
Walton (cited in [2])	3.93	–	1.40	–	55.4	46.7
	2.92	–	1.75	–	36.3	–
					100° C	400° C
Donaldson (cited in [2])	3.20	–	1.50	–	50.6	45.2
	3.18	–	1.59	0.99 Cu	44.4	41.0
	3.18	–	1.49	1.98 Cu	46.0	38.9
	3.16	–	1.44	3.10 Cu	46.0	41.0
	3.12	–	2.31	0.54 Cr + 0.77 Mo	49.8	45.6
	2.56	–	2.20	0.58 Mo	49.4	45.2
					100° C	400° C
Angus [2]	3.98	–	1.32	0.16 Cr + 0.31 Mo	57.0	42.0
					100° C	430° C
	2.75	–	6.49		37.0	34.0
	2.80	–	2.50		42.0	39.0
						100° C
400° C						
Roehrig [8]	3.74	–	1.02	–	52.0	44.9
	3.70	–	1.89	0.29 Cr + 0.33 Mo	47.0	42.8
					100° C	425° C
TPRC [6]	3.93	–	1.40	–	55.0	–
	2.98	2.23	1.94	0.49 Cr	42.3	–
	3.05	2.20	1.82	0.5 Cr	52.3	–
	3.82	3.17	2.02	0.19 Cr	56.5	–
	4.00	–	2.20	1.1 Ni	66.5	–
	2.70	–	0.96	0.95 Cr + 7.0 Al	33.0	30.1
	3.19	2.49	1.45	0.124 V	51.5	42.3
	2.70	–	–	7.0 Al	33.5	30.1
	3.02	–	4.20	–	41.0	38.5

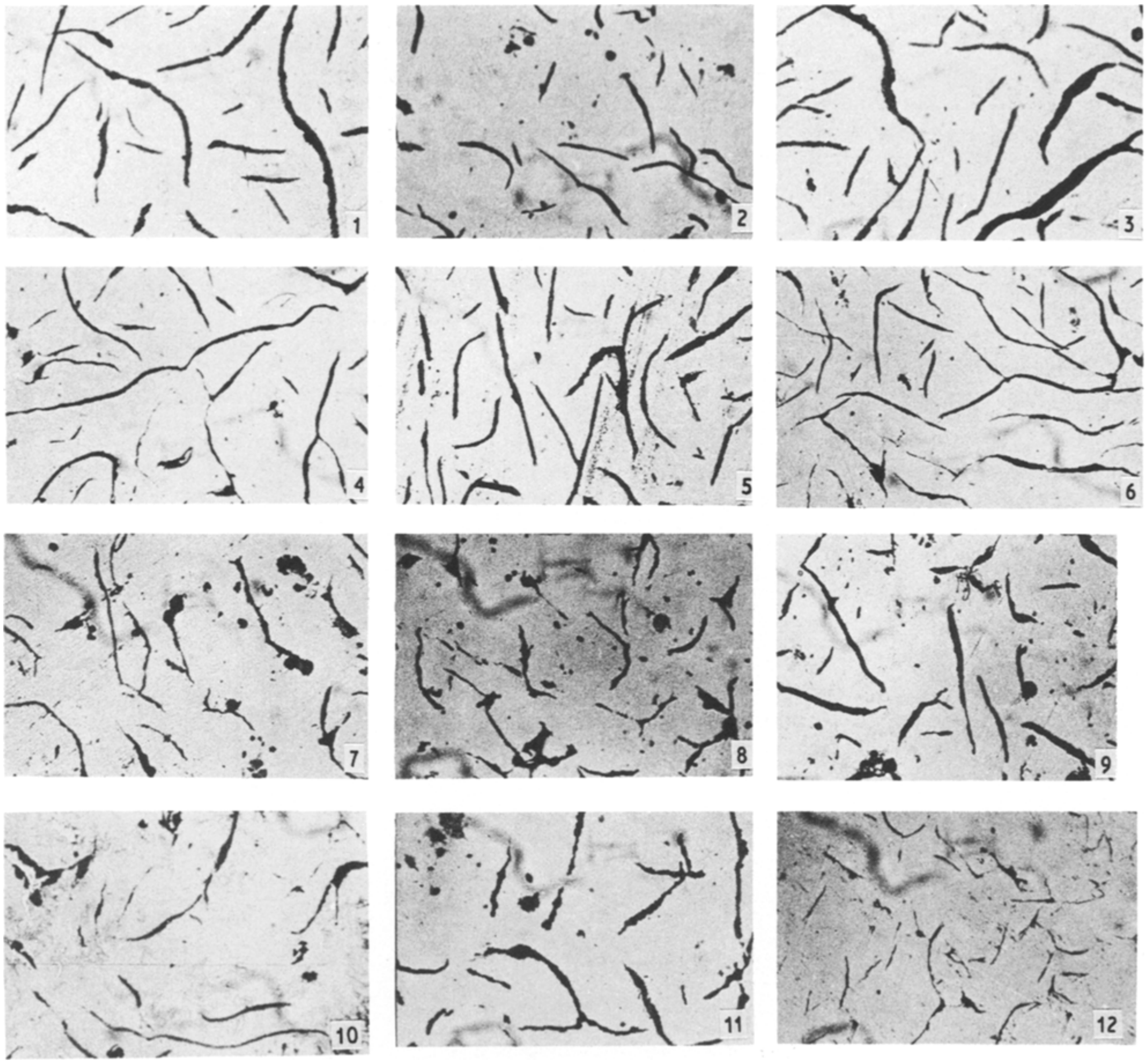

Figure 1 Optical micrographs of irons under study: unetched, × 150.

combinations in flake graphite cast iron and to throw light on the role of microstructure on thermal conductivity. The work was aimed at acquiring sufficient knowledge of thermal conductivity behaviour which will not only help in choosing the correct iron for elevated temperature applications but will also help in the design of newer iron alloys which have better thermal conductivity.

4. Experimental details

4.1. Melting and pouring

The base iron for all 23 grey cast iron was prepared in a 6000 kg mains frequency crucible-type induction furnace. The iron was produced by carburizing 5500 kg structural steep scrap, added in 500 kg liquid iron of 3.5% carbon, 2% silicon, 0.08% sulphur, 0.7% manganese and 0.12% phosphorous. The base iron composition was adjusted by additions of petroleum coke, ferro-silicon and ferro-manganese, added during the melting. Carbon, silicon and carbon equivalent (CE) levels were checked before tapping which was done at 1450° C. The melt was inoculated with standard calcium-bearing Fe–Si inoculant added at the 0.3% level. The alloy additions were done in the ladle. Standard tensile and transverse test bars were cast.

4.2. Chemical analysis

The samples for chemical analysis were poured along with the castings. The analysis was carried out on drillings from these samples and further checked with the analysis of shavings from the castings, obtained during the machining. The chemical analysis results were confirmed by spectrometric analysis. The sulphur, manganese and phosphorus levels of all irons were 0.06%, 0.71% and 0.08%, respectively. The chemical analysis of all irons is given in Table III.

4.3. Metallography

Specimens for metallographic examination were prepared from as-cast tensile test bars. The specimens were observed by both optical microscopy and scanning electron microscopy. All the irons exhibited a fully pearlitic structure with a different degree of pearlite refinement and different graphite morphology. The as-cast microstructures showing graphite morphology are given in Figs 1 to 4.

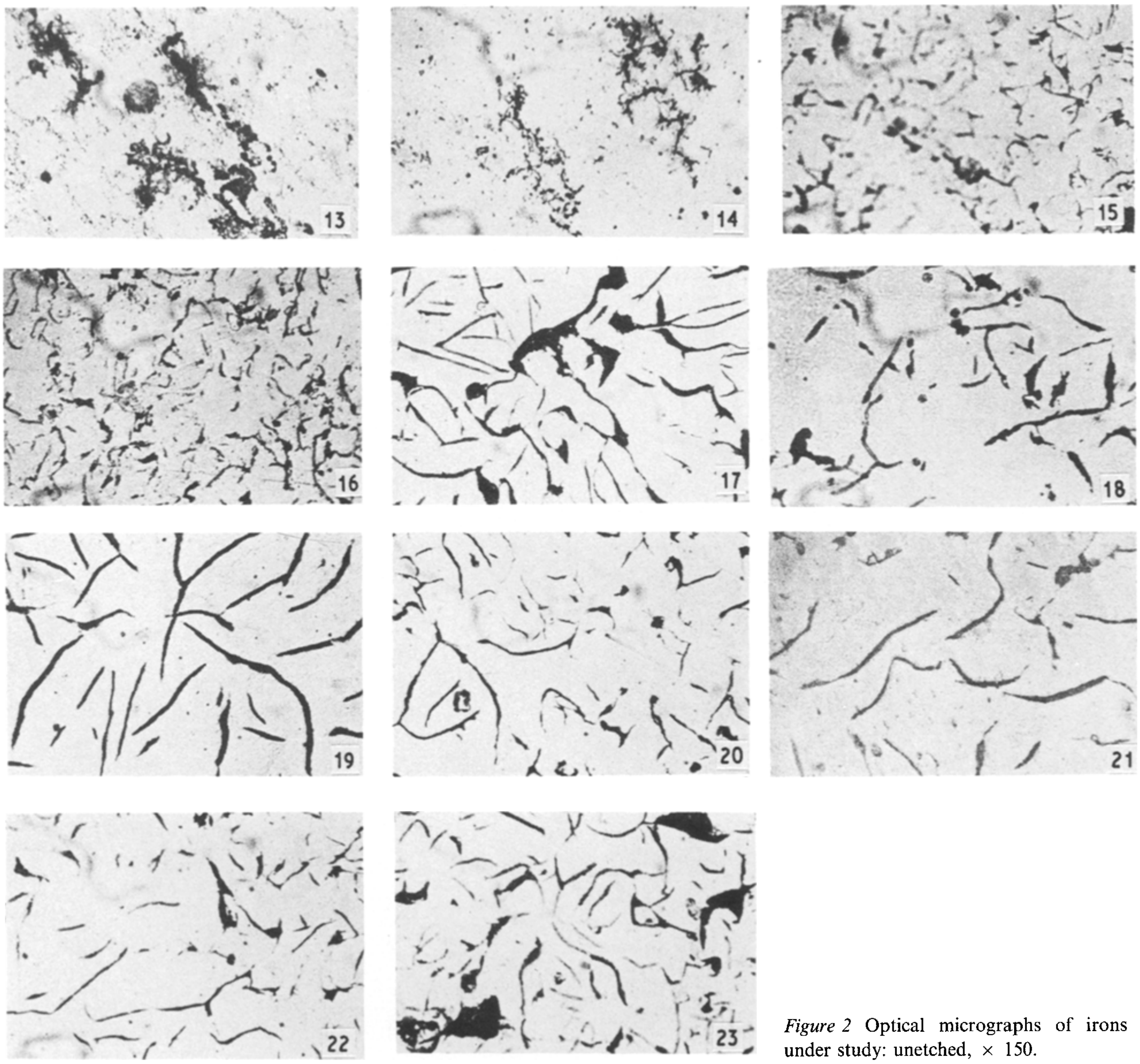

Figure 2 Optical micrographs of irons under study: unetched, × 150.

TABLE III Chemical analysis of irons under investigation

Iron no.	Chemical composition (%)			Alloy content (%)
	Total carbon	Graphitic carbon	Silicon	
1	3.93	3.13	1.06	–
2	3.00	2.30	1.98	–
3	3.93	3.17	1.06	Mo – 1.05
4	3.00	2.45	1.98	Mo – 1.02
5	3.93	3.11	1.06	Mo – 0.32, Cr – 0.72
6	3.00	2.30	1.98	Mo – 0.30, Cr – 0.68
7	3.93	3.14	1.22	Cr – 1.02, Ni – 1.08
8	3.00	2.27	1.98	Cr – 1.02, Ni – 1.04
9	3.93	3.10	1.40	Cr – 1.04
10	3.00	2.20	1.98	Cr – 0.98
11	3.93	3.11	1.40	Cr – 0.28, V – 0.69
12	3.00	2.18	1.98	Cr – 0.32, V – 0.72
13	3.93	3.15	1.60	Cr – 1.01, Sn – 0.11
14	3.00	2.17	1.98	Cr – 1.06, Sn – 0.11
15	3.93	3.09	1.60	Cr – 0.93, Sb – 0.05
16	3.00	2.14	1.98	Cr – 1.00, Sb – 0.054
17	3.93	3.11	1.06	Cr – 0.97, Cu – 2.11
18	3.00	2.26	1.98	Cr – 0.94, Cu – 1.98
19	3.93	3.16	1.06	Cr – 1.08, Cu – 3.10
20	3.00	2.12	1.98	Cr – 1.04, Cu – 1.04
21	3.93	3.12	1.06	Al – 5.1
22	3.00	2.25	1.98	Al – 5.2
23	3.00	2.30	1.98	Si – 3.73

Sulphur: 0.06%, phosphorus: 0.08%, manganese 0.71%.

4.4. Thermal conductivity measurement

Thermal conductivity (K) of grey cast iron can be measured by any apparatus which supplies the required boundary conditions to a particular solution of Fourier's equation of heat conduction [7] as given below:

$$H = \frac{-KA\Delta T}{L}$$

where H is the heat flow at one end of a rod of uniform cross-sectional area, A, and length, L, and ΔT is the temperature gradient along the length L.

The usual apparatus for measurement of thermal conductivity consists of an arrangement to ensure one-directional heat flow and measuring the temperatures at known lengths along the heat flow direction. The lateral heat flow in case of metallic rods can be avoided by either enclosing the specimen in tight dense insulation (as is done in the Searley method [4]) or by providing a guard cylinder (as is done in the NBS method [7]).

The experimental apparatus used for studying the thermal conductivity is given in Fig. 5. The guard cylinder has been incorporated to ensure one-dimensional heat flow along the length of specimen. Asbestos

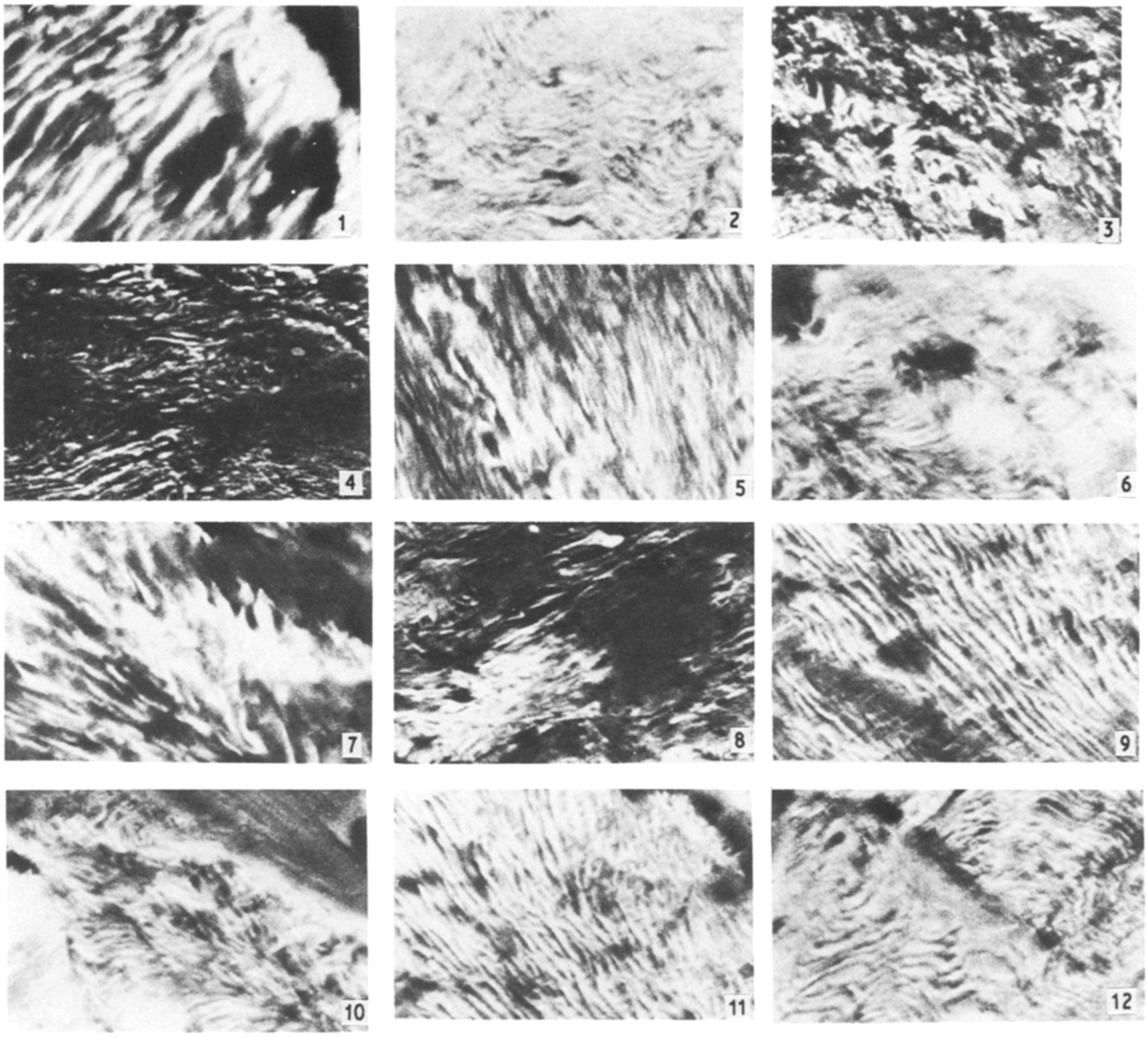

Figure 3 Scanning electron micrographs of irons under study: etched in 2% Nital, x 4000.

powder was used as an insulating material. One end of the specimen was heated by putting it in a closely packed and specially designed resistance heating furnace. The other end was cooled by maintaining a constant flow over it. The water flow was precisely measured. The heat flow (H) was calculated as the heat taken away by the cooling water. Chromel–alumel thermocouples duly calibrated were brazed at different known locations on the specimen. The temperature gradient (ΔT) was obtained by noting the temperatures at these locations. The tests were conducted up to 500° C.

The specimens were machined from 30 mm diameter as-cast bars. The specimen size was 20 mm diameter and 300 mm long.

Thermal conductivity values calculated by experimental measurements up to 500° C are represented in Fig. 6. The values are extrapolated to 700° C.

5. Discussion

The present work has provided detailed information on the thermal conductivity of several flake graphite irons. The alloy designs selected for the study covers most of the chemical compositions of commercially used flake graphite irons. The influence of all commonly used alloying elements on thermal conductivity of flake graphite cast irons can be predicted by using this information. In the present study thermal conductivity data can be correlated with the microstructure.

Steep temperature gradients are set up in a component subjected to repeated thermal shocks. This results in repeated severe thermal strains causing thermal fatigue. Flake graphite cast irons with high thermal conductivity are very much preferred to keep the level of thermal stresses to a minimum and thus improve upon thermal fatigue resistance of the component. Several alloy combinations from the present study have a high thermal conductivity to meet this requirement.

There is a vast difference between the values of thermal conductivity of various micro-constituents of flake graphite cast iron (Table I). In other words, the thermal conductivity of flake graphite cast iron largely depends on microstructure.

The ferrite in cast iron is really a silico-ferrite, i.e. ferrite with dissolved silicon. The presence of dissolved

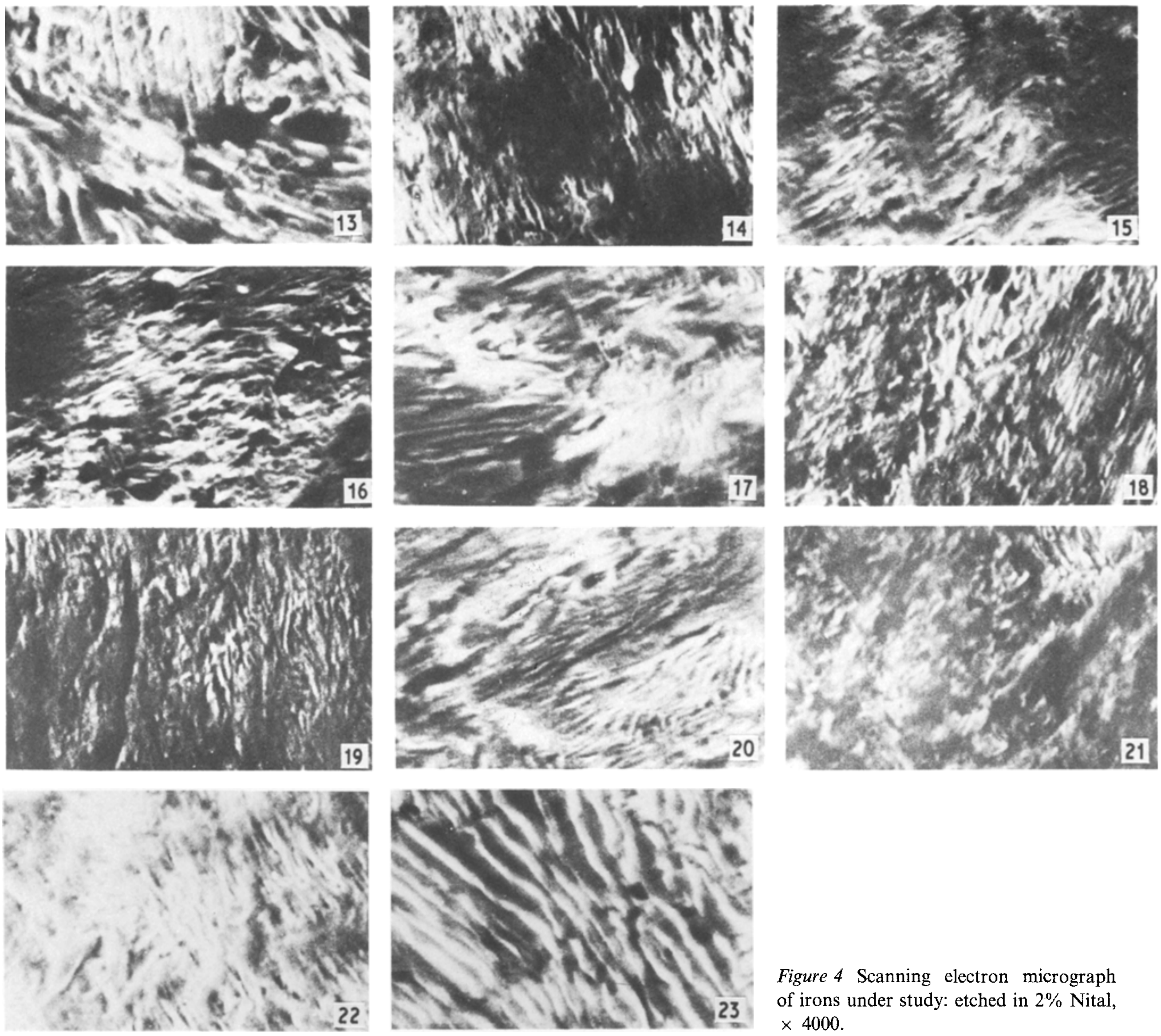

Figure 4 Scanning electron micrograph of irons under study: etched in 2% Nital, × 4000.

elements in ferrite substantially alters the thermal conductivity [1]. Silicon, by dissolving in ferrite, reduces thermal conductivity considerably. The results of iron 23 (Table III, Fig. 6) prove this. Aluminium also influences thermal conductivity in a similar way. This has been demonstrated from the results of irons 21 and 22 (Table III and Fig. 6). Silicon has reduced the thermal conductivity of the base iron by 15% in the temperature range 40 to 100° C, while aluminium has reduced it by 22% in the same range for high carbon-base iron. However, all three irons (21, 22, 23) are found to have a low rate of decrease with temperature.

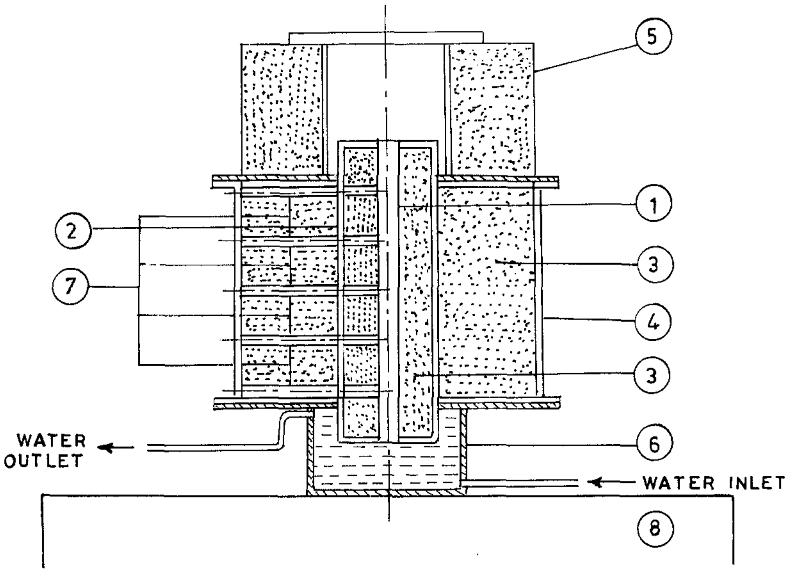

Figure 5 Thermal conductivity measurement apparatus. 1, Specimens; 2, guard cylinder; 3, insulation; 4, insulation container; 5, heating furnace; 6, cooling chamber; 7, thermocouple guide tube; 8, support table.

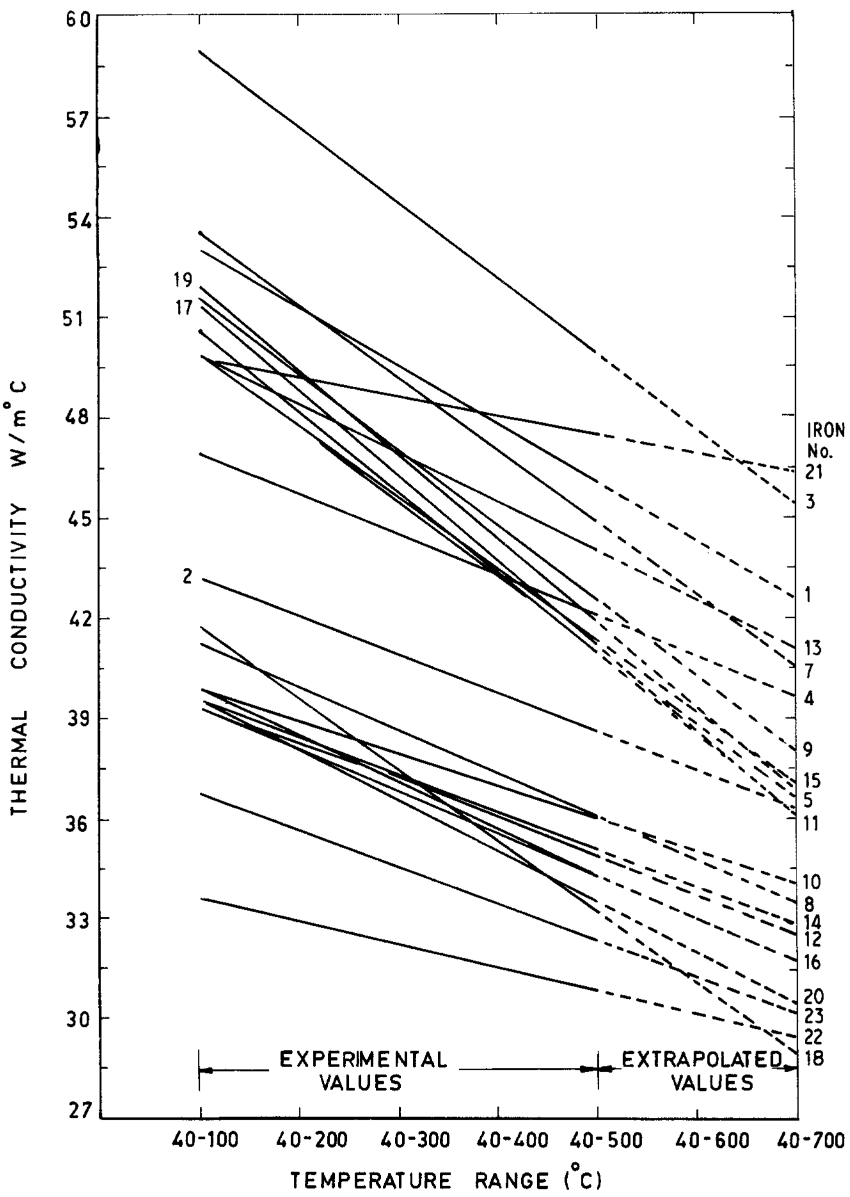

Figure 6 Variation of thermal conductivity with temperature for irons under study.

Aluminium and silicon are both strong graphitizers and increase the carbon equivalent appreciably (approximately equivalent to one-third of their content). The ratio of graphitic carbon to carbon equivalent in the case of these irons is very low.

The most influential element on thermal conductivity is carbon. Carbon in the form of graphite, increases the thermal conductivity, but in the form of combined carbon, reduces it (Table I). The shape, size and orientation of graphite is also important. There is a vast difference in the thermal conductivity values of graphite along the *c*-axis and basal plane (Table I). Therefore, the shape of graphite has a pronounced effect. Nodular graphite iron has the lowest thermal conductivity among grey cast irons; compacted graphite iron has an intermediate and flake graphite iron has the highest thermal conductivity.

In the present study, finer and long type A graphite (irons 3, 4, 5, 6, Table III, Fig. 1) in large quantity has been found to increase favourably the thermal conductivity. On the other hand, undercooled graphite such as type D (irons 14, 15, Table III, Fig. 2) and at low ratio of graphitic carbon to carbon equivalent, has been found to deteriorate thermal conductivity. The presence of combined carbon (irons 9, 10, 11, 12, Table III, Fig. 3) has resulted in lower thermal conductivity.

Alloying elements have been found to influence thermal conductivity through their influence on microstructure. Elements that dissolve in matrix such as aluminium (irons 21, 22) and silicon (iron 23) lower thermal conductivity through their influence on the matrix. Tin (irons 13, 14, Table III) and antimony (irons 15, 16, Table III) have been added in microquantities and may have been dissolved partially in the matrix to influence thermal conductivity. Chromium (irons 9, 10) and chromium–vanadium (irons 11, 12) additions have promoted the formation of some carbides (Fig. 3) and thus have deteriorated thermal conductivity by influencing the matrix. The addition of nickel has been found beneficial when added along with chromium (irons 7, 8, Table III); the addition of copper is also beneficial but to a lesser extent (irons 17, 18, 19, 20, Fig. 5). These elements have influenced the matrix by partially or fully nullifying the carbide-forming tendency of chromium.

Addition of molybdenum (irons 3, 4) has been found to be most favourable in increasing thermal conductivity. Molybdenum has refined the graphite (irons 3, 4, Table III, Fig. 1) and thus has a beneficial influence.

TABLE IV Decrease in thermal conductivity with increase in temperature for irons under investigation

Iron no.	Decrease in thermal conductivity per 100° C increase in temperature (W m^{-1} °C^{-1})
1	1.486
2	0.986
3	1.958
4	1.043
5	1.100
6	1.100
7	1.857
8	1.100
9	1.970
10	0.986
11	2.090
12	1.010
13	1.270
14	0.914
15	1.857
16	1.057
17	1.257
18	1.257
19	1.200
20	1.286
21	0.486
22	0.600
23	0.943

Further molybdenum is a ferrite promoter and has not promoted any carbide formation (irons, 3, 4, Fig. 3): it also strongly refines pearlite. The combination of molybdenum and chromium (irons 5, 6, Table III) has been equally as effective as molybdenum alone in refining graphite (irons 5, 6, Fig. 1) and refining pearlite (irons 5, 6, Fig. 3). Tin or antimony additions in combination with chromium have resulted in the formation of type B and type D graphite, respectively (irons 13, 14, 15, 16, Table IV, Fig. 2) which has the detrimental effect of lowering the thermal conductivity.

The thermal conductivity of all irons under study has been found to decrease linearly with temperature (Fig. 6). Most of the alloy additions have altered the rate at which this decrease occurs. Table IV gives the rate of decrease of thermal conductivity for all the irons. In general, irons having a high ratio of graphitic carbon to carbon equivalent have a high rate of decrease of thermal conductivity. Additions of molybdenum, chromium, vanadium, nickel and antimony have further accelerated this rate in such irons, while tin and copper additions have reduced the rate to some extent. Irons having a low ratio of graphite carbon to carbon equivalent have a low rate of decrease of thermal conductivity with temperature.

6. Conclusions

1. Thermal conductivity of flake graphite cast iron depends on microstructure. Alloy additions in solid solution with iron or those which promote carbide formation reduce the thermal conductivity through the matrix. For a similar nature of matrix, graphite morphology has a pronounced effect. High graphitic carbon and type A graphite increase the thermal conductivity.

2. Thermal conductivity depends on chemical composition of flake graphite iron. Molybdenum addition increases thermal conductivity appreciably, nickel and copper additions increase it moderately whereas aluminium and silicon strongly reduce it. Chromium, vanadium, tin and antimony reduce it moderately.

3. The thermal conductivity of flake graphite cast iron decreases linearly with increased temperature and most of the alloy additions alter the rate of such a decrease.

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