PREPARATION OF IRON-SULPHUR ALLOYS FOR DESULPHURISATION STUDIES

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BY

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SCOPE AND CONTENTS:

A levitation apparatus has been constructed for investigating the behaviour of liquid iron drops containing sulphur, whilst suspended in a moving gas stream.

To further this investigation, a source of iron-sulphur alloys, in form and size suitable for levitation, was required. Four methods for the preparation of the desired alloys were suggested, and each was experimentally examined in sequence.

The first 2 methods involved the quenching of a liquid solution of sulphur in iron, to give a solid alloy. The well-known behaviour of sulphur, to segregate on solidification, was observed, and the non-uniformity of the resulting alloys could not be tolerated. The third method involved preparing a large number of individual iron-sulphur samples by allowing drops of iron to fall and quench on particles of sulphur or iron sulphide. The repeatability of the method was found to be unsatisfactory. In the final attempt a levitated liquid drop of iron was equilibrated in a gas mixture of hydrogen-hydrogen sulphide. This method was considered more successful than the earlier three, and has the advantage that the prepared alloy drop is levitated and at the desired temperature.

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CHAPTER I

INTRODUCTION

The presence of sulphur in steel has always been a source of concern to the steelmaker, in view of its effect on the mechanical properties of the finished product. Problems associated with sulphur removal are likely to become more severe in the future, as the demands for cleaner steel become more widespread. Much of the previous work (1,2,3) on the behaviour of sulphur in liquid iron has been thermodynamic in nature, although there have been a few investigations into kinetics of sulphur removal from molten iron contained in refractory crucibles(4,5,6,7).

Recent developments concerning spray-refining(8,9,10) of hot metal, have given considerable optimism for the commercial use of this process for steelmaking purposes. As a result, much interest is now centred on the phenomena associated with a multicomponent liquid sphere falling in a moving gas, allowing mass transfer and chemical reaction. Since the desulphurisation data, available from crucible studies, are not applicable to the desulphurisation of molten iron alloy drops, there is a need for quantitative data in this area. An experimental technique which has been useful in the past for studying the behaviour of molten iron alloy drops, exposed to a reactive gas phase, is based on levitation melting.

In the following chapters a report is presented on two aspects of this problem:

(i) The construction of equipment, and development of a technique, suitable for studying the desulphurisation of levitated molten iron-sulphur alloys;

(ii) The development of a suitable procedure for preparing iron-sulphur alloys of known sulphur content, for use in subsequent desulphurisation studies.

CHAPTER II

LITERATURE REVIEW

2.1. Desulphurisation of Steel

Desulphurisation studies with industrial application(11,12,13) make little contribution to the basic understanding of the phenomena. While other studies(1,2,3) have been made to obtain thermodynamic data, comparatively little work has been done on the non-equilibrium state. The rates of sulphur transport from metal to slag have been examined(4,5,6,14) in crucibles, but the results are often specific to the particular laboratory system employed. Such studies also suffer from the limitations associated with crucible experiments; eg. contamination of the melt by the refractory material. They are of little value with regard to either conventional steelmaking processes or spray-refining. Masson et al.(7) found that sulphur could be removed from a liquid iron surface, exposed to hydrogen-helium gas mixtures, but the data cannot be extended to systems which differ in geometry from the one investigated.

More recently, a few data have been reported(15) for the removal of sulphur from drops of pure iron, iron-silicon, and iron-manganese alloys, falling through oxygen. This study represented a close simulation of the conditions which are likely to exist within a spray-tower. However, the data reported were very sparse and were based upon the behaviour of drops which varied in size from about 1 to 6 m.m. in diameter.

2.2. Levitation Melting

The feasibility of levitation melting has been known for many years, and received some detailed investigation in 1952 by Okress et al.(16). The technique has found a variety of uses in the metallurgical field, which are well referenced in the scientific literature. The history and uses of this technique, have been thoroughly reviewed by Peifer(17) and more recently by Rostron(18).

One of the applications of levitation melting has been for thermodynamic studies of reactions between molten alloy drops and a gas phase(19,20). An extension of this type of work has been reported by Baker et al.(21,22) who measured rates of carbon removal from droplets of iron-carbon alloys. The droplets were levitated in a moving gas mixture of carbon dioxide, carbon monoxide and oxygen at various partial pressures. It is considered that the type of kinetic data obtained by Baker for decarburisation, could also be obtained by a similar technique, for desulphurisation. Since the geometry of the system is accurately defined, the data may be interpreted mathematically, and should have application in both conventional and spray-steelmaking processes.

It is worth noting that, although experimental utilisation of the levitation technique has been successful in the past, a full understanding of the detailed electromagnetic phenomena involved, has never been established. However, the salient factors involved are known qualitatively, and the lack of fundamental theory concerning the operation of a levitation coil has in no way handicapped the work. Detailed studies(23,24) of electromagnetic theory with reference to levitation, have been made recently, which serve to confirm what has been known qualitatively concerning the actual operation of a levitation system.

When connected to a high frequency source, the levitation coil produces a magnetic field which both heats and levitates the metal sample. The temperature is generally controlled by varying the velocity of the gas past the sample(25), and by varying the power input to the coil. While this procedure is suitable for thermodynamic studies, variations of the gas velocity may have significant effect on the transport rates for kinetic investigations. As a result the gas velocity must be held constant, and the temperature of the sample controlled by adjustments of the power input alone. It is worth noting that the temperature is also governed to some extent by the drop size and coil geometry.

2.3. Preparation of Iron Alloys

After surveying the literature on desulphurisation and levitation melting, confidence was gained in the feasibility of future work. The immediate objective was thus the development of a technique for the preparation of iron-sulphur alloys, (1-4%S), which could then be used for subsequent desulphurisation studies.

Iron-sulphur alloy melts could be prepared in a crucible(7), and then allowed to solidify as rapidly as possible to yield a small ingot. In this way Baker(21) prepared 200 gm. ingots of iron-carbon alloys, which were of uniform composition. However, the general character of sulphur, and the behaviour of iron-sulphur alloys as indicated by the phase diagram, suggest that there is a possibility of non-homogeneity in ingots prepared in this way. Nevertheless, such a procedure has the advantages of simplicity, and speed, whilst yielding a large number of specimens suitable for levitation. These advantages clearly warrant further investigation of this procedure.

The possibility of sulphur segregation is reduced by more rapid quenching. This may be achieved by withdrawing large suction samples from the melt with quartz tubes and quenching in water. In the past, this technique has been widely used to obtain samples from liquid iron alloys. It has been found satisfactory(15) for melts of very low sulphur content, (approximately 0.1%) and suction tubes of small diamter (1 to 3 m.m.). Both these factors tend to reduce sulphur segregation. However, specimens taken from rods of such a small diameter would not be suitable for levitation purposes. Rods greater than 6 m.m. in diameter are necessary in order to provide suitable specimens. If such rods are obtained they must be homogeneous in composition.

It should be noted that when a sample is analysed for sulphur, the sample is destroyed, (see section 3.4.). It is necessary therefore, that the large alloy mass, part of which may be taken for analysis and part for experiment, be uniform in solute distribution. If such a condition cannot be satisfied, it may be obviated by making up many, small independent samples of a particular composition, and conducting the analysis on several complete samples. The total sulphur content of the sample is then known, irrespective of the distribution within it. If alloys of the same composition can be prepared systematically, with reliability, then the remaining samples may each be taken for levitation experiments.

An application of the latter approach was made by Shiraishi(26) in preparing 1 gm. samples of iron-chromium alloys for levitation. A weighed amount of chromium was inserted and sealed into a hole which had been drilled in a weighed piece of iron. The sample was then levitation melted to give a uniform drop of known chromium content. This method is ideal, when the alloying component melts at a higher temperature than iron, and is electrically conducting.

A modification of this procedure is to levitate pure iron and allow it to fall onto the alloying element contained in a copper mould. The two components weld together to some degree during the solidification process and yield a product in a suitable form for relevitation. This method has been used successfully(27) in the past for the preparation of a variety of iron alloys, including those of chromium, nickel, molybdenum and manganese sulphide.

Another possible method for the preparation of iron-sulphur alloys is based on the work of Chipman(28) who used a crucible technique to measure the equilibrium constant for the reaction:

$$Fe + H_2S = FeS + H_2$$

If the crucible-melt system is replaced by a levitated iron drop, then equilibrium may still be established with a gas mixture of hydrogen and hydrogen sulphide. The iron-sulphur drop, so formed, would be available at known composition, already levitated and molten for further experiment. To achieve such an equilibrium, the gas mixture must be low in hydrogen sulphide, (less than 1%). Chipman's work required considerable experimental sophistication to prepare and maintain such a gas mixture. Also, efforts had to be made to prevent thermal diffusion occurring within the gas phase, which would alter the ratio of the components of the gas, in the vicinity of the hot metal.

CHAPTER III

EXPERIMENTAL CONSIDERATIONS

3.1. Materials

A description is given below of the various materials used for the experimental work.

The analysis of the Armco. iron was as follows, (figures are in weight percent):

C - 0.024
Mn - 0.033
P - 0.005
S - 0.015
Si - 0.001
Cu - 0.018
O - 0.075

The sulphur was in a finely powdered form, manufactured by precipitation, and satisfying the specification of U.S.P.

The iron sulphide was granular and contained a minimum of 85% of iron sulphide. In view of the variation in sulphur content that this figure permitted, it was checked and confirmed analytically, on pieces as small as those used in later experiments.

A typical analysis for the hydrogen sulphide gas was as follows:-

	Mole Percent
Hydrogen sulphide	99.70
Carbon disulphide	0.09
Carbon dioxide	0.13
Methyl mercaptan	0.02
Carbonyl sulphide	0.01
Sulphur dioxide	0.05

The hydrogen supplied, was of a minimum purity (on a helium-free basis) of 99.999%. A typical analysis was as follows:

	P.P.M. by vol.
Oxygen	1
Carbon dioxide and monoxide	1
Hydrocarbons	0.8
Helium	50
Moisture	5

The helium which was used for purging was in excess of 99.0% purity.

3.2. Levitation Procedure

In order to determine the feasibility of using a levitation technique for desulphurisation studies of iron, in a manner similar to that of previous work(21,22) on decarburisation, several experiments were made using iron, and subsequently iron-sulphur alloys.

The equipment is shown in Figure 1. Apart from the sealing plate of aluminium at the base, the apparatus was made

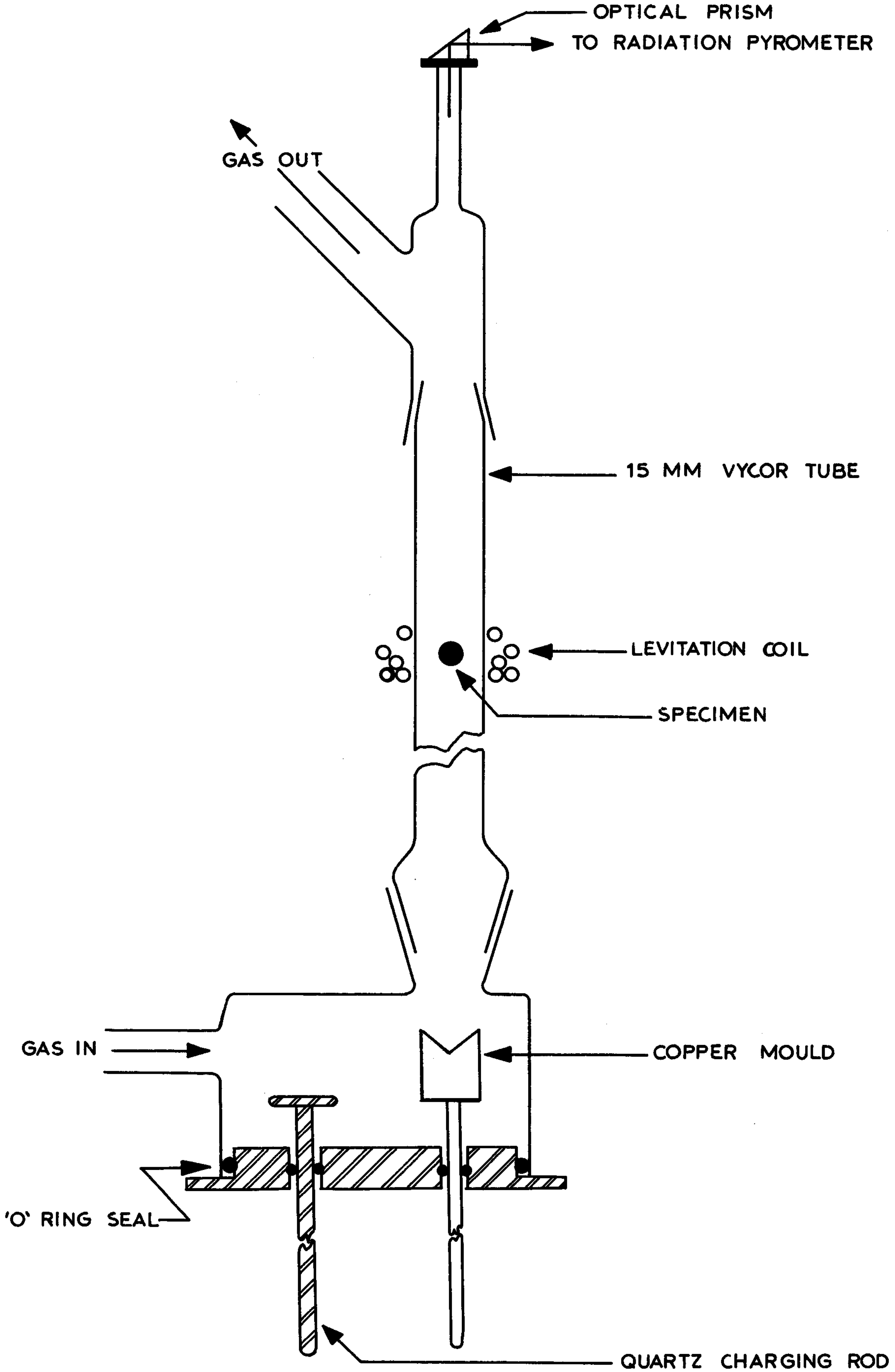


FIGURE 1– SECTION OF THE ORIGINAL EXPERIMENTAL APPARATUS FOR LEVITATION.

of Vycor glass, which tolerated limited contact of molten iron, without softening or shattering.

In the past, various types of coil design have been tried each with its own particular features (17,18,29). The design of 5 turns and two reverse turns, was used here in the early stages, and found satisfactory. The coil shown in Figure 1, with 4 turns in the lower section and one reverse turn in the upper section, was used during most of the present work. The coil was manufactured from 0.125 inch, O.D. copper tubing, by winding on a brass former, and finally dipped in an epoxy resin, which hardened to give the coil mechanical rigidity. The power for levitation was supplied to the coil, which was water-cooled, by a Toccotron high-frequency generator, giving 10 K.W., at 200 amps and 450 k.c. per sec. The current was conveyed to the coil through a 7.5:1, step-down transformer.

The temperature of the specimen was measured using a Milletron two-colour, radiation pyrometer. Temperature measurements with this pyrometer depend upon the ratio of the intensities at two particular wavelengths, which are selected by the instrument from the band emitted by the specimen. The measurement is thus largely independent, of any variations in emissivity of the surface, and also of any absorption of the rays, if both wavelengths are equally attenuated. The risk of absorption was reduced by the presence of the narrow tube on which the prism was located. In the early stages of the present work, temperature measurement from above the sample was found to be satisfactory. However in later stages, (see method described in section 3.3.4.) some difficulty was experienced, which may have been caused by the absorption of the light by fume or deposits in the upper section of the reaction tube. This difficulty was obviated by re-location of the prism below the sample, as shown in Figure 2.

The aluminium base could be rotated so that, either the copper mould or the charging rod, was directly below the sample. The charging rod was raised into the coil, thus supporting the cold specimen, whilst the system was purged with helium. The power was switched on, the specimen levitated and the charging rod withdrawn. At the conclusion of the levitation period, the specimen was quenched by raising the copper mould into the reaction tube and switching off the power. Provided that the quench is sufficiently rapid, the cast specimen should have the same composition as the liquid melt.

As mentioned previously, variations in gas velocity could have a significant effect on the reaction kinetics. Thus, for a particular sample and coil geometry, the temperature had to be controlled by the power input to the coil. This was found to allow temperature adjustment over only a narrow range. When the power was decreased, the levitation force was reduced, causing the specimen to locate itself at a null-point, which was at a lower position in the coil. The heating effect was greater and thus the temperature increased. However, the extent to which the power could be reduced, was limited by

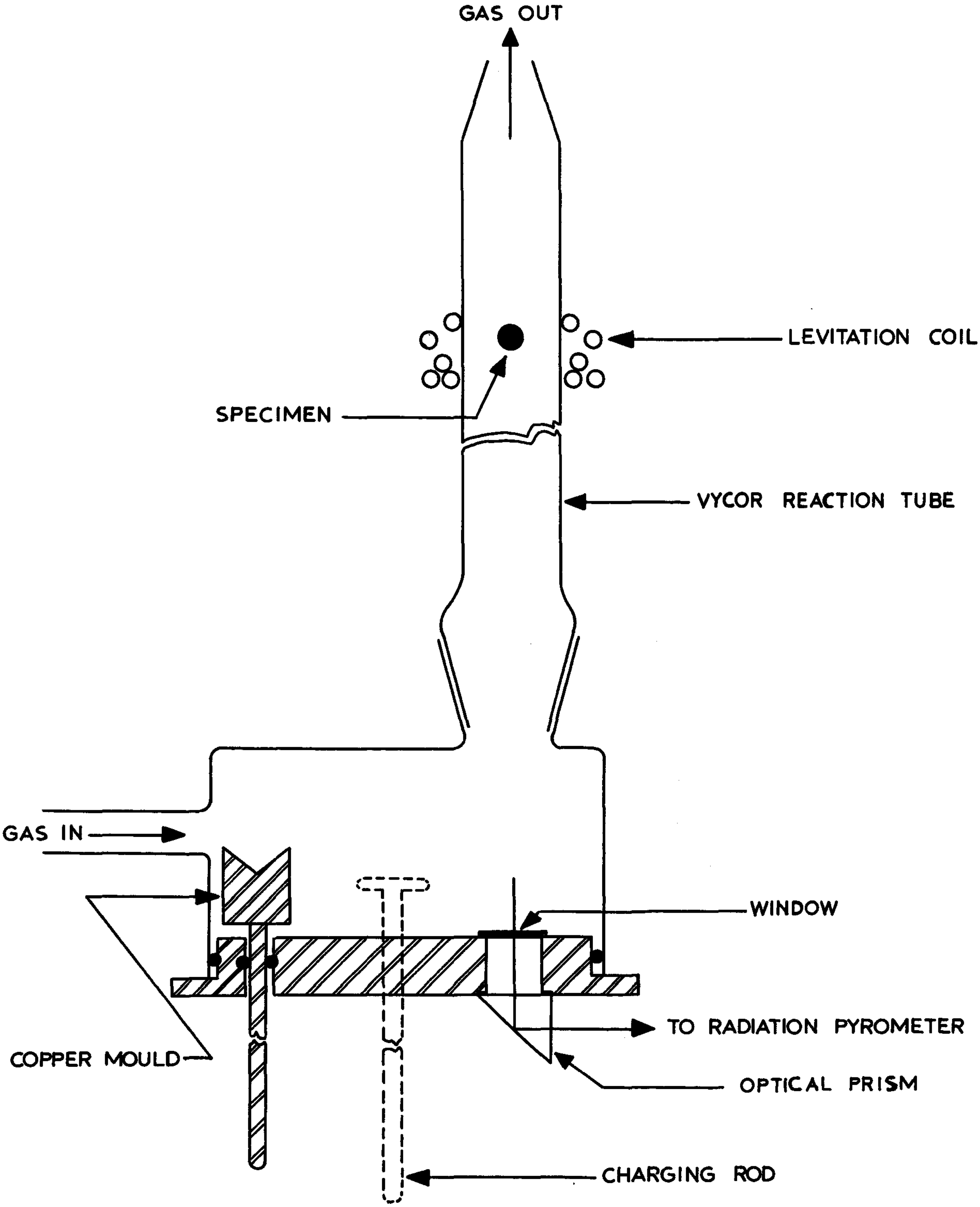


FIGURE.2 – MODIFIED APPARATUS FOR LEVITATION the minimum required for levitation of the sample. On the other hand, the lowest temperature was obtained when the drop was located at the highest point in the coil, which corresponded to the maximum power output of the generator. In consequence particular attention was paid to the other factors which affected the droplet levitation force and therefore its temperature. These factors, (drop size, coil geometry and electrical coupling to the coil) were selected so that the required temperature ranges could be attained by adjusting only the power input to the coil.

3.3. Preparation of Iron-Sulphur Alloys

3.3.1. Crucible Method

Alloys were prepared by placing about 100 gm. of Armco. iron in a recrystallised alumina crucible (Morganite Purox XN 20). The crucible was placed in the apparatus shown in Figure 3. The iron was melted under helium, by induction heating with the power supplied from the 10 K.W., high-frequency generator. The liquid was held just above the melting point, in order to reduce evaporation of the iron and ensure rapid solidification on cooling. The molten iron was deoxidised by passing hydrogen through the system for about 30 minutes.

Powdered sulphur was melted and cast in a mould to give a compact, bullet-shaped pellet of about 5 gm. in weight. This was added to the liquid iron through a quartz tube which was dipped into the melt. Some sulphur was lost as gas due to evaporation on immediate contact, but the greater portion of it

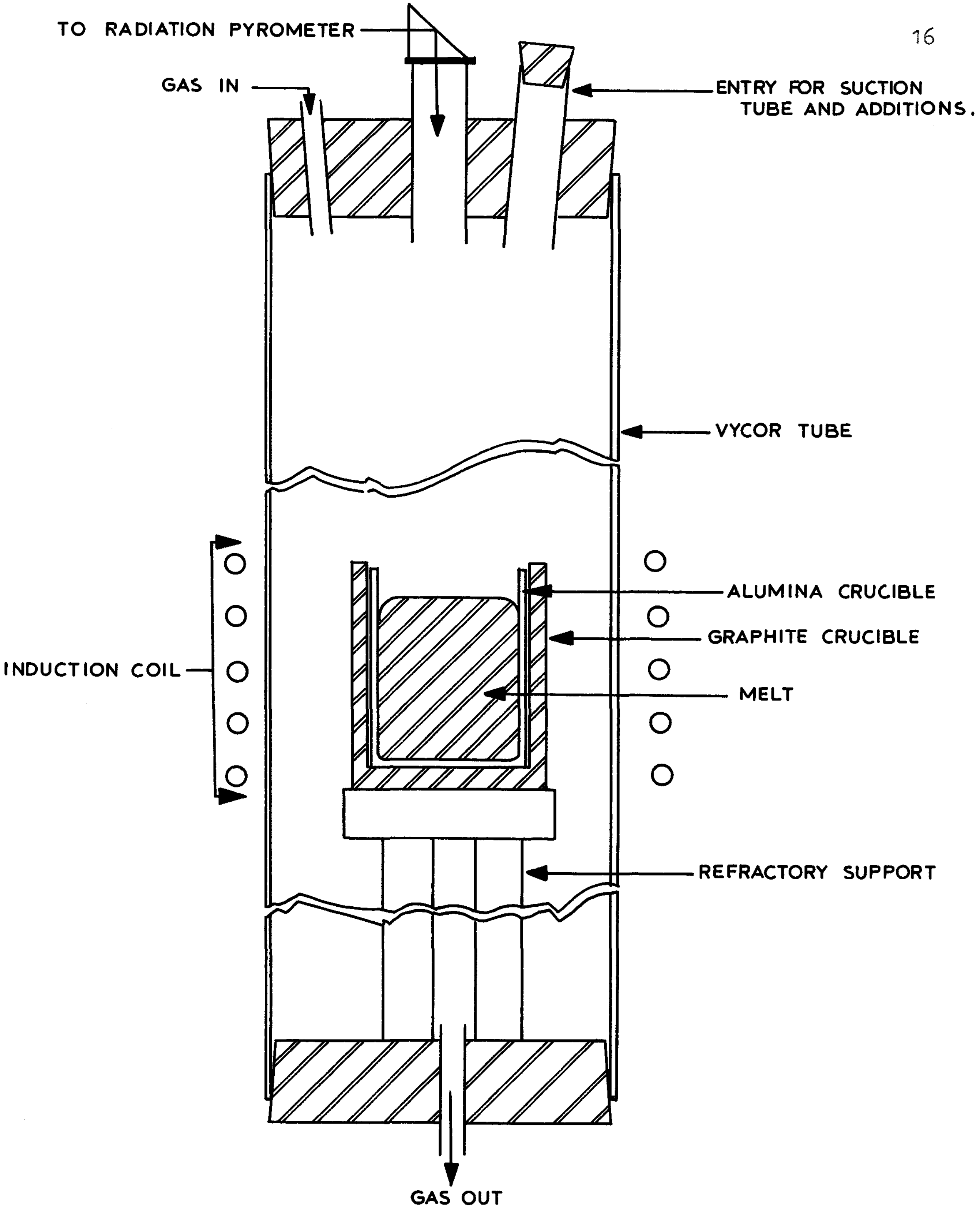


FIGURE 3 – APPARATUS FOR PREPARING IRON SULPHUR MELTS

was taken into solution in the iron.

About 5 minutes after the sulphur addition, the power was switched off, and the melt cooled as quickly as possible under a stream of helium. The resulting cylindrical ingot was removed from the crucible, and cut into small sections. Each section was analysed for sulphur content, to check the uniformity of the distribution. A section of the solidified ingot was mounted, polished, etched in 2% Nital and examined under the microscrope.

The first attempts to prepare iron-sulphur alloys were made without the outer graphite crucible. However, it was found that even with slow heating over prolonged periods, (up to 8 hours), the non-uniform heating by induction in the iron, produced temperature gradients in the alumina crucible, which were sufficient to cause fracture. When pure iron was contained within the crucible, these hair-line fractures could be tolerated without inconvenience, since the surface tension of liquid iron was sufficiently high to prevent leakage. However the presence of sulphur, even in small amounts, caused a marked decrease in the surface tension. This was sufficient to allow the liquid alloy to drain freely through the cracks. This refractory problem was overcome by introducing the outer graphite crucible, as shown in Figure 3. The graphite fitted closely around the alumina, with space for expansion, but without contamination of the melt. The power was dissipated in the graphite crucible, which then provided uniform heating within the alumina. In this way, thermal stresses in the alumina were eliminated, and spalling prevented.

3.3.2. Suction Sampling

The method of suction sampling, from a melt contained in a crucible, employed the same apparatus as that described above and shown in Figure 3. The liquid alloy of iron and sulphur was prepared in an alumina crucible, as outlined above. Suction samples were then drawn from the melt with the aid of an 8 m.m. O.D. quartz tube and an aspirator bulb. After immediate quenching in water, samples about 4 - 7 inches long were obtained. The ends, about ½ to 1 inch, were removed and discarded, and the surface of the rods cleaned by grinding and acid washing. The rods were cut into discs which were suitable for levitation. Some of the samples along the length of each rod were analysed. Sections of other samples were polished, etched and examined microscopically.

3.3.3. Mould Quenching

Sulphur weighing about 0.01 to 0.03 gm. was placed in the copper mould at the base of the reaction tube of the apparatus shown in Figure 1. An accurately weighed piece of iron, (0.5 to 0.7 gm.) was levitated and held at a temperature just above the melting point, in a helium gas stream. The copper mould was raised, the power switched off, and the drop quenched. The mould was shaped such that the iron enveloped the sulphur. If the envelope were not complete, considerable difficulty would follow on relevitation of the casting, even though its overall shape from the mould was ideal for a levitation specimen.

This procedure was repeated many times, until a number of satisfactory samples were obtained. The samples were weighed, before determining the sulphur content of each. A check was made between the weighings for iron and sulphur, and the final analysis.

This procedure was repeated using iron sulphide in the mould, rather than elemental sulphur.

3.3.4. Gas-Metal Equilibration

The final laboratory attempt employed a gas mixture, consisting of hydrogen and hydrogen sulphide. The mixture was supplied in a gas cylinder, and after standing for some time, was assumed to be completely mixed.

The apparatus used was that shown in Figure 2. A sample of pure iron was levitated in the reaction tube. Whilst in an inert atmosphere, the temperature was adjusted to the desired value. Great care was taken in purging the apparatus with helium, and in avoiding leaks, before switching over to the hydrogen/hydrogen sulphide gas mixture. The gases were passed over the molten iron for about three minutes, whilst the temperature was maintained constant. The sample was then quenched in the copper mould, and analysed. Several samples were prepared in this way, with the same gas in order to check for reproducibility.

Initial attempts at preparing alloys with this technique were made using the apparatus shown in Figure 1. However, when using the hydrogen/hydrogen sulphide gas, difficulty was experienced with the temperature measurement of the drop, as mentioned previously. The difficulty was overcome by mounting the prism on the aluminium base and sighting the pyrometer from below the drop, as in Figure 2. This apparatus was used for all subsequent work.

3.4. Chemical Analysis for Sulphur in Iron

The analysis of the iron-sulphur alloys was made by a standard combustion technique, followed by titration, using a 'Leco' unit.

The weighed sample, contained in a zirconia crucible, was combusted by induction heating in a stream of oxygen. The sulphur passed off as sulphur dioxide which was dissolved in the titration solution. In solution, any free iodine present was consumed, and sulphuric acid formed, according to the following reaction:

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$$

The free iodine was continuously generated by the addition of potassium iodate solution from a burette. Starch was used to indicate the presence of free iodine. The titration solution consisted of excess hydrochloric acid and potassium iodide, which, on addition of the iodate released iodine according to the reaction:

$$KIO_3 + 5KI + 6HCl = 6KCl + 3H_2O + 3I_2$$

The reproducibility of this analytical technique is discussed in more detail in Appendix I.

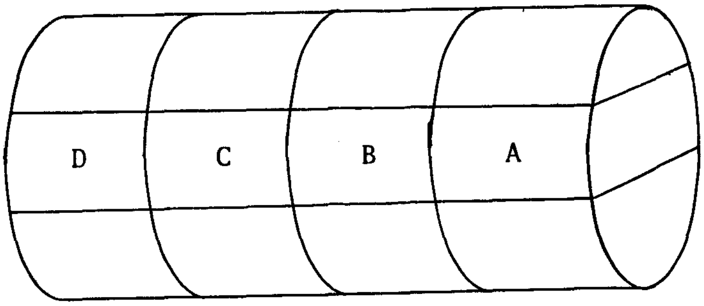
CHAPTER IV

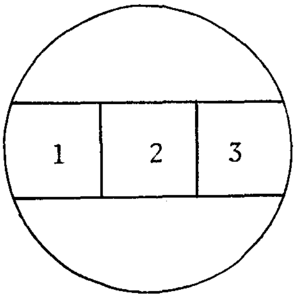
RESULTS

Typical data which resulted from the attempts at the various methods, are presented in the following tables, which are in the same sequence as the attempts. The sulphur content of various sections taken from one of the ingots produced from a crucible melt, is shown in Table 1. Each section is located by the reference number shown on the accompanying diagram.

TABLE 1 - Variation in Sulphur Content within a Small Ingot.

Section Reference	Sulphur Content Weight Percent		
	1	2	3
A	1.18	2.21	1.60
B	1.49	1.76	1.51
C	1.49	1.12	0.91
D	1.38	1.39	1.55





The sulphur content of seven suction samples taken from the same melt is shown in Table 2. The analysed samples were discs cut from the top, centre and bottom of each rod.

TABLE 2 - Variations in Sulphur Content of Suction Samples

Suction Sample	Sulphur Content % Wt.		
	Top	Centre	Bottom
1	3.7	2.9	3.5
2	2.0	2.1	0.65
3	1.9	1.7	1.4
4	0.84	2.4	2.8
5	3.2	2.5	1.4
6	3.1	1.6	2.0
7	3.2	2.3	2.4

The sulphur content of samples levitated in helium, and quenched in a copper mould containing sulphur, is shown in Table 3. The table does not include the large number of samples which were rejected after preparation, due to losses during quenching. This effect is discussed in section 5.3.

TABLE 3 - Sulphur Content of Drops Quenched in a Copper Mould containing Sulphur

Sample	Weight of Iron gm.	Weight of Iron + Sulphur gm.	Weight of Sulphur gm.	Predicted Sulphur Wt. %	Sulphur Analysis Wt. %
1	0.65241	0.65358	0.00117	0.179	Negligible
2	0.56446	0.56497	0.00051	0.090	0.064
3	0.70113	0.70106	-	-	-
4	0.62793	0.62844	0.00051	0.081	0.012
5	0.56796	0.56852	0.00056	0.098	0.037
6	0.66550	0.66540	-	-	-
7	0.55245	0.55201	-	-	-
8	0.68538	0.68871	0.00333	0.484	0.719
9	0.56889	0.56931	0.00042	0.074	Negligible
10	0.59190	0.59207	0.00017	0.029	0.848
11	0.63360	0.63415	0.00055	0.087	0.026
12	0.58373	0.58760	0.00387	0.657	0.073
13	0.65215	0.65843	0.00628	0.954	1.34

The results for samples which were levitated in helium and quenched in a copper mould containing iron sulphide, are shown in Table 4. The sulphur content obtained by analysis is compared with that predicted from a knowledge of the original weights.

TABLE 4 - Sulphur Content of Drops Quenched in a Copper Mould containing Iron Sulphide

Sample	Weight of Iron gm.	Weight of Iron Plus Iron Sulphide gm.	Weight of Iron Sulphide gm.	Weight of Sulphur gm.	Predicted Sulphur Wt. %	Sulphur Analysis Wt. %
1	0.53965	0.56137	0.02172	0.00792	1.41	1.18
2	0.58795	0.61283	0.02488	0.00907	1.48	1.40
3	0.57918	0.60418	0.02500	0.00912	1.51	1.16
4	0.63822	0.66292	0.02470	0.00901	1.36	0.815
5	0.59638	0.62094	0.02456	0.00896	1.44	0.773
6	0.49350	0.52204	0.02854	0.01041	1.99	1.84
7	0.64992	0.66756	0.01764	0.00643	0.96	0.899
8	0.54838	0.57692	0.02854	0.01041	1.80	1.21
9	0.55380	0.57360	0.01980	0.00722	1.26	1.19
10	0.63458	0.65380	0.01922	0.00701	1.07	0.857
11	0.58404	0.61213	0.02809	0.01025	1.67	1.54
12	0.63247	0.65840	0.02593	0.00946	1.44	1.12
13	0.56829	0.58819	0.01990	0.00726	1.23	0.884
14	0.55606	0.57980	0.02374	0.00866	1.49	1.48
15	0.63113	0.65744	0.02631	0.00960	1.46	1.40
16	0.63889	0.65934	0.02045	0.00746	1.13	0.880
17	0.58670	0.60011	0.01341	0.00489	0.81	0.966
18	0.52405	0.54761	0.02356	0.00859	1.57	0.877
19	0.60598	0.63190	0.02592	0.00945	1.50	1.30
20	0.63487	0.65046	0.01559	0.00569	0.87	0.707

The table below shows the sulphur content of specimens which were levitated, melted and allowed to equilibrate in a gas mixture of 0.05% hydrogen sulphide in hydrogen. Each specimen was maintained at a temperature of 1,600°C for approximately 3 minutes to establish equilibrium.

TABLE 5 - Sulphur Content of Drops Equilibrated in a Gas Mixture

Specimen	Weight of Specimen gm.	Sulphur Analysis Wt. %
1	0.6721	0.08
2	0.5756	0.10
3	0.5360	0.11
4	0.4786	0.09
5	0.5110	0.08
6	0.4794	0.12
7	0.4685	0.13
8	0.5737	0.10
9	0.5130	0.12
10	0.5424	0.11
11	0.5318	0.11
12	0.5510	0.11
13	0.4797	0.12
14	0.4428	0.09
15	0.5217	0.11
16	0.5403	0.11

Arithmetic Mean = 0.1056
Standard Deviation = 0.0141

CHAPTER V

DISCUSSION

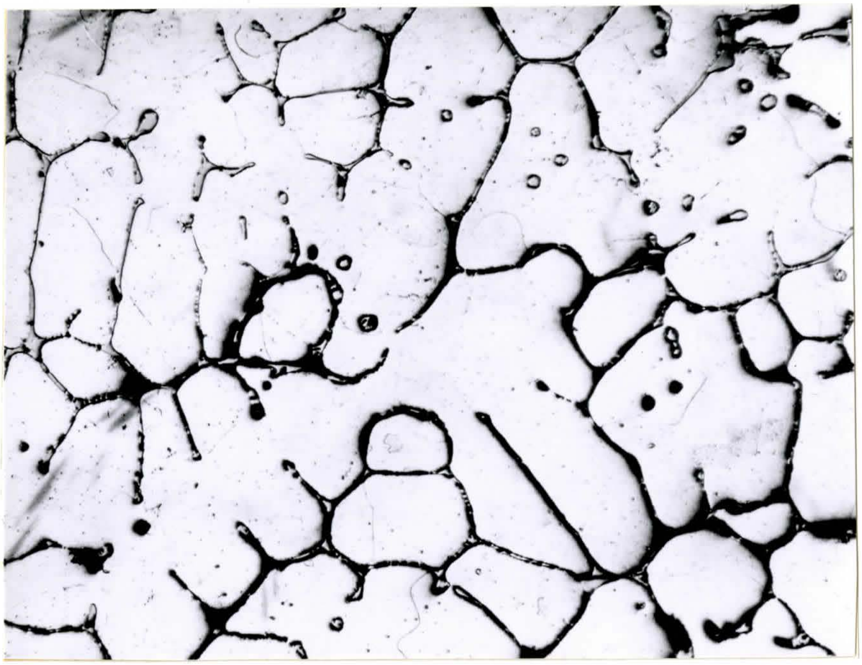
5.1. Crucible Method

As shown in Table 1, the distribution of sulphur throughout the alloy was quite irregular. The slow cooling of the ingot permitted pronounced segregation, and the sulphur concentration in various sections of the ingot, ranged from 1.0 - 2.5%.

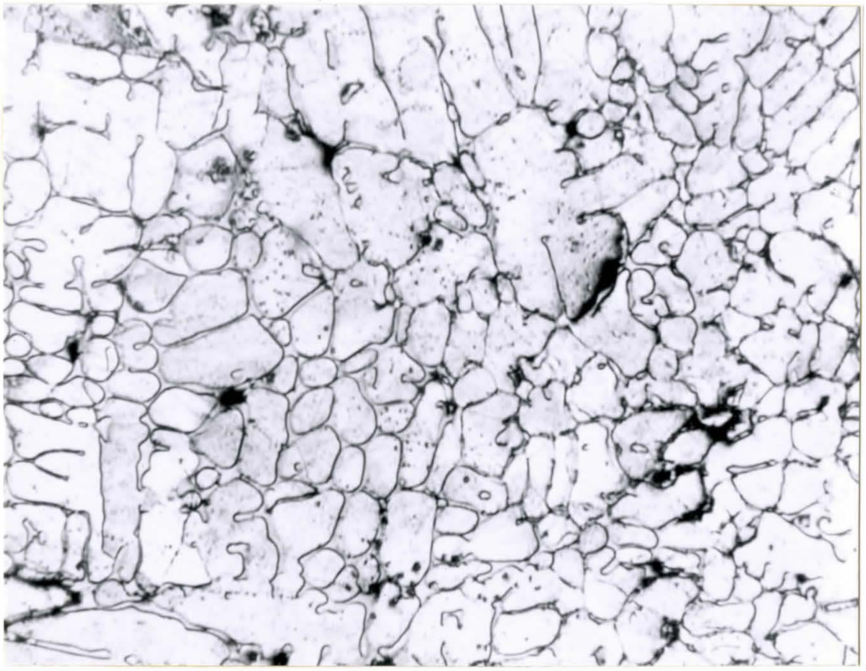
Microscropic examination of a polished section of the ingot, etched in 2% Nital, confirmed the slow rate of cooling and the segregation of the sulphur. A photomicrograph of the section is shown in Figure 4.a. The main features shown in this photograph are the large iron grains, indicative of slow cooling, and the broad grain boundaries, where the sulphur (dark areas) has collected in the form of iron sulphide. The iron sulphide at the grain boundaries forms a brittle network, which leads to poor mechanical properties in the finished steel. For this reason, alloying elements which have an affinity for sulphur, greater than that of iron itself, are generally added to steel in practice. In these circumstances the sulphur is present in the form of discrete particles rather than a continuous network around the grains, and consequently there is an improvement in mechanical properties.

5.2. Suction Sampling

Analysis of the rods obtained by suction sampling, (see Table 2), indicated a degree of non-uniformity along the length of

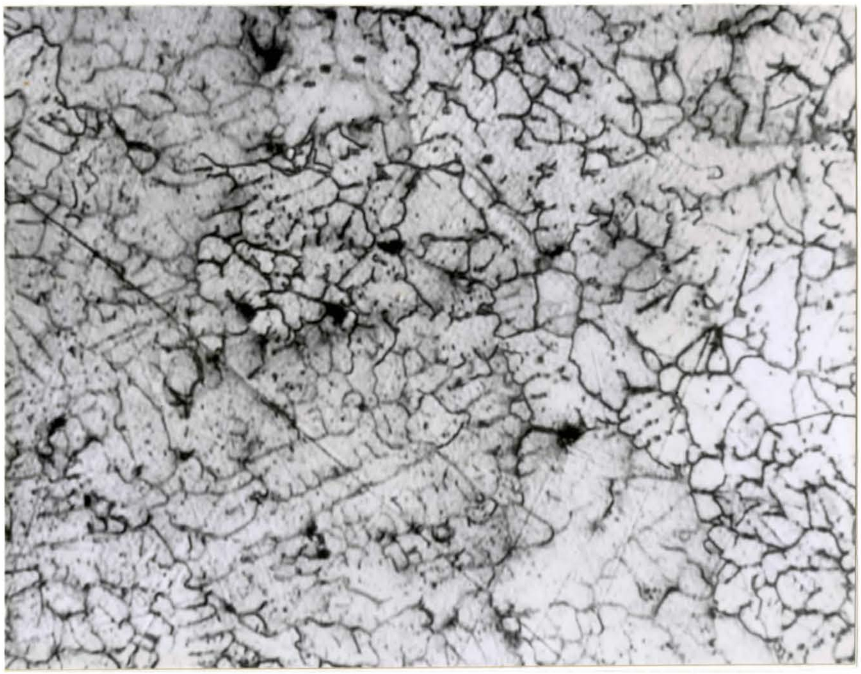


(a) Sample from an ingot - Magnification 150 x

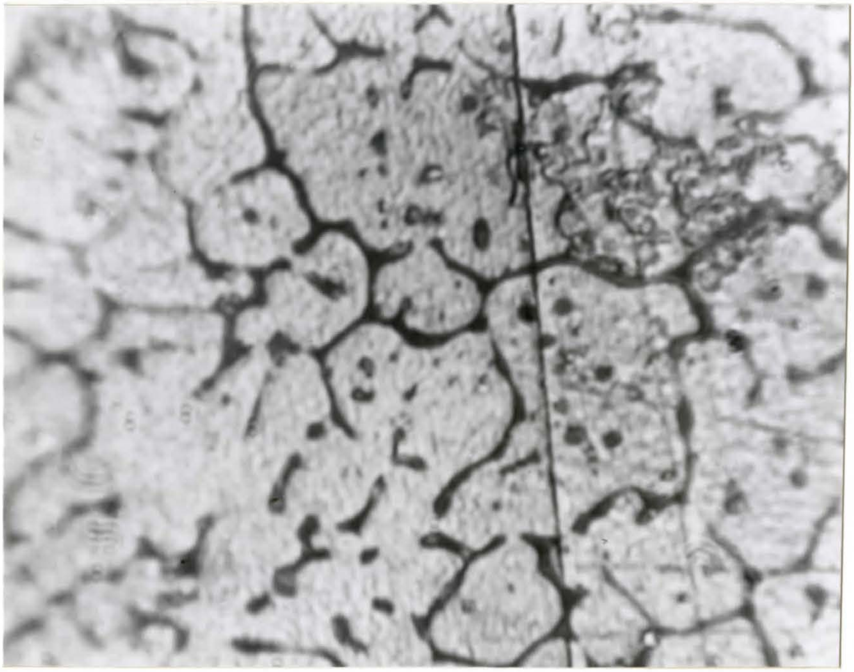


(b) Section from a suction sample - Magnification 300 x

FIGURE 4 - PHOTOMICROGRAPHS OF VARIOUS IRON-SULPHUR ALLOYS



(c) Section from a mould quenched specimen - Magnification 300 x



(d) Section from a hammer quenched specimen - Magnification 920 x

FIGURE 4 - PHOTOMICROGRAPHS OF VARIOUS IRON-SULPHUR ALLOYS

of the rods, comparable in severity to that of the ingots discussed previously.

A transverse section from one of the rods was polished and etched for microscopic examination. The type of structure obtained is shown in Figure 4.b. This is similar to that shown in Figure 4.a., although, as would be expected, the grain structure is much finer due to the more rapid quench.

Examination of the transverse section, clearly demonstrated the effect of cooling rate on the grain structure. As any diameter of the rod was transversed from the outer edge to the centre an increase in grain size could be detected, which corresponded to a decrease in cooling rate from the outside of the rod to the inside.

While suction sampling has been found to be satisfactory for the preparation of iron-carbon,(19) iron-chromium,(27) and iron-manganese(15) alloys, the present work indicates that the cooling rate is not sufficient to prevent segregation in the case of iron-sulphur alloys, of the size suitable for levitation studies.

5.3. Mould Quenching

In many cases, when the iron drop fell onto the sulphur the impact and high temperature were sufficient to cause some loss of sulphur and iron due to spatter and/or evaporation. When these effects were observed the resulting samples were discarded. The number of samples discarded, with respect to those considered acceptable, was high. This was a major disadvantage with this method, irrespective of the value of the acceptable samples.

The analysis and weighings for samples which were not discarded, are shown in Table 3. The data obtained indicate that considerable losses occurred during the process, and the final sulphur content bore no relationship to the original amounts introduced. After prolonged operation traces of sulphur were detected on the cooler, upper walls of the reaction tube.

The number of failures during the experimental procedure, rather than the results shown in Table 3, was the main reason for changing from elemental sulphur to iron sulphide. This procedure was more successful, and the number of samples to be discarded was reduced. The results, for the analysis of samples not discarded, are shown in Table 4. The improvement is attributed to the relatively high melting point of iron sulphide, (1193°C), compared to that of sulphur, (119°C, and boiling point of 444°C). However, despite the improvement, there was still disagreement between the analysed sulphur content and that predicted. Some disagreement may be explained by the impurity of the iron sulphide, which would permit the predicted sulphur content to extend over a range of values. However, the disagreement was greater than the limits of such a range. The prediction of the actual sulphur level was extremely uncertain, and thus the samples could not be used as starting material for future desulphurisation studies.

5.4. Gas-Metal Equilibration

Levitated samples of pure iron were allowed to reach equilibrium in a gas mixture containing 0.05% hydrogen sulphide. The results obtained for 16 experiments conducted at 1600°C are shown in Table 5. The error involved in the chemical analysis for the sulphur concentration is comparable to the standard deviation of these data. It is considered that the variation of the sulphur content for the results obtained so far, may be improved with further work. Improvement is possible, particularly in view of the fact that the reasons for poor reproducibility are experimental in nature, rather than inherent in the technique.

Additional attempts were made in which the period to establish equilibrium was varied, covering a range from 2 to 15 minutes. The data indicated that the inconsistencies typified in Table 5, were not due to insufficient time for the attainment of equilibrium.

Equilibrium values, derived from crucible measurements at this sulphur potential and at 1600°C, would indicate that the sulphur level in the iron should be approximately 0.19%. From Table 5 it can be seen that the final sulphur content of the levitated drops was of the order of 0.11%. This difference may be due to the occurrence of thermal diffusion within the gas mixture. The large difference between the molecular weights of the two gaseous components, and the severe temperature gradients near the drop, are both conditions which would promote thermal diffusion. If this effect is pronounced, the ratio of the components at the hot surface of the droplet may be different to that at the inlet. Further experiments are planned in order to investigate this effect in more detail.

One of the alloy specimens made by this method was sectioned, polished and etched to give the photomicrograph shown in Figure 4.c. This was done to examine further the effects of cooling rate on sulphur segregation. This section, from a levitated specimen quenched in the copper mould, received a more rapid quench than the sections shown in Figures 4.a. and 4.b. The separate sulphur phase may be clearly seen, indicating that the non-uniformity due to sulphur migration may still persist, despite the more rapid cooling rate. For purposes of comparison, Figure 4.d. is included. This shows a section from a sample which was quenched between the hammer and anvil of Caryll and Ward, (30). The initial cooling rate of the sample which this apparatus achieves, is of the order of 10^5 degrees C per second.

A particular advantage of the gas-metal equilibration technique is that the alloy droplet is already levitated and directly available for further experiments. In these experiments the droplet may be either exposed to, or allowed to fall through, a desulphurising gas phase.

CHAPTER VI

SUMMARY

Considerable experience has been obtained in the use of the levitation technique for supporting liquid metal droplets. The feasibility has been demonstrated, of studying the kinetics of desulphurisation of a sphere of an iron-sulphur alloy using this technique. Experimental apparatus for such studies is available for immediate use.

At high sulphur levels, there is little hope of producing a solid iron-sulphur alloy which is homogeneous. Only with extremely rapid quenching, may the pronounced segregation of the sulphur be eliminated.

The procedure for alloy preparation, whereby a levitated drop of iron is quenched on the second component which is located in the copper mould, was unsuccessful for iron and sulphur. This procedure is not recommended for iron alloys, where the melting point of the second component is much lower than that of iron.

The most successful method for the preparation of iron-sulphur alloys, was that based upon the use of a gas mixture of controlled sulphur potential. It is hoped to improve this method further. A particular advantage of this technique is that the levitated, alloy droplet is then directly available for desulphurisation experiments.

CHAPTER VII

FUTURE WORK

Equipment is available to enable the levitation technique to be used for further droplet studies. The removal of sulphur from iron, to a gas stream, will be examined in the future.

The present work with the gas mixture indicates that the technique may be used for thermodynamic studies of the activity of dissolved sulphur in multicomponent iron solutions. A fixed sulphur potential may be provided over the solution by hydrogen-hydrogen sulphide gas. The concentration of the sulphur in the solution may be measured as it varies with the effect of additional elements in the liquid iron. The elements which are normally used as deoxidisers in steelmaking, are of particular interest in this respect, since the effects of such elements are difficult to study by conventional crucible techniques.

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APPENDIX I

When any analysis was to be carried out on a batch of samples, a standard sample of known sulphur content was first analysed. This was always performed in order to ensure that the analytical apparatus and solutions were yielding results of the correct absolute value.

The accuracy of the method was examined by conducting analysis on 12 standard samples of known sulphur content. The standard used was supplied by N.B.S., standard sample number 129B, (high sulphur). The table below shows the sulphur contents obtained during the analysis.

Sample	Weight of Sample gm.	Sulphur Analysis Wt. %
1	0.9218	0.222
2	0.6820	0.227
3	0.8448	0.227
4	0.7961	0.210
5	0.7443	0.223
6	0.8195	0.209
7	0.8247	0.221
8	0.7337	0.211
9	0.7911	0.216
10	0.8225	0.215
11	0.8090	0.229
12	0.9251	0.223

Arithmetic Mean = 0.2194

Standard Deviation = 0.0070