ASSESSMENT OF THE EFFICACY OF SOME CARBONATE MINERALS AS ENERGIZERS IN PACK CARBURISATION OF MILD STEEL

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ABSTRACT
The efficacy of some carbonate minerals (marble, limestone and dolomite) as energizers in pack-caburisation of mild steel has been compared with that of barium carbonate. Mild steel samples were pack-carburised for suitable lengths of time at 900^{0}C in carburising compounds containing charcoal plus varying amounts (up to a maximum of 20%) of $BaCo_3$ and/or either marble, limestone or dolomite as energizers. The resultant carburisation depths obtained with different compounds were compared by means of hardness measurements using a microhardness testing .machine. The results showed that $BaC0_3$ can almost be completely substituted with marble or limestone, and that a combination of $BaC0_3$ and marble was a more effective energizer than solely $Baco_3$; whereas dolomite was the least effective energizer. The deepest and best^{3}defined case was obtained with a combination of 15% marble and 5% $BaC0_3$•

1. INTRODUCTION

Pack carburisation of steel parts is conventionally carried out at about 850 to950^{0}C using carburising compounds made up of charcoal and an energizer (a catalyst), traditionally barium carbonate. The energizer which usually amounts to some 6-20% of the compound is supposed to break down in the presence of carbon to form the active CO thus:-

$BaCo_3 \longrightarrow BaO + CO_2$…… (1)

$CO_2 + C \rightarrow 2CO$…… (2)

The CO then breaks down at the steel surface according to the reverse of reaction (2) above i.e.

$2CO \rightarrow CO_2 + C$ ……… (3)

The oxide of the energizing compound in turn reacts with CO_2liberated in equation (3) to reform the carbonate, i.e.

$BaO + CO_2 \rightarrow BaCO_3$……. (4)

While the carbon is readily dissolved by the austenite phase of the steel and diffuses into the steel which on subsequent quenching develops a hard case.

It is known [1] that for a give carburising time, temperature and steel composition, the depth of carburisation is determined by the carbon potential (activity) of the carburising medium. The higher the carbon potential the higher the equilibrium carbon concentration at the surface of the steel and thus the deeper the carburising depth. Thus the role of an energizer is thought to be related to its ability to raise the carbon potential of the carburising medium. How the energizer does this has not been clearly out- lined and indeed why a particular carbonate should be a more effective energizer is still a matter of some conjecture though chemical stability is thought to be an important factor. In some pack carburising operations [2] some quantities of

$BaC0_3$ have been replaced by Na_2CO_3. The replacement or substitution of $BaCO_3$ by other carbonates is of great interest. Apart from scientific and technical interests there may be some national considerations for evaluating the efficacy of other carbonates in pack carburisation, especially for those countries that have to import $BaCO_3$at great foreign exchange costs whereas they have abundance of other more common carbonate minerals. For example, while there is no known deposit of whiterite, ($BaCO_3$) in west African, many forms of other carbonate minerals especially limestone and marble abound in many parts of the sub-region; abundant deposits of high quality limestone being found in practically all parts of Nigeria, some of which have between 97-99% $CaCO_3$ content. Thus it is of great strategic interest to examine the possibility of substituting limestone (or any of its associated compounds) for $BaCO_3$ in such industrial applications as pack-carburisation.

2. PROPERTIES OF SOME CARBONATE MINERALS AND CHOICE OF CARBURISING COMPOUNDS AND TEST MATERIALS

Carbonate minerals generally fall into three structural groups [3]

(i) The Calcites (Hexagonal, with space group R3c) of which calcite $CaCO_3$, and magnesite $MgC0_3$ are common examples;
(ii) The Aragonites (Orthorhombic, with space group Pmcn) e.g. aragonite $caCo_3$, witherite $BaC0_3$; and
(iii) The Dolomites (Hex890nal, with space group R3) e.g. dolomite $caMg(C0_3)_2$ and ankerite $CaFe(co_3)_2$

In this classification it is worthy to note that calcium carbonate $CaCO_3$, can occur in two structure types i.e. calcite with 6 coordination of Ca to 0 and aragonite with 9 coordination of Ca to 0, since the ratio of the Ca and 0 diameters (i.e C:0) is O. 707.

The basic building block of the carbonates are the anionic $(Co_3)^{-2}$ complexes which are bonded to the central carbon cation (bond strength $1\frac{1}{2}$ ev). The bond is however not as strong as the covalent bond in CO_2 so that with the application of heat the carbonate can be broken down

$$\times CO_3 \rightarrow XO + CO_2 \ldots\ldots \quad (5)$$

as in equation (1) above. The efficacy of any carbonate as an energizer in pack caburisation is most likely to depend on its thermo-chemical properties e.g stability, the amount of heat generated, etc. Some of the physical and thermo-chemical properties [4] of these carbonate minerals are compared in table 1.

The limestone sample used in these experiments were from the lot supplied by the Cross River Limestone Limited from their Mfamosing Limestone Mines in Cross River state, the marble from Jakura Mines and the dolomite from Osara Mines both in Kwara state, were obtained from the National steel Council (Metallurgical and Tests Division) Jos. The $BaC0_3$ and $Caco_3$ power samples were of May and Baker Laboratory grade. The Chemical analysis of these carbonates as quoted by the

Table 1: Thermo-chemical properties (4) of carbonate minerals used in pack-carburisation

CaMg (co$_3$)		Baco$_3$		Caco$_3$
			calcite	Aragonite
decomposition				
Temp °c	730-760	1450	898	825
Density	2 8 72	4.43	2.710	2.930
Mol wt	184.41	197 .35	100.09	100.09
ΔH^0(kcal)		-291.3	-288.45	-269.53
ΔG°(cal)	-520.5	-272.2	-269.78	-269.53

Suppliers are given in table 2. Mild steel of RST 37 grade which is the common grade of steel rolled at Jos Steel Rolling Company Limited, Jos was selected for carburisation. (Table 3).

3. EXPERIMENTAL PROCEDURE

The steel samples for carburisation were cut from RST 37 grade mild steel rods 12mm diameter. Each sample measured 50mm in length. These 50mm long rods were thoroughly washed in acetone and dried and their faces (ends) coated with ceramic clay leaving the curved surfaces exposed for carburisation. Eleven carburising compounds of compositions listed in table 4 were prepared. Steel boxes used for the pack carburisation were constructed from heat-resisting steel (Ni-Cr steel). Each box measured 80 x 80 x 70 mm and had a lid with folded-down edges. The size of the box was chosen simply to ensure that it can accommodate at least 3 to 4 steel specimens and still have sufficient space for the carburising compounds.

To make a pack for carburising, a 20 ma thick layer of a chosen compound was first poured into the box, and three steel specimens were placed in position inside the box and the box filled up with the compound. The lid was sealed with clay in order to make the box air tight and eliminate possibility of air ingress during pack carburisation process. A large muffle furnace with a temperature sentivity of ± 5°C was used.

The temperature distribution in the furnace over the 800-1000 ^{0}C range was first established and it showed the existence of a uniform temperature within the central region of the furnace extending over an area 320 x 320 mm and up to 150 mm high from the furnace floor.

For carburisation at the given temperature for any given time the eleven boxes (packs) containing the test specimens corresponding to the eleven carburising compounds A to K in table 4 were all placed in the muffle furnace within the uniform temperature zone which had already attained the carburising temperature. The heating-up time needed to make up for the sudden temperature drop which followed the introduction of the packs into the furnace was less than 10 minutes and is therefore negligible compared to the carburising time varying from 2-8 hours. Pack carburisation runs with all the

Table 2: Chemical Analyses of Carbonates used as Energizers in pack-carburisation (as quoted by the suppliers)

	Osara dolomite	Mfamosing limestone	Jakura marble	$BaCO_3$ (powder	$CaCO_3$ (powder)
L.I.O.	45.78	43.69	43.58		
CaO	28.04	54.61	55.23		
SiO_2	0.99	0.88	0.31		
$A1_20_3$		0.22	0.04		
MgO	24.09	0.96	0.45		0.01
Na_20	-	0.009	0.02		0.02
K_20	-	0.005	0.02		0.005
S	0.04	0.02	0.09		
Fe_20_3	0.80	0.17	0.60	0.008	0.01
p	0.02	0.0095	0.05		
Ba	-	-	-		0.01

Table 3: Composition of RST 37 steel (as supplied by Jos Steel Rolling Company, Jos

C	Si	Mn	P	S	Cr	Ni	Cu	Fe
0.14	0.21	0.50	0.023	0.006	0.02	0.02	0.07	Balance

Table 4: compounds used for the pack carburisation

Compound	Composition
A	100% charcoal
B	80% charcoal + 10% dolomite + 10% $BaCO_3$
C	80% charcoal + 10% marble + 10% $BaCO_3$
D	80% charcoal + 10% limestone + 10% $BaCO_3$
E	80% charcoal + 20% marble
F	80% charcoal + 20% dolomite
G	80% charcoal + 20% limestone
H	80% charcoal + 20% $BaCO_3$
I	80% charcoal + 15% marble + 5% $BaCO_3$
J	80% charcoal + 15% dolomite + 5% $BaCO_3$
K	80% charcoal + 15% limestone + 5% $BaCO_3$

carburising compound were carried out at 900^{0}cfor 2 hours, 5 hours and 8 hours. At the end of a carburising time, the boxes were taken out of the furnace and air cooled. The experiment was repeated using fresh specimens for each pack-carburising period, yielding a total of ten rod specimens for each period.

Steel discs of 10 mm thick were cut from the central region of each of the carburised rod specimens and labelled. These disc specimens were thereafter solution treated at 850 C in the furnace for 10 minutes and water quenched. They were then prepared and polished for hardness measurement on a microhardness indenter. Michrohardness measurements on all the specimens were carried out on Vickers microhardness testing machine Model MHT-NO: 8331 made by Matsuzawa Seiki Co. Ltd. of Japan. The machine has a maximum test load of 1000gf with a load holding time of 5 -30 secs. Indentations were made starting 0.02mm from the edge and at intervals of 0.02mm right across the diameter, and was repeated on another diameter at right angles from the first traverse. From the hardness values obtained from each specimen the average hardness profile for each carburising compound and carburising time was plotted.

4. RESULTS AND DISCUSSION

The hardness profiles for specimens carburised at 900^{0}C for 2 hours, 5 hours and 8 hours are represented in figures 1(a,b and c), 2(a,b and c) and 3(a,b and c) respectively.

For a given steel specimen and carburisng compound it is known that the depth of carbon penetration at any given temperature is dependent only on time so long as all other parameters (e.g. packing conditions, (5) gas tightness, etc.) remain constant since our specimens are of the same size and composition and were quenched from the same temperature into the same medium (water) the depth of case hardening (case depth)is a good measure of carbon penetration. Thus the efficacy of an energizer can be assessed by the depth of case hardening (dc)which by ISO 2693-1973 as well as SS 11 70 08 is defined (1) as the distance from the surface to a plane at which the hardness is 550HV.From figures 1, 2 and 3 therefore, the case depths for all the compounds for each carburising time have been read off and tabulated in table 5.To compare the effectiveness (or efficacy) of an energizer in pack-carburising it is most appropriate to define a quantitative parameter. A convenaient parameter appears to be 'the relative efficacy (R_{ff}) of an energizer defined as the fractional increase in case depth obtained of a given enegerizer over that of all-charcoal compound, i.e.

$$R_{ff} = \frac{\text{case depth with a compound containing the energizer}}{\text{case depth with an all} - \text{charcoal compound}}$$

The average values of this parameter have been evaluated for each compound from each of the carburising times (2 hours, 5 hours and 8 hours) and incorporated in table 5 from which one can at a glance compare the effectiveness of all the energizers

It is evident from this table that compound 1 with 80% charcoal, 15% marble and 5% barium carbonate is the most efficacious compound, with R_{ff} = 3.43 and case depth of 2.04 mm 2.44 mm and 4.16 mm for 2 hours, 5 hours and 8 hours respectively. This is closely followed by compound H (80% charcoal. +20+ barium carbonate) with R_{ff} = 3.14.) The least effective compound is F (80% charcoal + 20% dolomite) with R_{ff} = 0.63 and case depths of 0.26mm, 0.40mm and 0.60mm for 2 hours, 5 hours

Table 5: The Case Depths and Relative Efficacy obtaining with different Carburising Compounds

CARBURISING COMPOUND						EFFECTIVE CASE DEPTH (mm) dc			AVERAGE RELATIVE R_{ff}
CODE						2HRS	5HRS	8HRS	
A	100%	Charcoal				0.52	0.92	1.12	1
B	80% c	Charcoal	+	10%	Dolomite + 10% Baco$_3$	1.30	1.60	2.24	2.08
C	80%	Charcoal	+	10%	Marble + 10% Baco$_3$	1.60	2.58	2.64	2.75
D	80%	Charcoal	+	10%	Limestone+ 10% Baco$_3$	1.40	1.76	2.72	2.34
E	80%	Charcoal	+	20%	Marble	0.68	1.96	2.00	1.74
F	80%	Charcoal	+	20%	Dolomite	0.36	0.46	0.78	0.63
G	80%	Charcoal	+	20%	Limestone	1.08	1.68	1.92	1.87
H	80%	Charcoal	+	20%	Baco$_3$	1.76	2.40	3.84	3.14
I	80%	Charcoal	+	15%	Marble + 5% Baco$_3$	2.04	2.44	4.16	3.43
J	80%	Charcoal	+	15%	Dolomite + 5% Baco$_3$	1.22	1.60	2.38	2.07
K	80%	Charcoal	+	15%	Limestone + 5% Baco$_3$	1.68	2.04	2.56	2.58

and 8 hours respectively

It is thus clear that marble (and to a good extent limestone) can be used as a substitute for nearly all the amount of barium carbonate required as energizer in pack carburising, though it appears that some amount of barium carbonate is still needed for the greatest effect. It is interesting to notice that compound I with 15% marble + 5% barium carbonate is a more effective energizer than compound H with 20% barium carbonate. The case depths obtained with compounds containing dolomite (especially F) shows clearly that dolomite is not an energizer; it appears to retard the carburising action. This could be due to its reduction of the carbon potential in the gas phase and hence lowering the carbon concentration at the

Surface of the steel.

To check the reasonableness of our data we obtain an estimate of the diffusion coefficient of carbon Dc , in steel from our values of case depths (extent of carbon penetration) and compare it with published data. Estimate of Dc can be made from the solution of the diffusion equation under similar conditions (semi-infinite medium, constant surface concentration and constant temperature) viz

$x \approx \sqrt[D]{t}$...... (6)

so that

$D \approx \frac{x^2}{t}$............. (7)

Where x is the depth to which appreciable diffusion of specie has reached in time t, and D is the diffusion coefficient of the specie.

Using equation (7) and the case depth (carbon penetration) data in table 5 for each of the eleven compounds we obtain an average diffusion coefficient of carbon in steel D_c as

$$D_c = 1.7 \times 10^{-4} mm^2/sec$$

$$i.e\ 1.7 \times 10^{-4} mm^2/sec$$

From literature, (7) the diffusion coefficient of carbon in iron is given by

$$D_C = 0.02\, exp(\frac{-20{,}100}{RT})$$

which at $900^0 c$ *gives*

$$D_c = 1.9 \times 10^6 cm^2/sec$$

which compares favourably with the value from our experimental data. This confirms that our data is reasonable.

5. CONCLUSION

Marble or limestone can replace most of the barium carbonate required as energizer in pack carburising; and indeed for the best effect it has been shown that the amount of barium carbonate should be reduced to about 5%. A mixture of 15% marble and 5% . Barium carbonate appears to be a more effective energizer than 20% barium carbonate.

Thus it is being suggested in this paper that in the absence of barium carbonate, limestone or marble can be used as an energizer but will generally require longer carburising times. Dolomite is not an energizer, it indeed appears to ·retard the carburising action.

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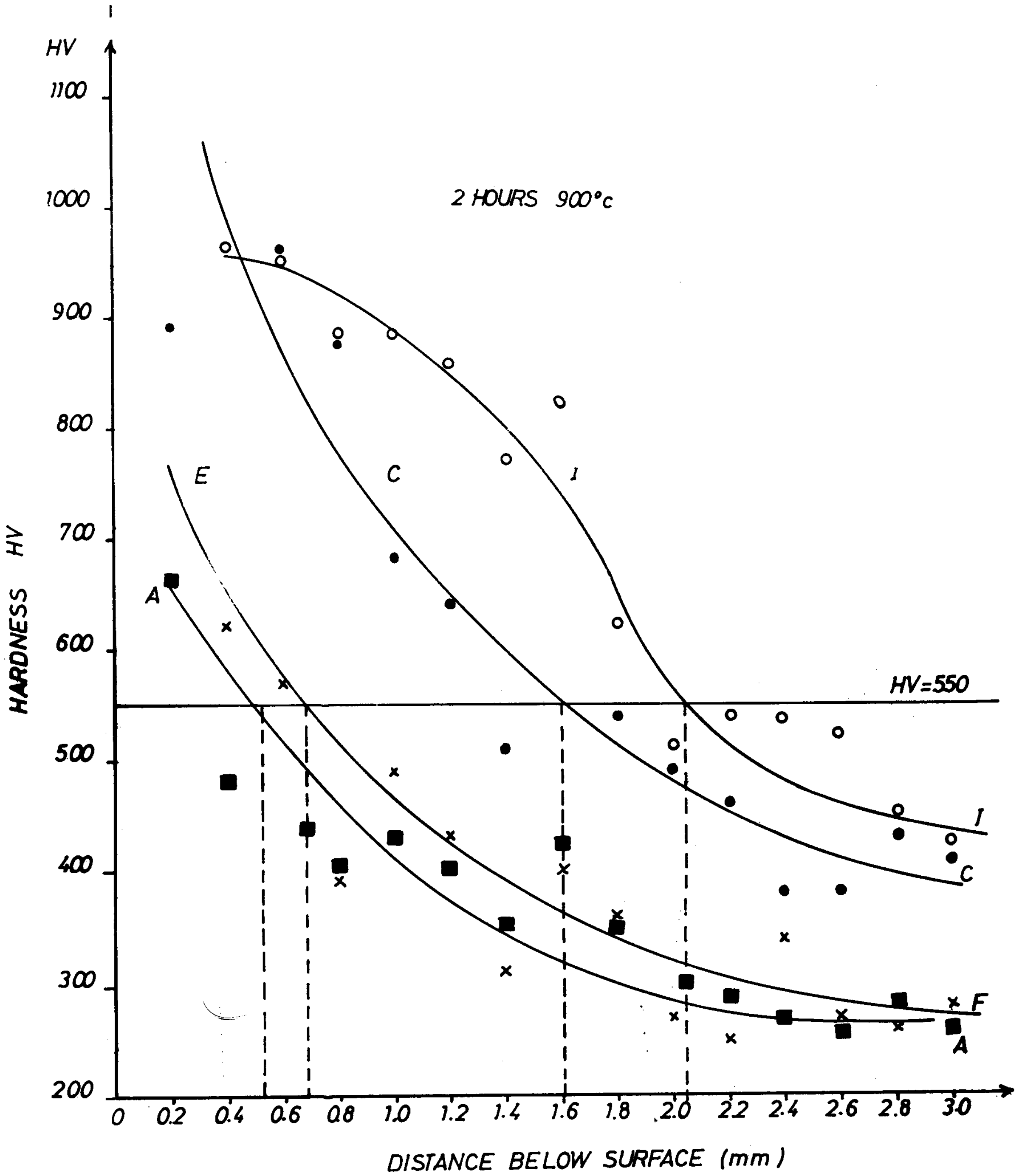

Fig 1(a): Hardness profiles with different carburising compounds after 2 hours at 90

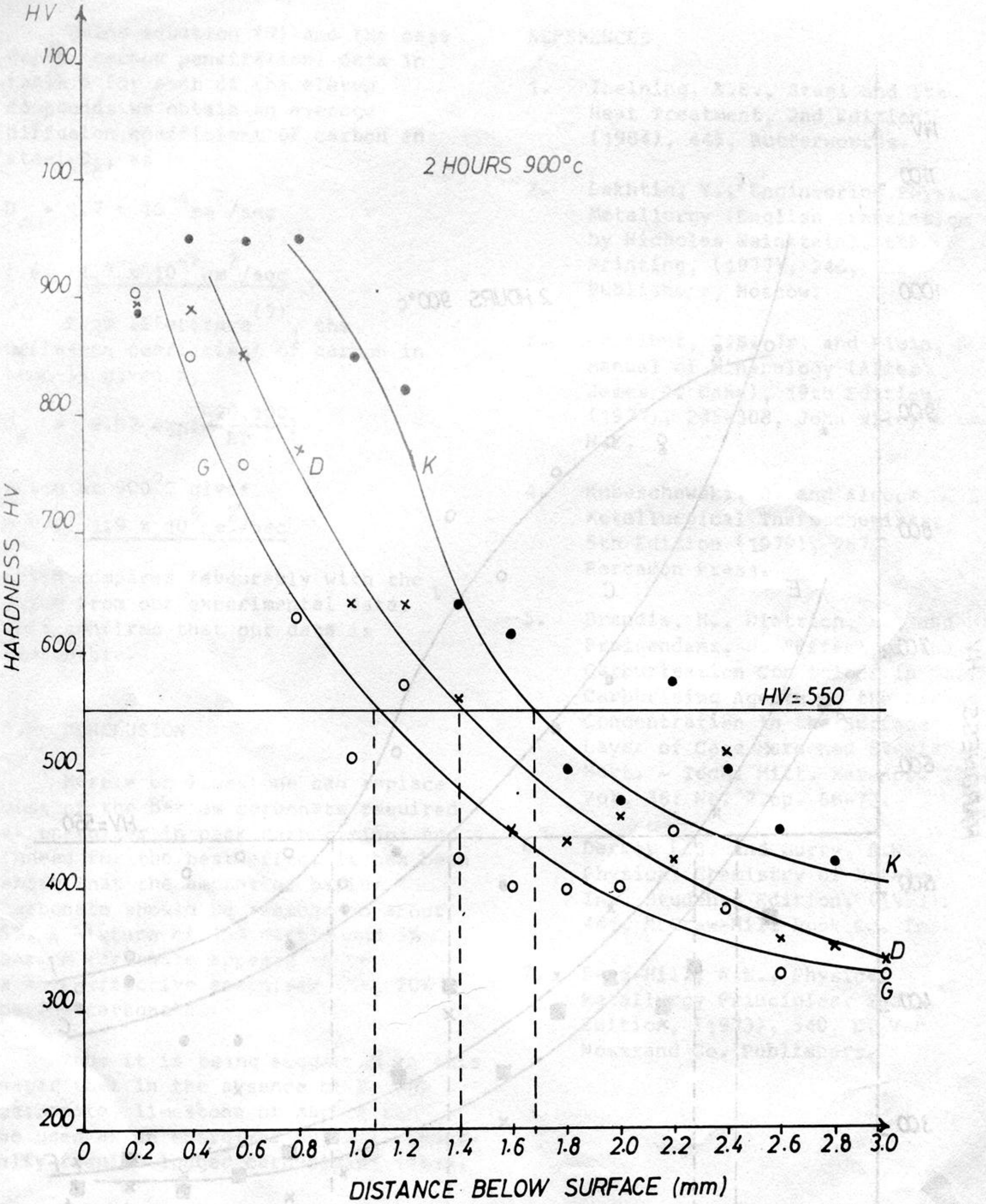

Fig 1 (b) Hardness profiles with different carburising compounds after 2 hours at 900°c

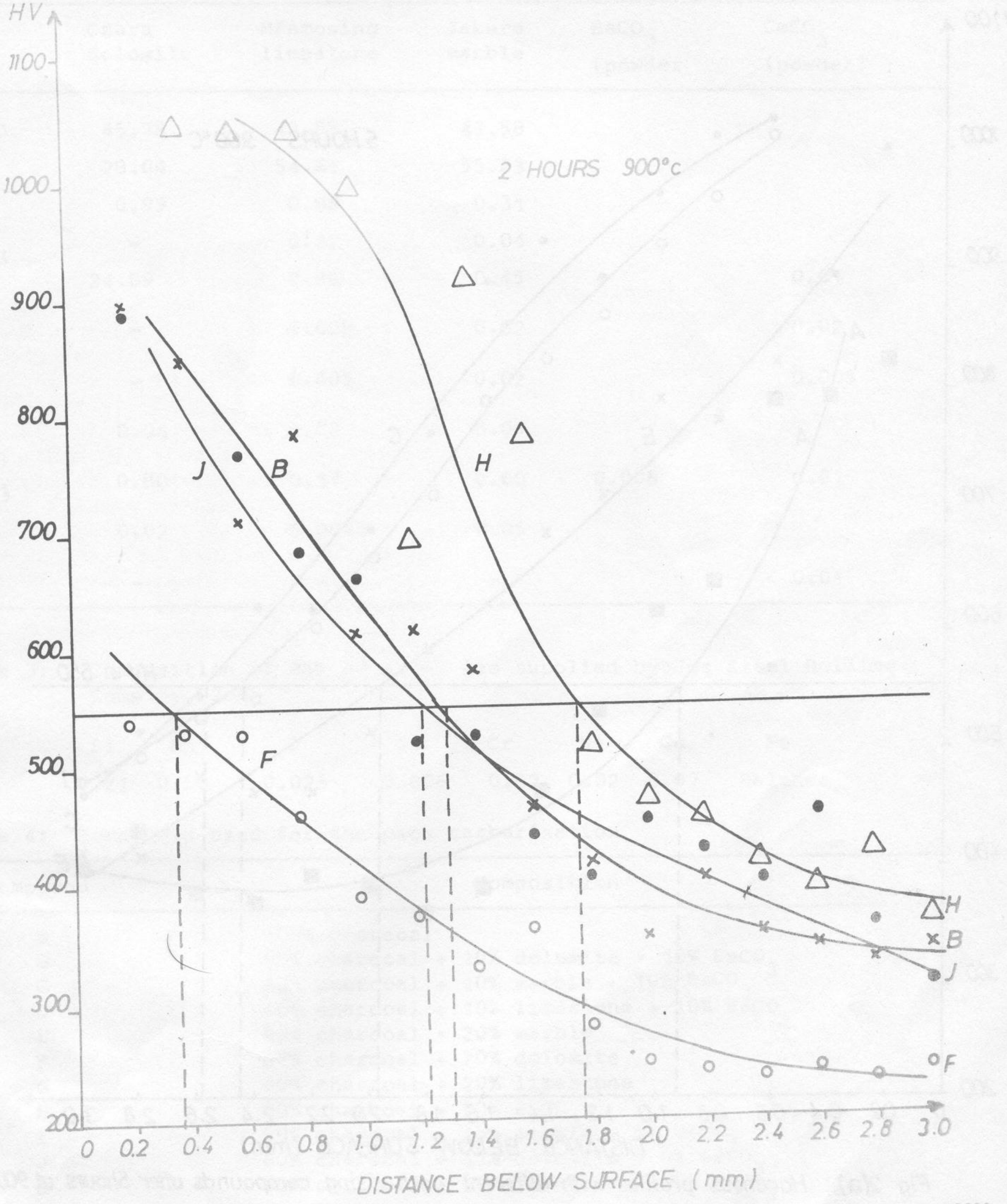

Fig 1 (c) Hardness profiles with different carburising compounds after 2 hours at 900°c

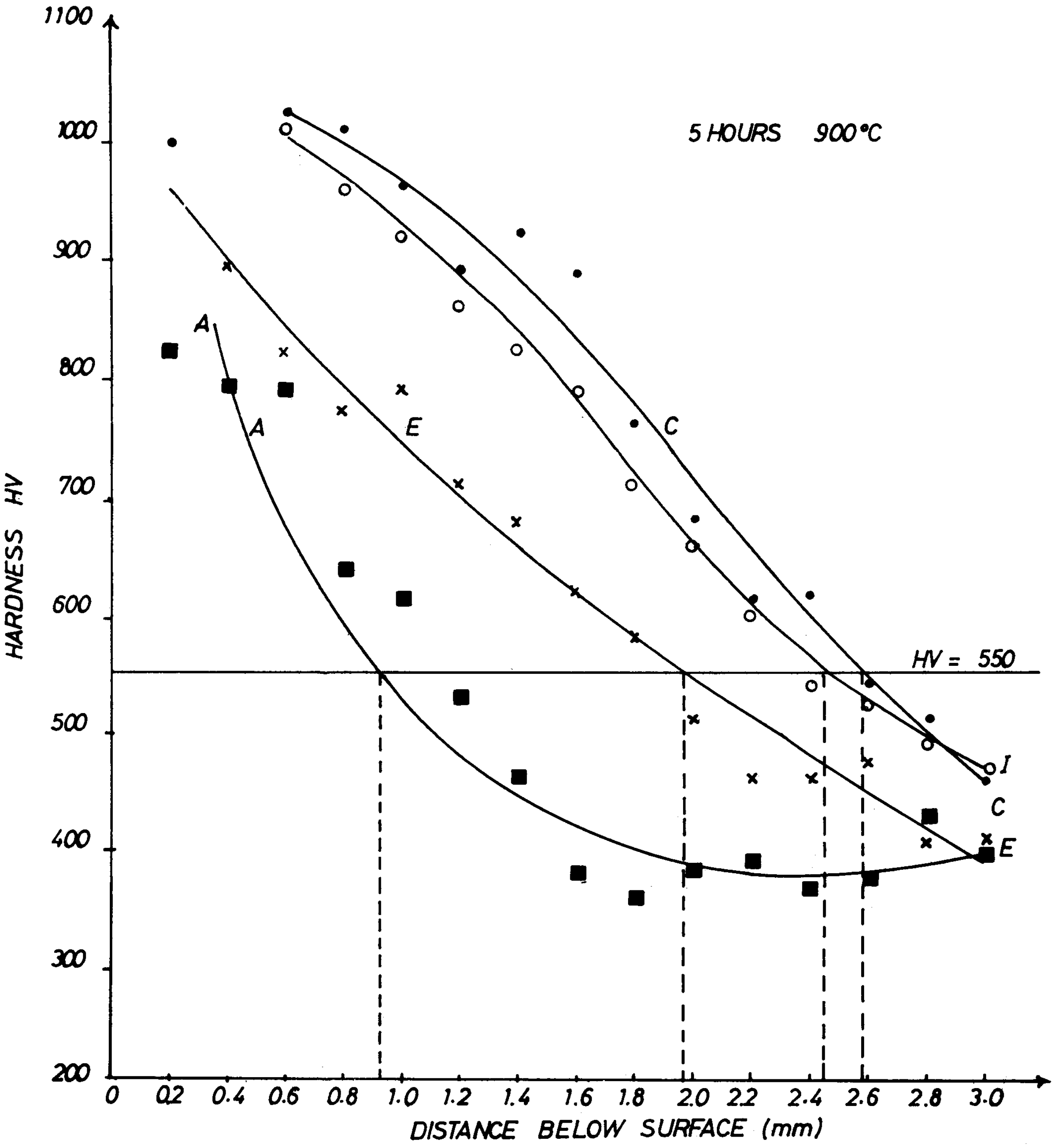

Fig 2(a): Hardness profiles with different carburising compounds after 5hours at 900°c

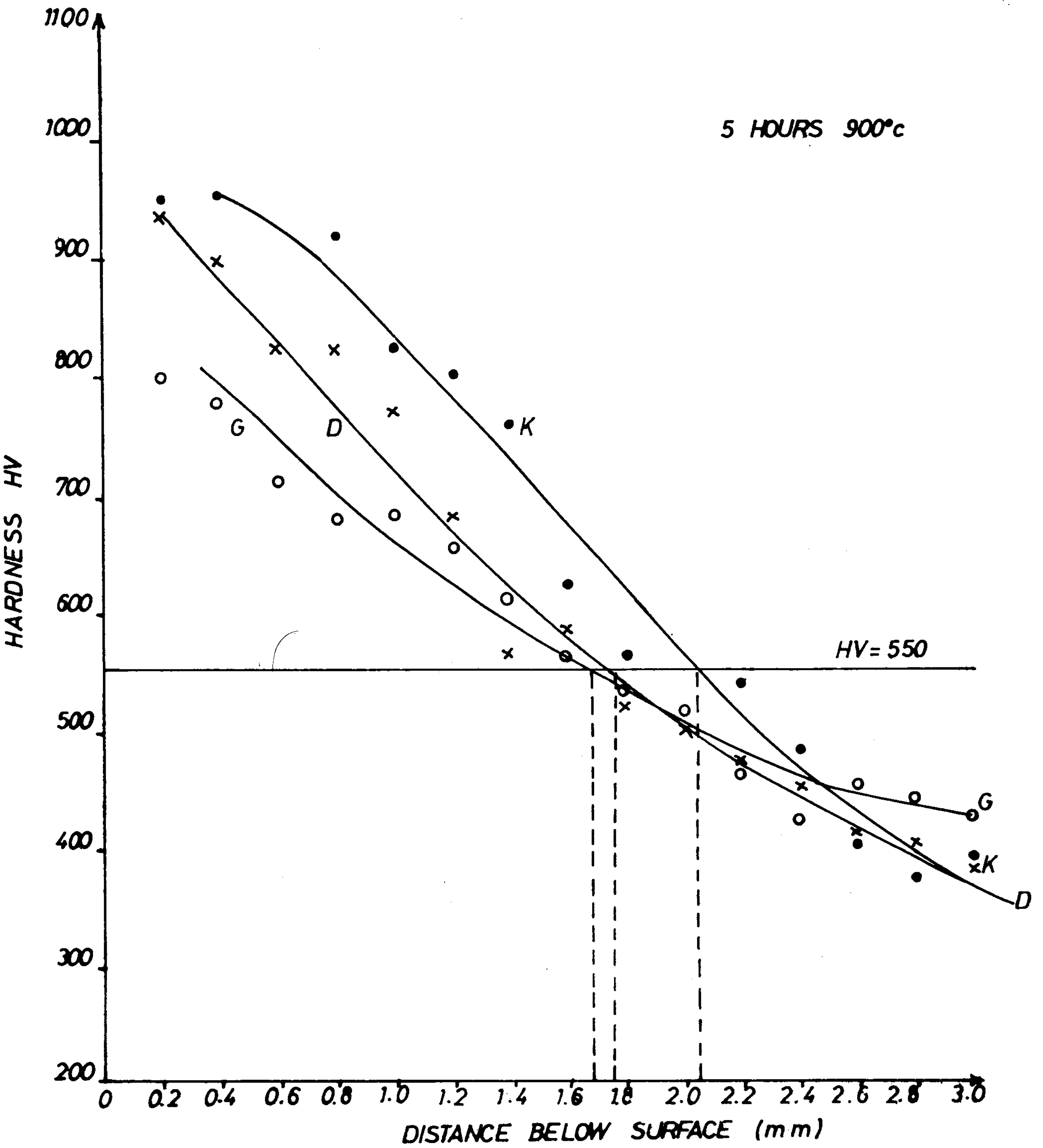

Fig 2 (b): Hardness profiles with different carburising compounds after 5 hours at 900°c

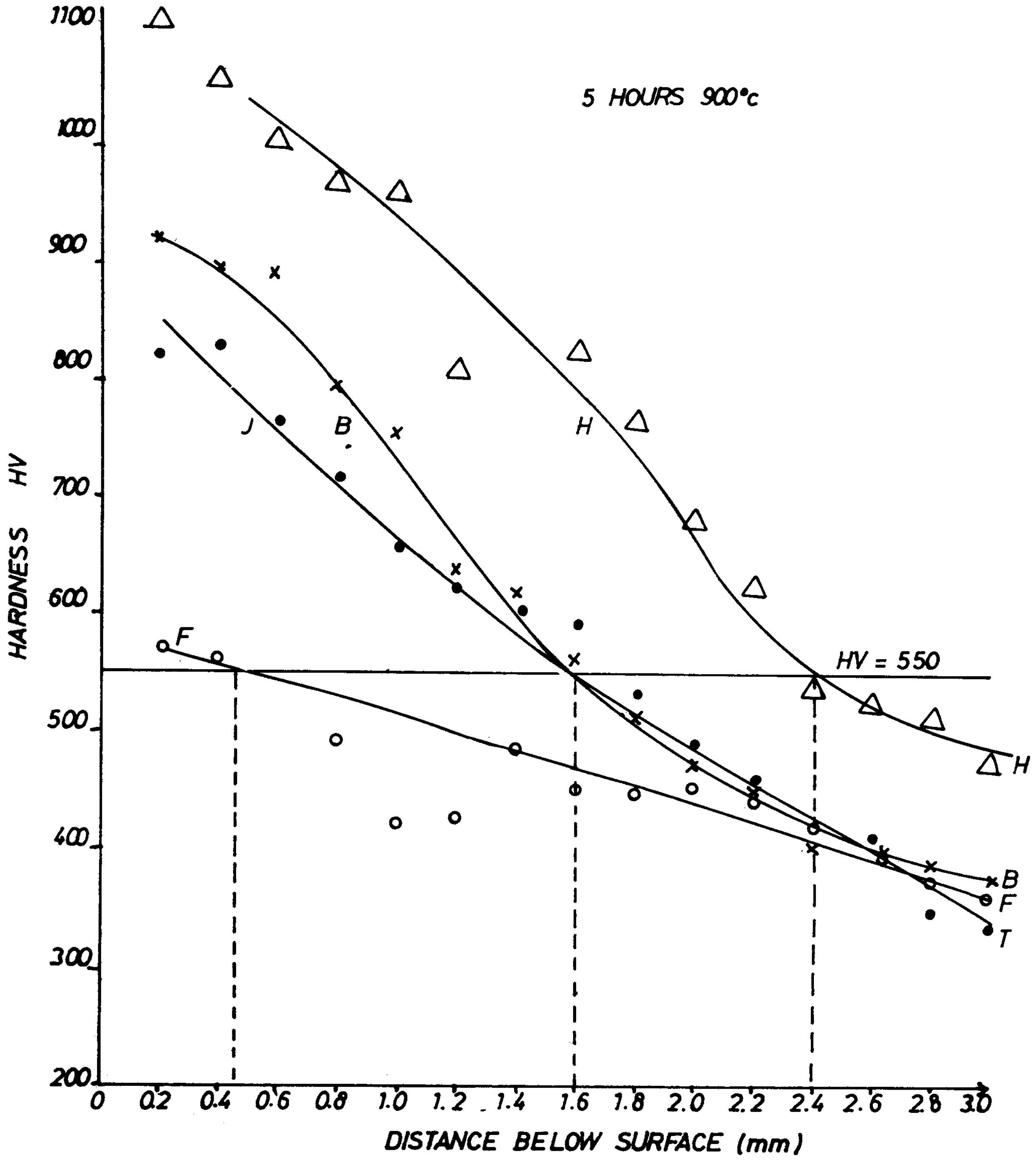

Fig 2(c): Hardness profiles with different carburising compounds after 5hours at 900°c

FIG 3(a): HARDNESS PROFILES WITH DIFFERENT CARBURISING COMPOUNDS AFTER 8 HOURS AT 900°C

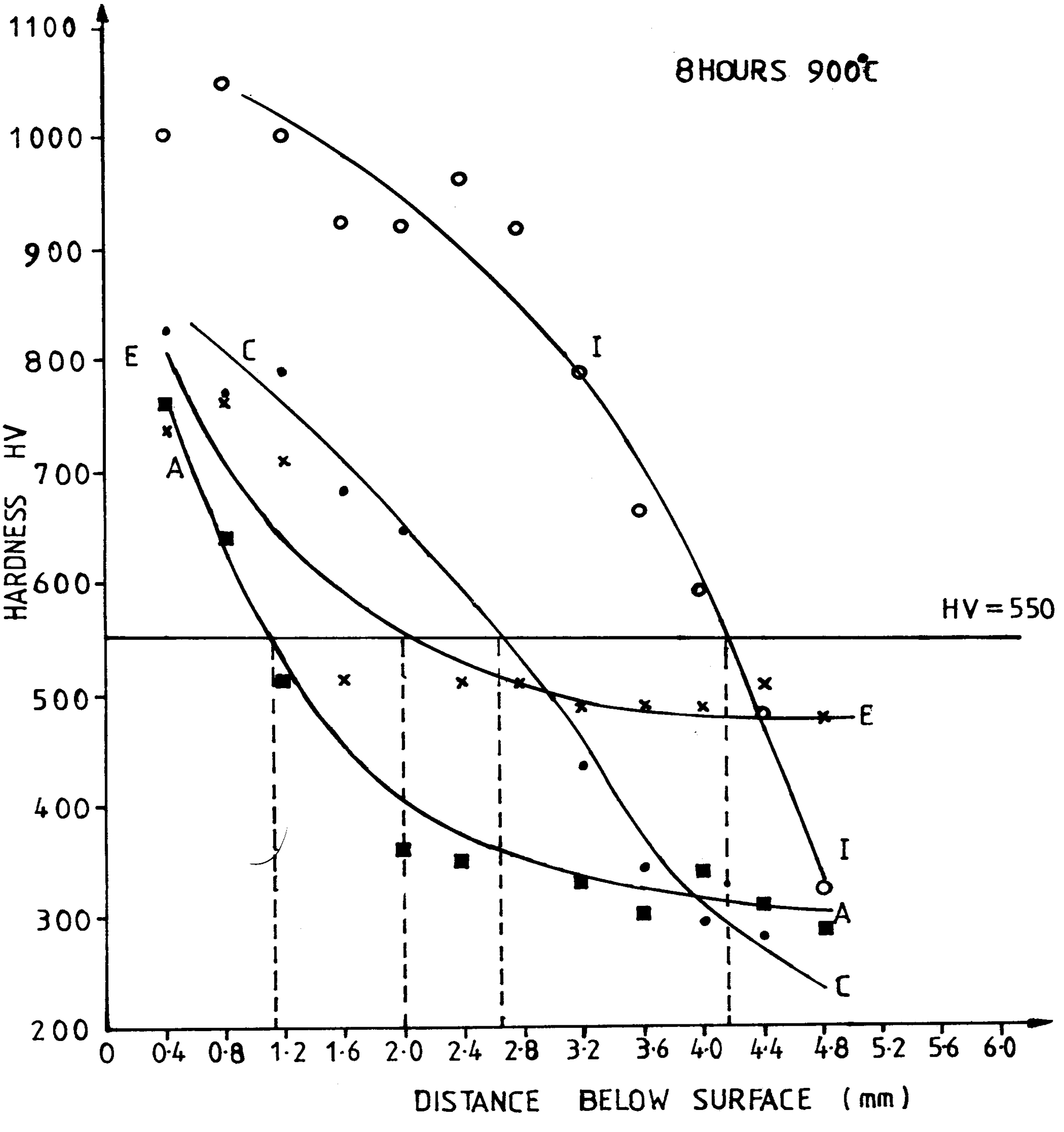

FIG3(b): HARDNESS PROFILES WITH DIFFERENT CARBURISING COMPOUNDS AFTER 8 HOURS AT 900°C

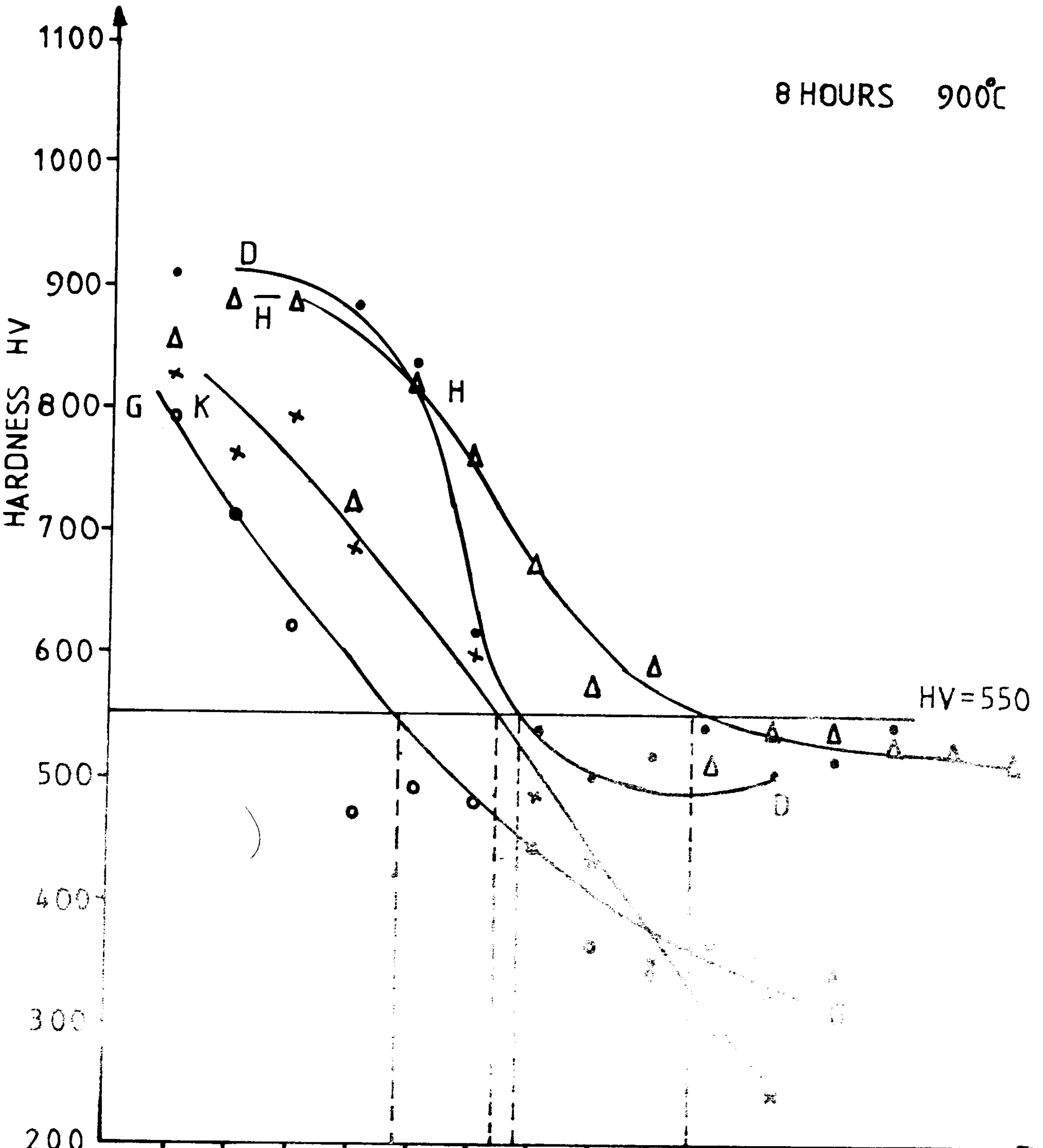

FIG 3(c): HARDNESS PROFILES WITH DIFFERENT CARBURISING COMPOUNDS AFTER 8 HOURS AT 900°C