A CASE STUDY OF THE INFLUENCE OF DEOXIDATION PRACTICE ON THE MORPHOLOGY AND CHARACTER OF NON-METALLIC INCLUSIONS IN CERTAIN GRADES OF STEELS

A DISSERTATION

submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF ENGINEERING
in
METALLURGICAL ENGINEERING
(With Specialization in Extractive Metallurgy)

By

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APRIL, 1991

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the dissertation entitled, **'A CASE STUDY OF THE INFLUENCE OF DEOXIDATION PRACTICE ON THE MORPHOLOGY AND CHARACTER OF NON-METALLIC INCLUSIONS IN CERTAIN GRADES OF STEELS'**, in partial fulfilment of the requirements for the award of the degree of **MASTER OF ENGINEERING** in Metallurgical with specialization in **Extractive Metallurgy** submitted in the Department of Metallurgical Engineering, University of Roorkee is an authentic record of my own work carried out for a period of 11 months from June 1990 to April 1991 under the guidance of **Dr. S.K. Goel**, Professor, Department of Metallurgical Engineering , University of Roorkee, Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree or diploma.

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Dated: 18th April, 1991

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ACKNOWLEGEMENT

I hereby express my sincere and heartful gratitude to Dr. S.K. Goel, Professor, Department of Metallurgical Engineering, University of Roorkee, Roorkee for his valuable guidance, time to time discussions and persistant encouragement throughout the period of my dissertation work.

I am grateful to Dr. M.L. Kapoor, Professor and Head, Department of Metallurgical Engineering for providing facilities in the departmental laboratories.

I am thankful to Sri D.D. Sharma, General Manager, and the management of M/S U.P.Steels for allowing me to stay at their premises, collect samples and other necessary data pertaining to different grades of steel from their Steel Melting Shop (SMS). Thanks are also due to Dr. Subodh Goel (Manager Quality Control) of M/S U.P.Steels for valuable discussions and keen interest he showed in this study.

The help rendered by the staff of Metallography, Heat-Treatment, Metal Forming and Drawing Office is greatfully acknowledged. Thanks are due to the staff of University Science and Instrumentation Centre (USIC) for providing Electron Probe Micro Analyser (EPMA) and Scanning Electron Microscope (SEM) facilities.

I am indebted to Dr. Jagpal Singh for his help at various stages of this work.

My sincere thanks to Sri Vinod Kumar Tyagi for providing facilities in Departmental Library and my special thanks are due to Miss Vijay Laxmi for neat and flawless typing of this thesis.

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ABSTRACT

A study of eight different grades of steels obtained from M/S U.P. Steels, Muzaffarnagar, has been made with a view to ascertaining the influence of deoxidation practice on the cleanliness levels of these steels. Specimens were drawn at different stages of the processing of above heats. These stages were : after melt-out, after refining (carbon boil), after reducing period and from the ladle. The morphology, volume fraction and approximate chemical composition of inclusions was ascertained with the help of optical, quantitative metallographic SEM and EPMA techniques respectively. It was found that the volume fraction of inclusions is fairly high during melt out and refining period and then their number decreases after the reducing period and in the ladle. The inclusions found at the melt out and refining stage usually conform to FeO-MnO-Al_2O_3 system and many times, the inclusions are only FeO. Because of alloy additions and deoxidation during reducing period, the composition of inclusions becomes very complex. Many times, the inclusions contain FeS-MnS-CaS, which must be slag inclusions. Indigenous inclusions formed due to deoxidation practice usually contain CaO-Al_2O_3-MnO-FeO. The inclusions found in the ladle sample were usually globular in shape and of very fine size (5-8 μm). But some eroded refractory pieces were also found in this specimen, which had reacted with the steel. Present studies revealed that some grades of steels manufactured by M/S U.P. Steels did show fairly low volume fraction of NMIs in the ladle, while others did show much higher volume fraction of non-metallic inclusions in the ladle. This signified that the steel making practice of the above works was not very consistent.

CONTENTS

CHAPTER - 1

INTRODUCTION

Non-metallic inclusions, however, undesirable they may be, are an integral part of all commercial steels. They are in general not welcome, and cause deterioration of properties, often leading to rejections of materials and occasionally resulting in damaging and disastrous failures. The extent of presence of these inclusions and their shapes therefore control the level of "cleanliness" of various steels. It is well known that the details of processing of a given heat and the deoxidation practice adopted greatly influence the shape, size and composition of non-metallic inclusions in steels and therefore control their "cleanliness ratings".

Considerable amount of scientific effort has therefore been devoted to an understanding of the mechanism of formation of non-metallic inclusions in steels. An understanding of the nature and distribution and origin of inclusions is helpful in controlling their quantity and shapes with in limits. The nature of inclusions in different steel varies depending upon the analysis of the finished steel and other factors such as deoxidation practice, change in equilibrium constants as the steel Cools coals down to freezing temperature, decreased solubility with decreasing temperatures and finishing operations etc. The most important factor among these variables is the deoxidation practice along. In addition, the inclusions in different ingots of the same heat may vary, as also the nature of inclusions in different regions of the same ingot. Clearly, therefore, to obtain a comprehensive knowledge of these inclusions in a particular grade of steel needs extensive study. The limitation is that inclusion studies with small laboratory ingots donot give the necessary information required for controlling NMIs in large commercial heats. Another possibility is that test specimens may be drawn from the liquid steel at various stages of the processing of a heat such as during melt out, refining, reducing period, deoxidation stage and from the ladle. But it should be appreciated that during all these stages the steel is in a dynamic state because numerous changes continue to occur even after the specimen is drawn. Despite these limitations, these studies can lead to specific conclusions as to the changing state of non-metallic inclusions throughout the course of a given heat.

The above strategy of withdrawing samples at different stages of the processing of the heat has been followed in the present study. The present study is concerned with the occurrence of non-metallic inclusions in eight different grades of steels manufactured by M/S U.P. Steels, Muzaffarnagar. Four of these grades belong to the forging quality and the remaining four belong to the foundry grade. Since these specimens were quenched, they were too hard and therefore had to be annealed at 950°C for periods ranging from 12 to 18 hrs. These specimens were then sliced through the centre and then ground and polished using standard metallographic techniques in order to examine their both transverse as well as longitudinal sections for the occurrence of NMIs. For this purpose, various grades of silicon-carbide polishing papers were employed and all the specimens were wet polished. The specimens were finally mirror polished using diamond paste of 0.25 µm fineness on a valvet cloth. Sometimes suspended Al_2O_3 slurry of ultrafine quality was also employed to obtain the mirror polish on the specimen. The specimens were polished virtually under their own weight and no external pressure of hand was applied. This is a special precaution required to be observed in such cases otherwise some abrasive particles may get embedded into the surface of specimens. These embedded particles may be mistaken later for NMIs.

In the present work, non-metallic inclusions were observed optically to precisely study their morphology. These studies also revealed that the inclusions were usually complex and contained more than one mineral in them. The occurrence of NMIs was quantified in a given microsection of the specimen using quantitative metallographic techniques. It was found that generally larger number of inclusions were present in the longitudinal section compared to the transverse one. The composition of inclusions was studied with the help of JEOL Super Probe Micro Analyser Model JXA8600M. Using this instrument, spot analysis of several inclusions was carried out at many locations.

It was concluded from the above studies that the morphology and composition of inclusions is greatly influenced by the steel making practice in general and the deoxidation practice in particular. The morphology and composition of inclusions is a function of the sequence in which the deoxidizers are employed and the stage when these deoxidizers are added. Adequate holding time is also necessary to permit the inclusions to float out of the liquid steel. It was concluded from the present study that the steel making practice followed at M/S U.P. Steels is not very perfect and consistent and much desires to be done to improve the practice so that "Cleanliness Ratings" of all the steels manufactured by them is further improved.

CHAPTER - 2.0

A COMPREHENSIVE STUDY OF NON-METALLIC INCLUSIONS IN STEEL

2.1 General:

In the modern context when the specifications of steels for various applications are becoming more and more stringent, the basic consideration of cleanliness of steel assumes paramount importance. One of the criteria for judging the cleanliness of steel is to assess the content and character of non-metallic inclusions besides the presence of dissolved gases such as hydrogen and nitrogen. In order to judge the quality and fitness of a given steel for a particular use, the amount and nature of non-metallic inclusions must be carefully assessed. The non-metallic inclusions are considered and desirable basically because they are incongruent with the metal lattice and therefore represent considerable amount of discontinuity in steel structure. At the same time, it should be appreciated that inclusions are sometimes purposely introduced to gain certain desirable effects such as when sulphur is added to improve machinability and Al_2O_3 seeds are introduced to achieve grain refinement. It is also a fact that no steel can be entirely free from non-metallic inclusions. In regard to detrimental effects of inclusions, there is more unanimity of opinion that harder the steel, the worse their effect, and the several restrictions are probably put on materials for ball bearing or roller bearing steels.

The distribution and character of inclusions seems to be at least equal in importance to the content, it has been shown, for instance, that in cast steel the ductility varies widely with the distribution of sulphides even though the quantity remains the same.

The eutectic type of sulphide, which causes loss of ductility in castings has also been found to produce hot shortness in wrought steels. In a large majority of the cases where steel failures have been definitely traced to non-metallic inclusions, the responsible inclusions have been found to be large ones of the "stringer" type; that is, preponderantly exogenous inclusions.

From the standpoint of origin, inclusions can be classified into two major categories; (a) Those occurring as a result of reactions taking place in the body of molten or solidifying metal generally termed as indigenous or natural or native inclusions and (b) Those resulting from mechanical incorporation of refractories or other materials with which molten steel comes in contact and are generally termed as Exogenous or accidental or foreign inclusions.

Non-metallic inclusions are composed principally of oxides and sulphides but carbides and nitrides sometimes play an important role. In the case of indigenous inclusions the reactions by which these particles are precipitated from molten or solidifying steel may be caused by:

(1) Oxidation such as may occur during refining or during tapping and teeming.

(2) Deoxidation by added alloys.

(3) Change in equilibrium constants as the steel cools to freezing temperature.

(4) Decreased solubility with lower temperature and,

(5) Change in concentration owing to segregation during freezing, with resultant saturation of still liquid portion.

Exogenous or foreign inclusions may be bits of solids and practically unchanged material picked up and entrained by flowing steel but usually are molten globules from fluxed and eroded surfaces of refractories over which steel flows. Some of the latter types of inclusions are altered in composition by reaction with the molten steel.

The materials composing the precipitated inclusions are chemical compounds or mixtures of compounds but seldom are pure or simple compounds. While in contact with liquid steel, they maintain as close an approach to equilibrium with the steel as the velocity of the reaction and diffusion will allow. Thus, particularly when small in size, they are quite dependent on steel composition for their own composition. Some inclusions are precipitated as solids or freeze before steel does, and these usually assume the natural external crystalline form for the material unless it is glass, which does not crystallize. Those formed as liquids, which freeze later than surrounding steel, are probably constrained to remain as globules, although they may have internal crystalline characteristics. Some formed as homogeneous liquid inclusions separate into two or more constituents when they solidify or cool. The formation of separate constituents may be by the process of liquation, in which the more refractory constituent freezes out first, or again by the formation of a eutectic. Some inclusions forming materials, notably some sulphides have such a high solubility in steel that they are precipitated with the last of mother liquid and form films or eutectics in the primary grain boundaries.

The inclusion types are largely independent of the steel analysis. But the type of steel based on the process of manufacture (Basic or acid, electric, high frequency, kaldo etc.), details of methods of steel melting and deoxidation and teeming and the casting operations all have a much greater influence on the formation of inclusions than the steel composition itself. For the most part, inclusions in steels are oxides, sulphides and nitrides; or various combinations of these. The different inclusions phases observed in steel have usually been named by minerologists and these names have been adopted by the metallurgists.

The quantitative results on the composition of inclusions and their identification are of fundamental importance for the understanding of their formation and properties. A number of techniques have been developed to identify the inclusions. The most common technique applied for this purpose is microscopic examination of polished sections in plane and dark-field illuminations. Features commonly observed are outline, reflectivity and colour. In other cases it is necessary to remove inclusion from metals and subject them to examinations under a petrographic microscope or analysis by x-ray diffraction. In the modern times, the revolutionary method of Electron Probe Microanalysis has now become available to the metallurgists, making a quantitative analysis of inclusions possible in-situ and important developments have also occurred in x-ray diffraction techniques (mono-chromatic x-ray techniques, micro methods etc.). In addition to above, quantitative metallographic techniques are usually employed to quantify the distribution of non-metallic inclusions and their sizes in the finished steel.

In the present chapter, an effort has been made to critically review and examine the existing literature in regard to the presence of non-metallic inclusions in different quality steels.

2.2 The Concept and Criteria of Steel Cleanliness

One of the criteria for judging quality and fitness of a given steel for a specific application is the content and character of non-metallic inclusions. For a variety of steels, certain cleanliness standards have come to be accepted and applied by both the manufacturer as well as the consumer. This has led to the development of standards and charts in different countries defining the content, nature and size of variety of inclusions commonly found in different steels. These standard charts, therefore, become the reference point for both the manufacturer as well as the consumer. The fact that non-metallic inclusions are in congruent with the metal lattice and therefore are considered undesirable. It is also well known that these inclusions influence the properties of finished steel considerably. For this reason, cleanliness ratings have been specified for numerous quality steels.

A number of operating parameters have been found to influence the cleanliness of steels which are listed below;

(a) Control of deoxidation
(b) High pouring temperatures
(c) Clean furnace bottom
(d) Avoidence of late ore addition

(e) Maintenance of high residual manganese

(f) A prolonged ore-boil, airy boil

(g) Slag control to maintain lowest FeO content conducive to elimination of phosphorous.

(h) Holding ladle and mould additions to aminimum.

(i) Good pouring practice which may include basket pouring or the use of refractories that will not erode badly and flux away in appreciable amounts.

Good pouring practice entails the minimum of running stoppers, mould splashes, and fan shaped streams caused by eroded or partially clogged nozzles. Using an oxygen lance is often necessary with cold heats to clear clogged nozzles, but it also often damages the bore of the nozzle and causes a ragged, irregular stream to flow.

Sulphides constitute well over 50 percent of all the natural or precipitated inclusions present in most steels. In as much as practically all the sulphur forms sulphide inclusions, one of the most profitable means of reducing the inclusion count is to keep sulphur as low as possible.

The oxide inclusions found in solid steel are thought to be largely those precipitated very late before the freezing of steel. It is because the oxide inclusions formed earlier as a result of deoxidation practice rise to the top of liquid steel and join the liquid slag. For this reason, reoxidation from contact with air during tapping and teeming is considered an important source of oxide inclusions.

As mentioned earlier, high grade refractories will promote the production of cleaner steels. Pouring steel hot gives exogenous inclusions a better chance to float out of the steel in the ingot mould before they are trapped by advancing solidification interface. Using Stoke's law it can be shown that a particle 1mm in dia would rise at the rate of approximate 2 ft/sec.

2.3 Methods for the Estimation of the Type and Amount of Inclusions:

Both steel maker and user are interested in not only in the type but also in the size and distribution of inclusions, and in their total quantity. Two methods are adopted for this study. The first procedure is concerned with the counting of inclusions in the polished specimen using optical microscope. The inclusions are observed at a fixed magnification with regard to their shape and size and are compared with standard sets of charts such as J.K. charts showing various combinations of length, breadth, continuity and type of inclusions [1]. For this purpose I.S.; 4168;1982 concerning the method of inspection of non-metallic inclusions in steels is also extensively employed in the Indian steel industry [2]. The second approach to this problem is the extraction of non-metallic matter from the steel by dissolving the metal, whereby a residue is obtained which may then be analysed by appropriate chemical or microscopic means. This method however is very useful for research purposes but is considered slow and difficult for routine testing in the industry. Generally the findings of these studies are reported according to the codes developed by different countries as the one mentioned above (I.S.;4168;1982). Thus, broadly two methods are followed; (1) Those using standard comparison charts and (2) Those that count and measure the inclusions. There are also the combinations of two methods [3]. For simplicity and speed, recourse to visual examinations of sample sections of steel has been general.

In any such test, sampling is of great importance, for at best only a small portion of steel can be examined, and this portion must be as truly representative as possible. When one considers the infinite variety in which inclusion may occur as far as concentration, distribution, dimensions and characters are concerned, it is readily apparent that reporting the findings of an examination is not simple. In sampling, it is generally recommended that the samples include the mid-radius of the bar or billet and the face to be examined should be a plane exactly parallel to the long axis of the inclusions i.e. parallel to the direction of rolling.

Preparation of metallographic specimen needs to be done very carefully for inclusion counts. The polishing is required to be carried out in such a manner that inclusions are retained in the polished surface and polishing pits are not produced, for the latter may be mistaken for inclusions at the low magnification often used in such studies. These measurements are done to establish "cleanliness rating" of a given steel. The number, size, continuity and distribution are determined either by measuring intercepts on a micrometer scale or grid superimposed on the microscope image of the polished section or by comparison of the image with a "standard" set of photomicrographs of inclusions. Sometimes an attempt is made to classify the type of inclusion as well as to ascertain the size and amount [1]. As mentioned by

Pomey and Trentini [4]. The development of automatic counting methods will greatly increase the number of determinations and thereby provide some basis for a statistical solution to this problem. These automatic counting systems, however, present some specific problems. The main obstacle to the progress of automatic counting technique is the difficulty in distinguishing inclusions by differences in their reflectivity as suggested by Pomey and Trentini [4], this problem could perhaps be tackled by selective etching techniques or by improving the sensitivity of equipment e.g. by adjusting the spot size to the size of the particles to be measured. It is hoped that these systems will eventually be able to count inclusions by nature, shape and size so that appropriate histograms can be drawn up for each type of inclusion. When these diagrams have been established for the different ranges examined, they may be used to determine inclusion distribution (covariogram) and their distribution over the whole batch of steel. Finally, these methods will be required to provide a satisfactory count of inclusions in clusters or stringers which can have a harmful influence beyond that of their constituent inclusions in isolation.

The solution of these problems will require development of instrument technology and methods of application. The combination of automatic scanning potential with mathematical morphology theory (shape recognition) for investigation of a metallographic sample opens new avenues in quantitative metallography, and particularly in the physical assessment of steel cleanliness. By the help of above technique, it will be possible to give a more accurate definition of steel cleanliness [4,5].

Automatic inclusions counting methods have been developed to a high degree of refinement for the electronic processing of images. The most important feature of these methods is that the relations between different physical properties of steel and the size, shape, and distribution of inclusions can be evaluated, based on a larger population of inclusions than can be studied using manual techniques. Correlations can thus be established on a firmer statistical basis.

As an example of the importance of time saved in routine inclusion assessment, manual microscopical assessment of inclusions by the method of comparing fields on a sample with JK scale takes about 15 min. for 100 fields each of area 0.5 mm^2, giving a total surface area examined about 50 mm^2. A typical automatic technique requires only 50 seconds to calculate and print out oxide and sulphide inclusion area fraction data from 500 fields each of 0.32 mm^2, giving a total area examined of 160 mm^2. Manual counting gives a typical rate of about 10 inclusions counted per minute, compared with about 3500 inclusions in the same time using an automatic image analyser. Examples of the automatic techniques given in the references include: the assessment of inclusions in relation to fatigue, surface crack in cold rolled tubing, and shape control of sulphides in free machining steels.

It must be stressed, however, that most automatic inclusion assessment methods rely on conventional optical imaging. They are limited, therefore, to the resolution and contrast conditions given by suitable combinations of objective, microscope, and metallographic preparation. There are some aspects of inclusion morphology which are of considerable importance and cannot be dealt with adequately using optical methods. For the study of very clean steels, increasing use will be made in the future of SEM imaging techniques in combination with automatic image analysis.

Macroscopic examination for inclusions may largely superseed microscopic methods because it is apparent that "In the great majority of the cases the interest is not in the uniformly distributed inclusions which can be observed only microscopically, but in larger inclusions and segregates which can also be detected macroscopically. These larger inclusions and segregates are not uniformly distributed but are scattered at random through steel, so that large areas of steel should be examined to determine the size of larger inclusions present. For such large scale sampling a macroscopic test procedure is far superior to a microscopic one" [3].

Samples for macroscopic examinations may consist of cross sections or longitudinal sections of a billet or bar or may be step down tests. In the step down test, a round bar, for example, is machined into the form of a telescope to expose concentric layers at various depths. Sample surfaces are usually finished by grinding. Further preparation of sample may consist in macroetching the surface or magnetizing for magnaflux testing. Both methods are fairly satisfactory but latter has the advantage of revealing large, unexposed inclusions near the surface.

Magnafluxing is conducted by placing the piece to be tested in the circuit of a heavy direct electric current to magnetize it. A fine magnetic powder is then sprayed over the surface. Because steel is very highly permeable to magnetic flux as compared with air or any non-metallic solid, magnetic lines of force will spread out at any discontinuity in steel, whether caused by a crack, a hole or any inclusion. The magnetic powder, also being highly permeable, will be drawn in, in an attempt to bridge the gap, and thus produce a concentration outlining the defect.

Magnaflux is a particularly searching and valuable test and has the further advantage of being a non-destructive test usable on finished product without reliance on sample specimens, which may or may not be representative. As was pointed out earlier, macroscopic inclusions largely if not wholly exogenous in origin, are the potentially dangerous kind and cause most concern. They have such a haphazard occurance that it is only by mere chance that sampling will show their presence or absence.

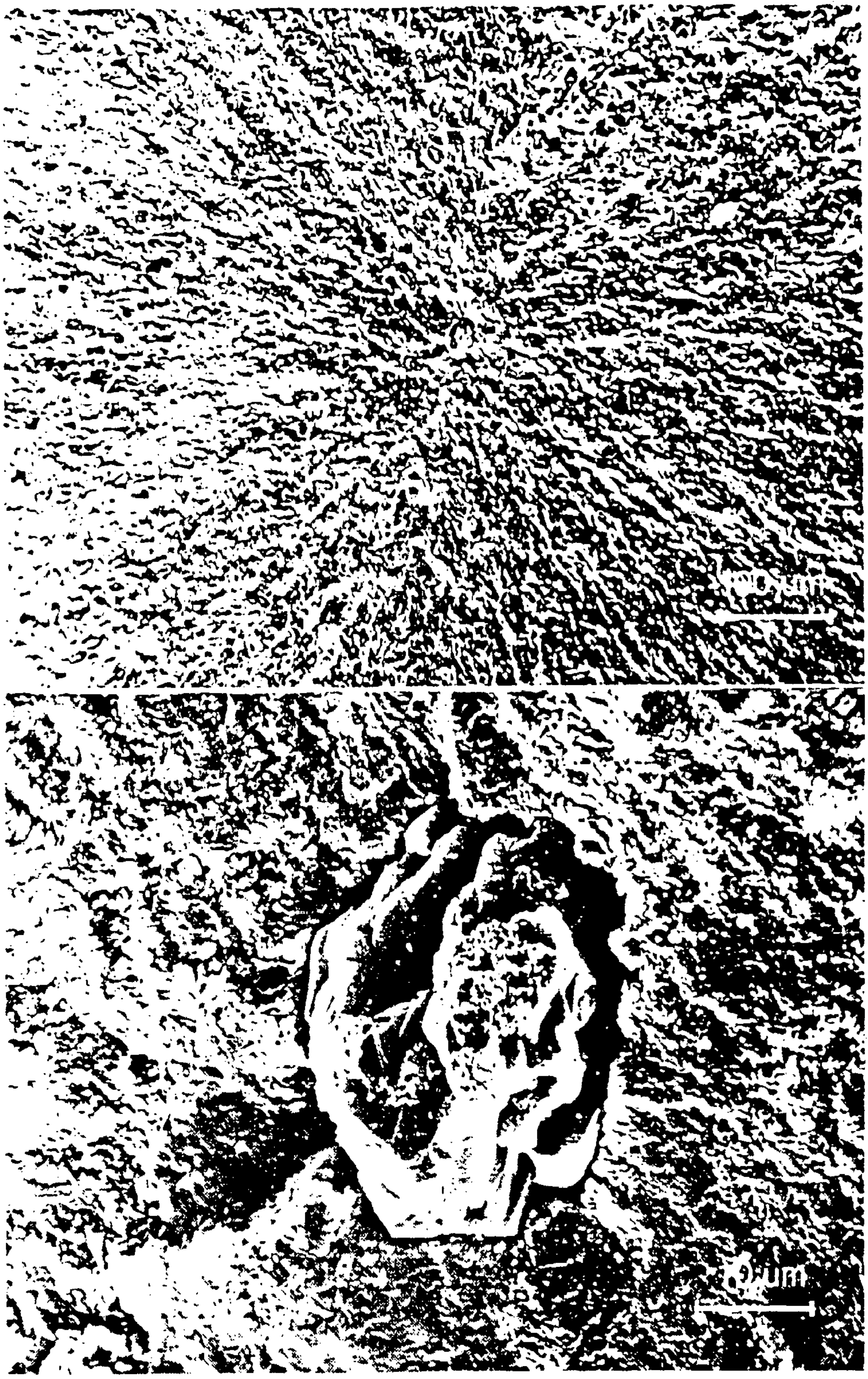
The important thing is to discover finished pieces containing such inclusions. Test and experience have shown, moreover, that these large inclusions are detrimental to service life only when they occur in certain strategic positions, notably at or near the surface. The magnaflux test shows these if present and makes it unnecessary to accept or reject the whole heat.

The standard inclusion atlas or inclusion charts, as they first appeared some thirteen years ago, were based on experimental observations of non-metallic inclusions in steel, observed and studied in-situ. The revolutionary method at that time was electron probe microanalysis, and this technique for composition determination on the microscale was combined with optical microscopy and x-ray diffraction. The combined techniques made it possible to identify the different phases present in inclusions, confirming their identity by comparison with phases in experimentally prepared synthetic slags. These sophisticated experimental techniques, however, were employed only for phase analysis of inclusions exclusively and their basic objective was not to determine the amount of inclusions. For the latter part of this study, automatic inclusion counting techniques discussed earlier have proved to be most useful. As mentioned in section 2.1, the sophisticated technique of electron probe microanalysis has made it possible to quantitatively analyse the different phases present in inclusion. This technique has further been supported by x-ray diffraction techniques (monochromatic x-ray techniques, micromethods) for the quantitative estimation of phases in inclusions. The latest technique that has been added to this sphere of study is the Scanning Electron Microscope (SEM). Its main advantage for the study of inclusion is its high resolution combined with a relatively large depth of focus, even at high magnifications. Much of the versatility of the instrument derives from its ability to relate features such as inclusions to the surrounding matrix, in specimens which may be fracture surfaces, conventionally prepared plane sections, or specimens deeply etched to reveal complex inclusion particle morphologies.

The SEM may also be used to obtain three dimensional images for sterometric analysis and is particularly valuable for the examination of particle morphology, features of the particle/matrix interface, and the formation of voids or cracks at particles as a result of deformation. On the specialized SEM techniques, semi quantitative in-situ chemical analysis is perhaps the most useful in inclusion studies. Although not yet refined to the standards of quantitative analysis permitted by wave length-dispersive x-ray detectors used in conventional microprobe analysis, non-dispersive x-ray energy analysers are of great value when combined with SEM. In particular, their high count rates permit the qualitative analysis of small particles in rough surfaces such as fracture.

Scanning Electron Microscopy has been used as a complementary method in studies of many inclusion phenomena. These include the location and effect of inclusions on fracture surface (Fig.1), the precipitation patterns and solidification mechanism for sulphides (Fig.2a & b) identification of inclusions at very high magnification [7], [8], and identification of electrolytically isolated inclusions [9]. Other studies embrace the relation between microcracks & inclusions [10], the formation of voids around inclusions, and corrosion around inclusions [11].

A new development of SEM technique has recently been reported [12]. The object has been to perform tensile tests in-situ in the scanning electron microscope by simultaneous video recording of the microscope image and a load-elongation curve. The nucleation and growth of cavities around surface inclusions has thus been monitored quantitatively [13]. The technique is of particular interest for inclusion studies, as it makes possible dynamic behaviour at very high magnifications. Further studies are now in progress in order to observe the effects of temperature on inclusion deformation. The simultaneous recording of the SEM image and the load-elongation curve in order to relate the various



STEEL low-alloy chromium steel
INCLUSION calcium aluminate
COMMENT photograph illustrates depth of focus at high magnification given by SEM and topographic details in surrounding steel matrix.

Fig. 1. Scanning electron micrographs of fatigue failure initiated at an inclusion[29]

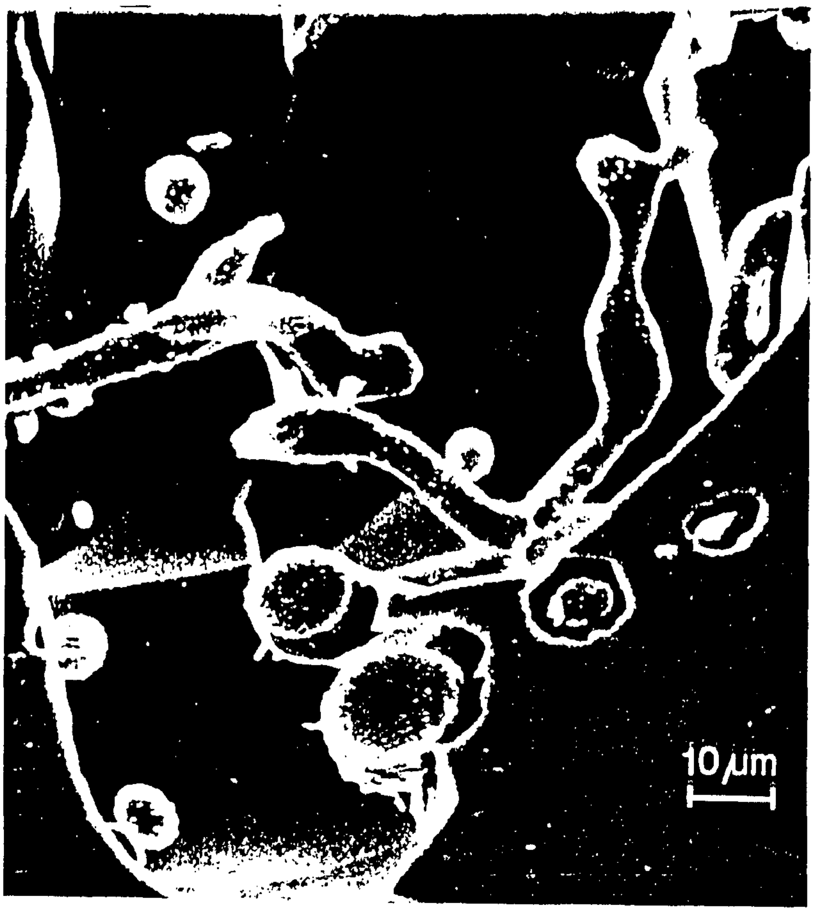


Fig. 2(a).

Fig. 2(b).

mechanical and microstructural events occurring in the same experiment is an important development.

2.4 Origin of Non-metallic Inclusions:

2.4.1 Non-Metallic Inclusions and the Phase Diagrams:

In considering the mechanism by which non-metallic inclusions are formed in molten steel, it is frequently helpful to know how oxides react with each other, What temperatures are involved, and whether the inclusions formed are solid or liquid under given conditions. An idea of these factors may be gained from equilibrium diagrams of the system involved, of which figs.3 to 7 are of especial interest in considering non-metallic inclusions. The first three of these approximations show the binary and ternary phase diagrams of common oxides found in steel. They do not explain the equilibrium relations of such deoxidizers as manganese, silicon, and aluminium with liquid steel but merely show how mixtures of oxides FeO, MnO, SiO_2, and Al_2O_3 flux each other or form compounds to give different melting points from those of pure oxides.

2.4.2 Origin of Different Kinds of Inclusions:

As suggested by Kiessling [6], the earlier classification of non-metallic inclusions into two broad categories such as indigenous and exogenous inclusions is rather over simplified. Detailed microprobe analysis of inclusions has shown that overall composition of inclusions is very complicated and its origin cannot be attributed to only one particular source. It is mainly because, starting from the point of nucleation of such inclusions, they

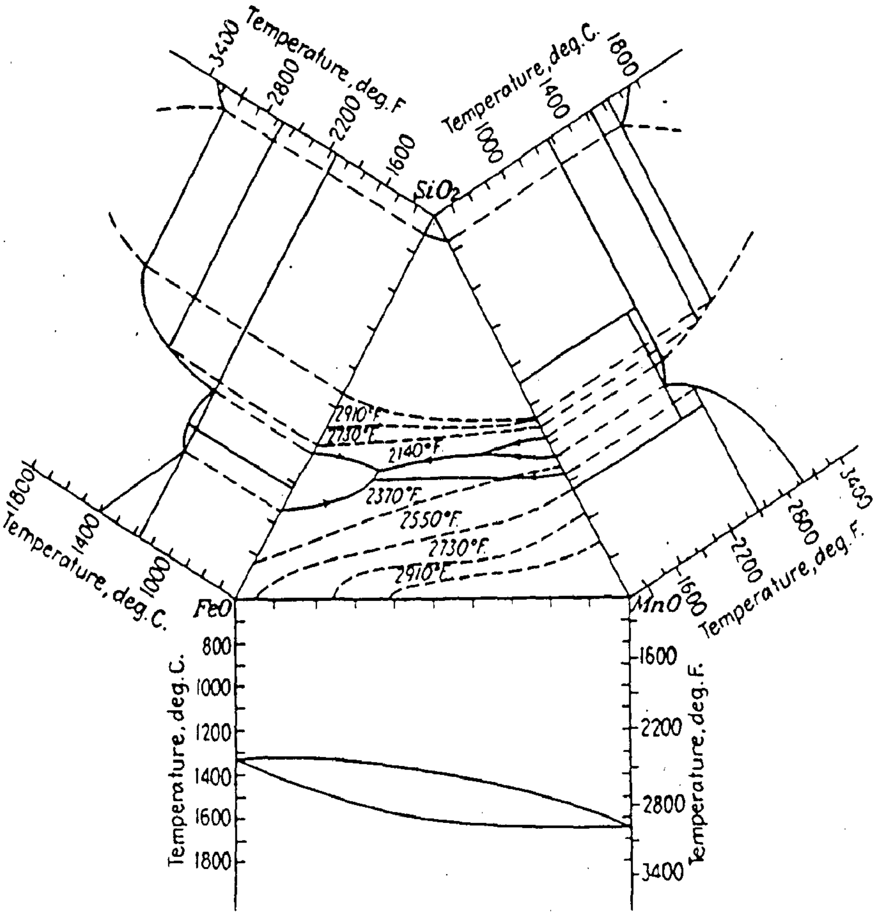


Fig. 3 . The MnO-SiO$_2$-FeO system. (After Wentrup.[24])

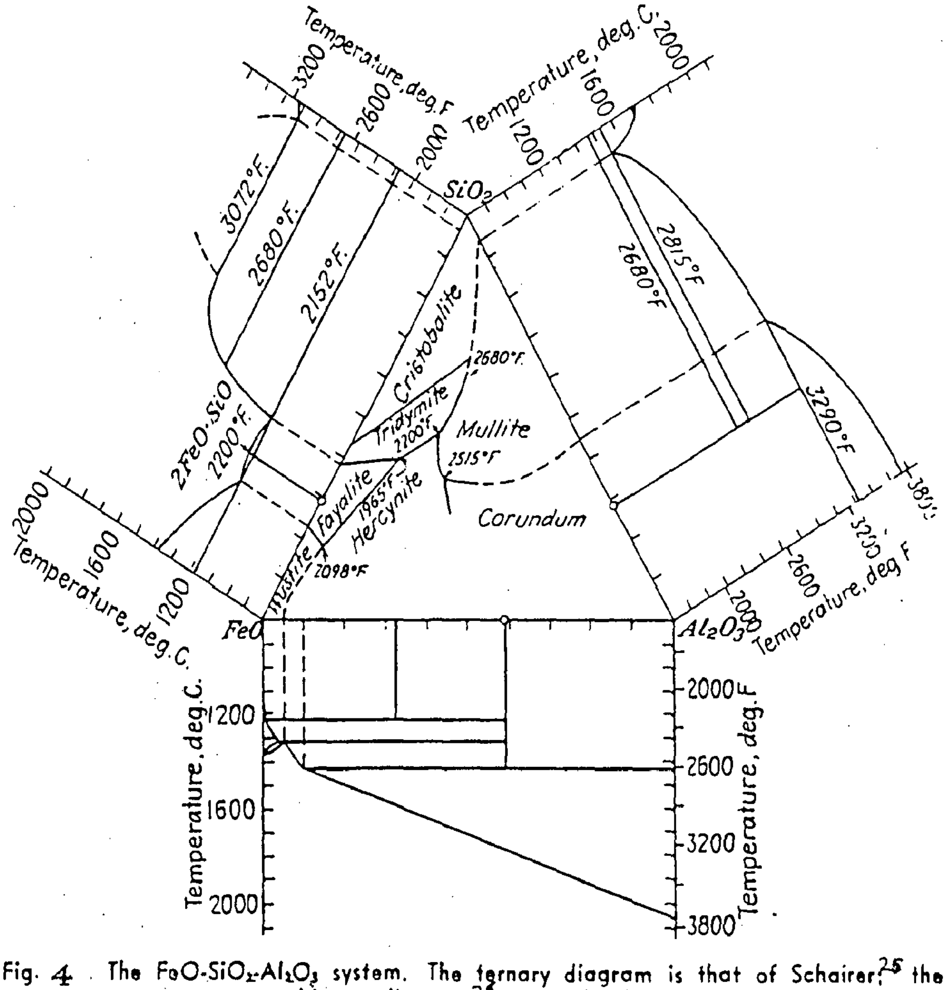


Fig. 4 . The FeO-SiO$_2$-Al$_2$O$_3$ system. The ternary diagram is that of Schairer;[25] the binary diagrams[26] were added.

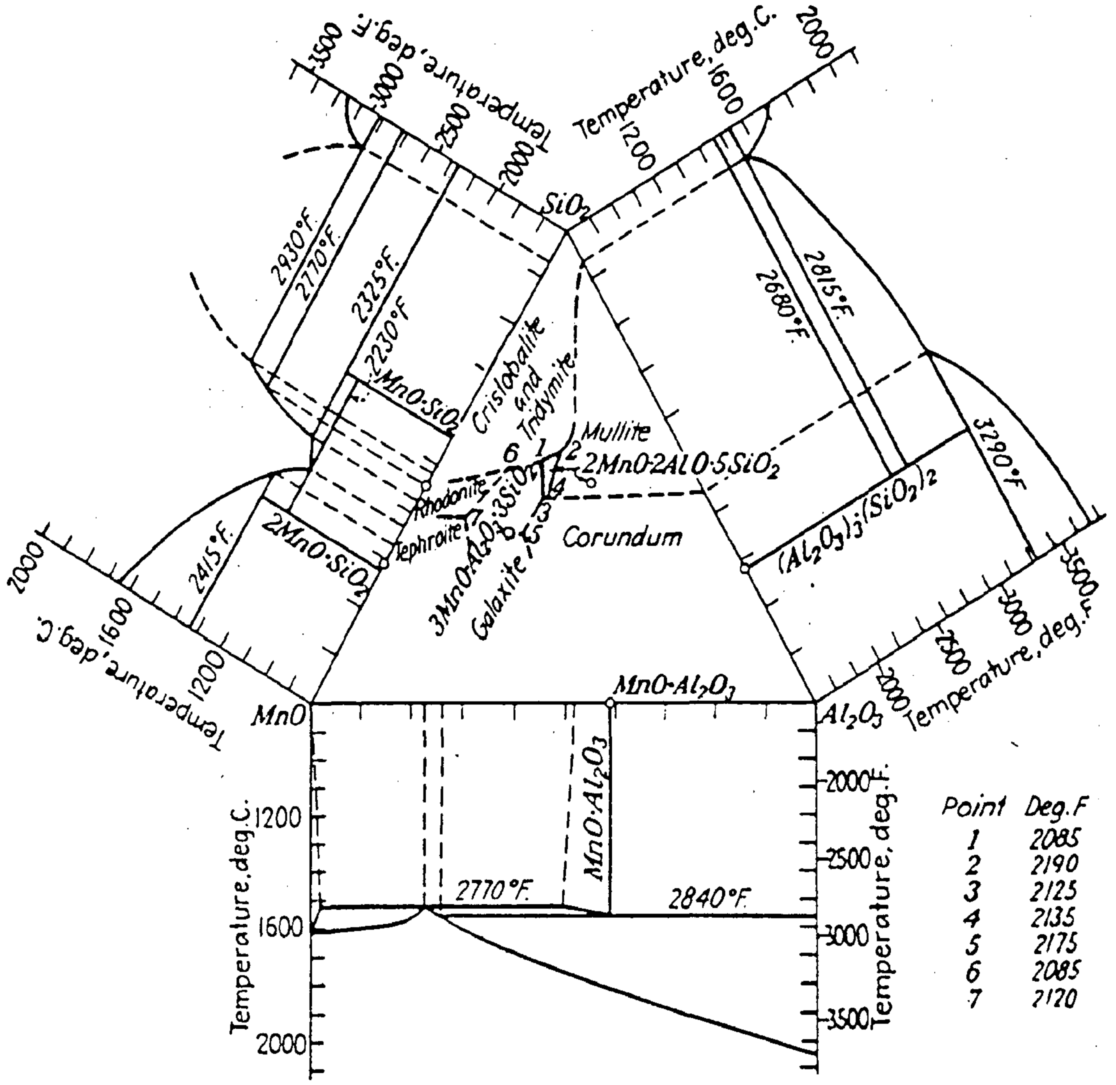


Fig. 5 The MnO-SiO$_2$-Al$_2$O$_3$ system. The ternary diagram is that of Snow;[27] the binary diagrams[26] were added.

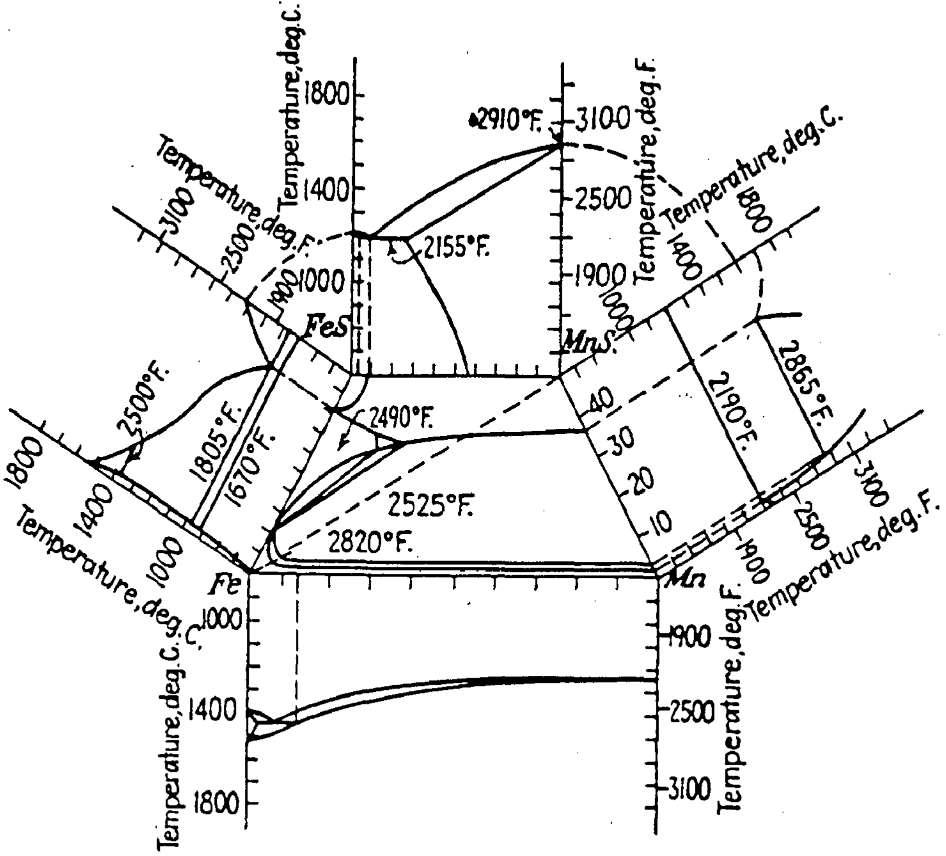


Fig 6 The Fe-Mn-S system. (After Wentrup.[24])

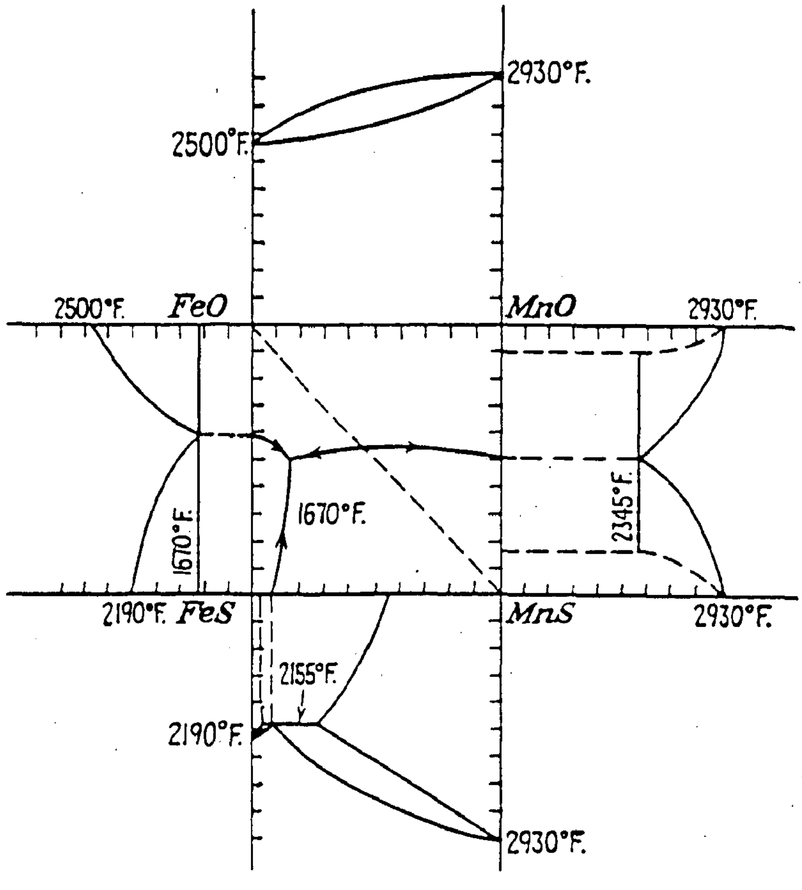


Fig. 7 The FeO-MnO-FeS-MnS system. (After Wentrup.[24])

TABLE - 2.1

The composition of different types of deoxidation alloys with calcium

Type of alloy	Composition,wt-% Ca	Si	Fe	Al	Ti	C
75/2	2.2	73.6	21.6	1.2	0.15	...
75/5	5.8	75.4	16.1	1.4	0.10	...
75/10	11.0	81.7	4.8	1.1	0.08	...
55/14 Ti Al	13.9	56.1	16.85	1.97	8.91	0.38
55/17 Ti	17.3	54.6	17.2	0.2	7.44	0.64
75/20	17.9	77.8	2.1	0.66	0.06	...
60/30	31.1	60.2	5.7	1.4	...	...

under go many changes during the process of deoxidation, tapping, and teeming of steel in the ingot moulds and its final solidification. e.g., a large multiphase inclusion with irregular shape and complex structure is not merely an exogenous piece of refractory which has entered the steel. The origin may be the refractory material, but the mean composition, and often also the structure of this type of inclusion, usually differ considerably from the original refractory due to indigenous precipitation of oxygen as different oxides. Sulphides may also be nucleated on oxide inclusion particle.

The composition and structure of inclusions are not the only factors of importance in tracing their origin. The inclusion shape, size and position in the ingot are all highly relevant. The formation of inclusions may be followed through the different stages of the bath, ladle, tapping process and solidification. The deoxidation mechanism is of fundamental importance for the formation of non-metallic oxide inclusions. It is therefore, apparent that different stages of steel making directly control or influence the kind of non-metallic inclusions found in the finished steel. In the earlier days the inclusions were broadly classified as: Oxides, sulphides, nitrides, carbides and refractory inclusions. This classification, however, seems incorrect in view of the facts mentioned above.

2.4.2.1 The Influence of Deoxidizing Elements Upon Inclusion Formation:

Table 2.1 shows that the solubility of oxygen in pure iron is a function of the temperature. If pure iron solidifies, a considerable part of the oxygen is precipitated

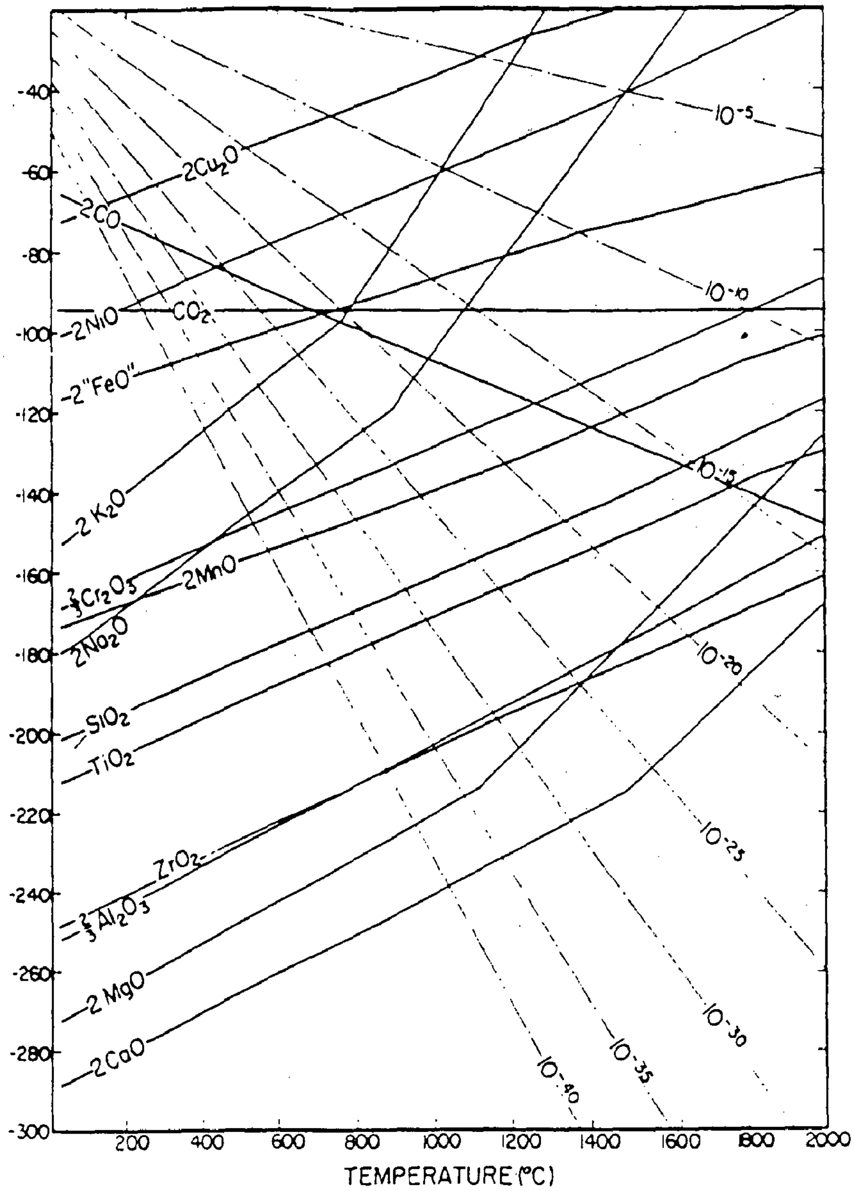
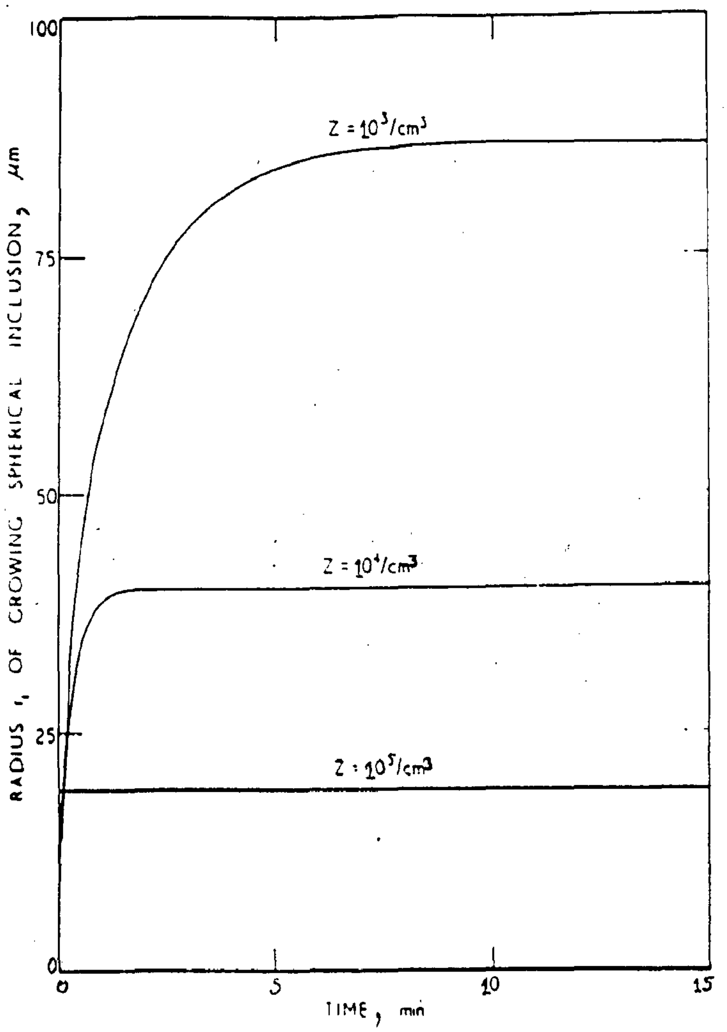


Fig. 8. Standard free energies of formation ΔG° (kcal) for various oxides of the elements as a function of temperature. Light dash-dot curves are lines of equal oxygen pressure, (atm) of the gas phase, as labelled on each curve. From Muan and Osborn,[28] Fig.1, p.4

as liquid FeO inclusions, which will be visible as a spherical inclusion in the solidified iron. In case of steel, the oxygen content of liquid steel depends upon the nature of the elements present in addition to iron, the most important element being carbon. Most of the oxygen is in solid solution in liquid steel but a part may also be present as small oxide inclusion in the melt. The purpose of deoxidation process is to decrease the amount of oxygen in the steel. This may be accomplished by adding to steel elements with a higher affinity for oxygen than iron, precipitation deoxidation and by the transfer of FeO to a suitable slag on the steel surface, diffusion deoxidation. Only the precipitation deoxidation results in the formation of inclusions in the steel. Relative deoxidizing power of different elements is shown in Fig.8.

Deoxidation occurring at a fix temperature results in the formation of primary deoxidation product. Deoxidation may also occur during cooling of both the liquid and solid steel at decreasing temperature due to decreasing solubility of oxygen. This is called secondary deoxidation. The primary deoxidation product have a greater opportunity for escape from the steel than those which form by the secondary formation on a falling temperature scale. Both primary and secondary processes are responsible for the formation of inclusions.

Bergh [14] studied the relationship between the oxygen content and the no. of oxide inclusions formed in a Si-killed steel. Turkdogan [15] has shown that the number of nuclei have a pronounced effect on the growth of oxide inclusions, on the extent of deoxidation reaction, and on the rate of floatation of oxide



The initial oxygen content of steel $[\%O]_0 = 0{\cdot}05\,\%$ and the final equilibrium oxygen $[\%O] = 0$. The figure illustrates the expected effect during deoxidation of the number of nuclei, in the liquid steel Z/cm^3, on the rate of growth (*a*) and distance of rise with time (*b*) for various values of Z.

While for $Z = 10^5$/cm^3 growth is complete in about 10 s, about 6–7 min are required for a number of nuclei $Z = 10^3$/cm^3. As the inclusions grow and rise in the melt with increasing reaction time, the liquid steel is progressively depleted of inclusions from bottom to top. From ref. 16

Fig. 9(a) The effect of number of nuclei in melt on the rate of growth of oxide inclusions as they rise in the melt and on the rate of ascent of growing inclusions

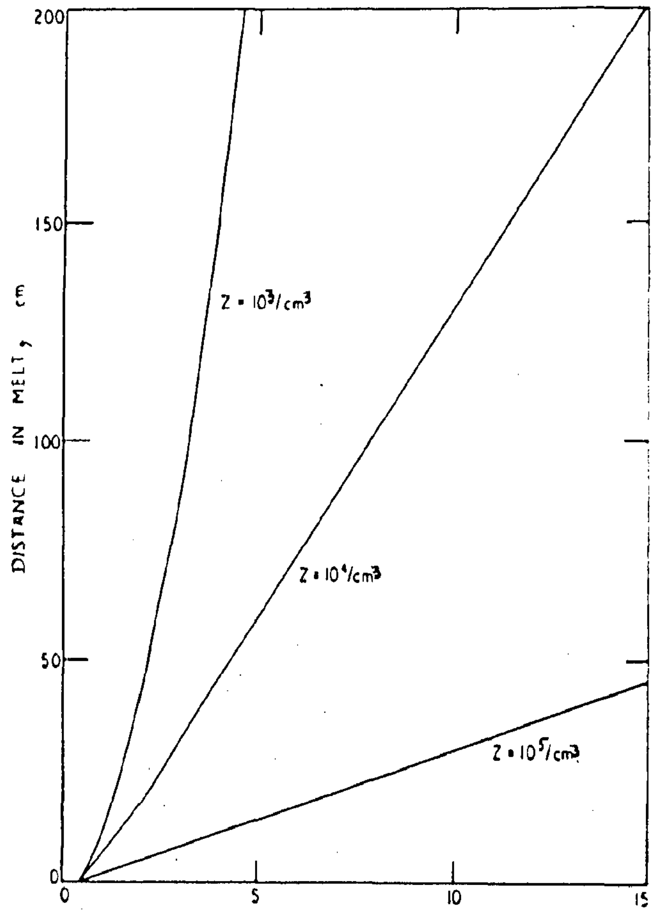
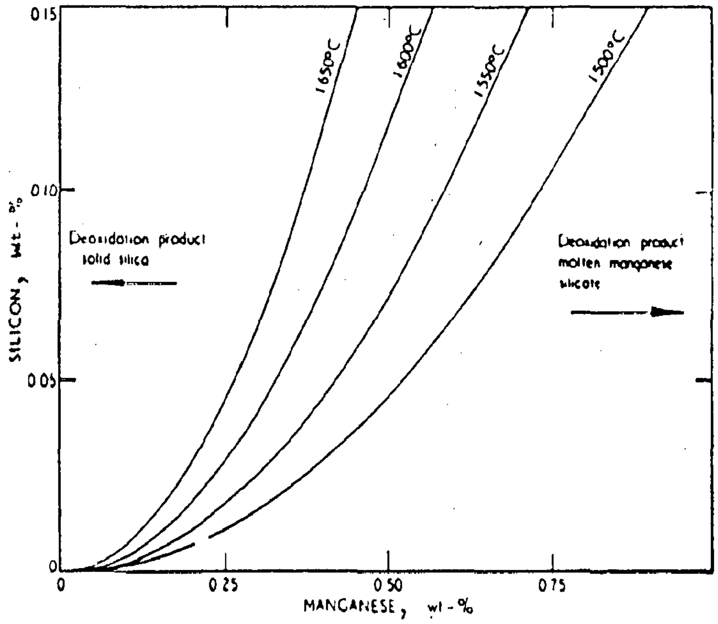


Fig. 9(b).

(*see* caption below Fig. 9a on previous page)



There is a critical ratio [%Si]/[%Mn] above which only solid silica forms as the deoxidation product. The figure gives the critical Si and Mn contents of steel in equilibrium with silica-saturated manganese silicate at various temperatures. If, for any particular temperature the composition of steel lies above the curve, Mn does not participate in the deoxidation reaction but solid SiO_2 is formed. In the region below the curve, the deoxidation product is molten Mn-silicate. From ref. 15

Fig. 10 Critical Si and Mn contents of steel in equilibrium with silica-saturated deoxidation product (manganese silicate) at different temperatures inclusions out of the melt. For instance, Turkdogan [15] showed that if the number of nuclei in the melt is $Z=10^5/cm^3$, a typical figure, then the spherical oxide inclusions formed by deoxidation will grow such that the majority will have a final radius of 20 microns. 10^4 particles will reach a diameter of about 40 microns whilst 10^3 will grow to about 85 microns. The time required for the completion of this growth process increases successively, however, to 6-7 minutes. The results of Turkdogan are shown in Fig.9(a&b).

The inclusions also rise in melt, and in Fig.9b the effect of the number of nuclei in the melt on the rate of ascent of growing inclusions is given. As the inclusions grow and rise in the melt with increasing reaction time, the liquid steel is progressively depleted of inclusions from bottom to top. Since there is insufficient supersaturation new nuclei cannot form in the inclusion-depleted part of the steel, and therefore the deoxidation reaction ceases before reaching the final equilibrium state. A significant point is his conclusion that, for any given deoxidation time, there exists a critical value Z_c of the numbers of inclusion nuclei. If the number of nuclei is less than this critical value, relatively large nuclei are formed which float out of the melt quickly; but a high residual oxygen content is left in solution. The steel may therefore be essentially free of inclusions at the time of pouring, but contain a high percentage of oxygen in solution leading to the formation of blow holes on solidification. For the case where critical nucleus density is exceeded, steel is effectively deoxidized but inclusions are small and have a slow rate of ascent in the melt. Even after prolonged holding times the inclusion content of melt is high and solidified steel may become rich in inclusions.

The rate at which suspended particles rise out of liquid steel is expressed by Stoke's Law [3]:

$$V = K \frac{2}{9\eta} r^2 g\,(d' - d) \qquad \ldots\ldots\ldots\ldots (2.1)$$

Where

V = rising velocity

K = settling constant

r = radius of particle

g = acceleration owing to gravity,

d' and d = density of liquid and particle, respectively,

η = viscosity of liquid

The important variable in this formula is clearly r, the radius of the particle, for the rate of rise varies as the square of the radius.

A detailed account of the effect of various deoxidizing elements such as carbon, manganese, silicon, silicon-manganese, aluminium, chromium, titanium, zirconium, calcium, etc. in forming different kinds of non-metallic inclusions in the steel has been dealt with in detail by Roland Kiessling (Edi) in his monograph on "Non-metallic Inclusions In Steels" Part-III, Page 17-29, [6]. Some very salient features of above deoxidizing elements and the resulting products are mentioned below:

(1) Carbon:

The deoxidation products are mainly gaseous. Such gas precipitations are potential causes of pin hole porosity in steel castings. At low pressures however, carbon can be an effective and useful deoxidizer. This is realized through vacuum treatment of liquid steel.

(2) Manganese:

It can be seen from Fig.8 that this element is a weak deoxidizer and it is not, at least in pure form, used as a deoxidizer. If manganese is added to an iron melt containing oxygen, inclusions of the type MnO-FeO are formed usually as solid solutions. The deoxidation inclusions are smaller and evenly distributed in the steel, and their morphology depends on the MnO/FeO ratio of the solid solution, i.e. on the Mn content of the resulting steel. These inclusions are usually globular.

(3) Silicon:

It can be seen from Fig.8, that Si is much more effective deoxidizer than Mn and it is often used in combination with that element. If pure iron is deoxidized with Si, the deoxidation products are either iron silicates which are liquid at the melting point of iron or solid SiO_2. According to Evans and Sloman [16], pure SiO_2 is formed if the silicon content is higher than 0.08%. The SiO_2 inclusions are usually glassy and globular with diameters upto about 50 µm. It is essential to establish the SiO_2 modification present in inclusion, if the origin has to be determined. SiO_2 may also be of exogenous origin e.g. from the refractories, and it is especially important to find whether or not low quartz is present. If that modification is identified the SiO_2 can not be a deoxidation product.

(4) Silicon-manganese:

Although deoxidation by silicon is more effective than by manganese, simultaneous deoxidation by these two elements gives much lower residual oxygen in solution. This was shown by Körber and Oelsen [17]. Normally in the deoxidation of steel both these elements are used together and the first stage of deoxidation is carried out by Si/Mn additions to the ladle during tapping. In this case the deoxidation product is essentially liquid manganese-silicate or solid silica with little or no iron oxide in solid solution. The non-metallic inclusions formed as a result of this deoxidation process therefore, belong to $MnO-SiO_2$ system. Turkdogan [15] has studied the equilibrium constant;

$$K = \frac{[\%Si]}{[\%Mn]^2} \cdot \frac{(a_{MnO})^2}{(a_{SiO_2})} \qquad \ldots\ldots\ldots\ldots (2.2)$$

He has concluded that there is a critical ratio $[\%Si]/[\%Mn]^2$ above which only solid silica forms as a deoxidation product ($a_{SiO_2}=1$) and thus manganese does not participate in the deoxidation reaction. He has given curves for the critical silicon and manganese contents of steel in equilibrium with silica-saturated manganese silicate at various temperatures (Fig.10). From these curves it is possible to predict the deoxidation products and therefore the type of inclusions formed in the steel. If, for any particular temperature, the composition of steel lies above the curve in Fig.10, manganese does not participate in the deoxidation reaction and solid silica is formed.

(5) Aluminium:

It can be seen from Fig.8 that aluminium is a strong deoxidizer and it is commonly used for that purpose. The deoxidation constant K = $[\%Al]^2 \times [\%O]^3$ for Al and oxygen in solution in the steel phase has been determined between 10^{-9}-10^{-14} at 1600°C. It has been found that the coarser particles of Al_2O_3 are eliminated in 7-10 minutes, but a finer suspension ($< 70\ \mu m$) probably remains in the liquid steel even after 20 minutes of the addition of Al. According to the phase diagram FeO-Al_2O_3 (Fig.11) three deoxidation products are possible as a result of the Al deoxidation of the steel: Liquid FeO-Al_2O_3 melts, solid hercynite and solid Al_2O_3. In actual deoxidation practice, the formation of liquid FeO-Al_2O_3 melts is very unlikely because the oxygen content of the bath is never high enough. The most common deoxidation product is Al_2O_3 usually in its α modification. Al_2O_3 inclusions in practice appear as clusters of Al_2O_3 particles. They are rather small in size, mostly in the range of 1 to 5 μm, irregular in shape or partly molten. They are usually trapped between the dendrites of the steel. The Al_2O_3 particles tend to stay together when they collide.

(6) Chromium:

This metal is rather a weak deoxidizer (Fig.8). Non-metallic inclusions from Fe-Cr-O system in steels give rise to the formation of chromite (FeO-Cr_2O_3) and Escolaite (Cr_2O_3) inclusions.

(7) Titanium and Zirconium:

These metals are strong deoxidizers (Figs.8) and titanium is often present in calcium deoxidation alloys. (Table 2.2). Oxide inclusions with titanium or zirconium oxides may therefore be formed

TABLE - 2.2

The solubility of oxygen in liquid iron at various temperatures. Two different equations have been used, namely

$$\log |\%O| = -\frac{6320}{T} + 2.734 \qquad (1)$$

$$\log |\%O| = -\frac{5762}{T} + 2.439 \qquad (2)$$

Temperature(°C)	$|\%O|$,eq.(1)	$|\%O|$,eq. (2)
1550	0.185	0.190
1600	0.229	0.230
1650	0.281	0.277
1700	0.340	0.330
1750	0.409	0.388
1800	0.483	0.456

from these different sources. TiO_2 and ZrO_2 are also present in some refractories used in steel making. The content of these oxides is usually low but oxide inclusions with different amounts of titanium and zirconium oxides may result from slag or steel reactions with these refractories.

(8) Calcium:

The free energy of formation of CaO is lowest among the common oxides (Fig.8). Ca has therefore a high affinity for oxygen and should be an effective deoxidant. On the other hand its solubility in steel is very low and the deoxidation process is complicated. Because of its low melting point Ca is usually added as different Ca-Si alloys (Table 2.2). The primary deoxidation inclusions are therefore usually different calcium silicates but often also contain varying amounts of Al_2O_3, FeO and MnO in solid solution, depending on the composition of the deoxidation alloy and deoxidation practice. They are usually present in the ingots as small, glassy, globules, which deform plastically if the steel is deformed. Sometimes different combinations of Ca-Al deoxidation are used and this may result in spherical Ca-aluminate inclusions which do not deform readily during steel deformation.

2.4.2.2 Vacuum Deoxidation:

The common effects of above treatment on non-metallic inclusions are as under:

(1) The amount and size of indigenous oxide inclusions decreases due to decreased oxygen level of steel.

(2) The precipitation pattern of sulphide inclusion changes.

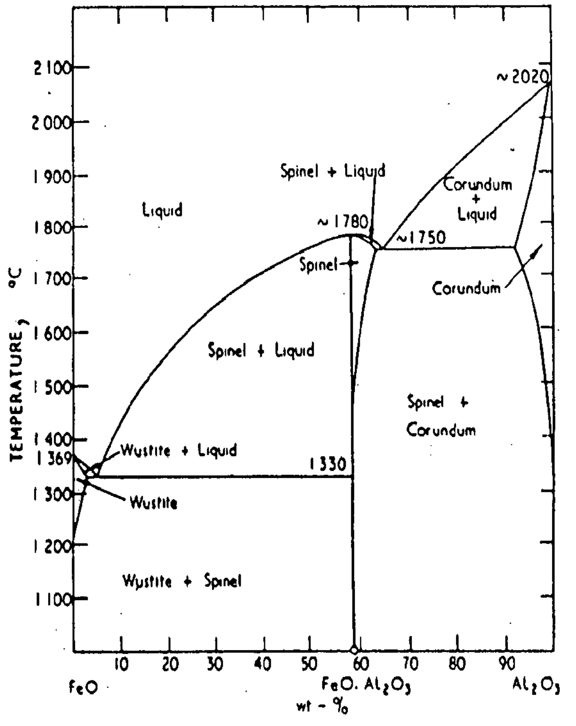
(3) There is an increased danger of large exogenous inclusions due to steel-refractory reactions or emulsified slags, since temperature and holding times are often increased as compared with conventional steel making, but in general an improvement is observed.

(4) The influence of inclusions is greater on high-carbon, low alloy steels than on low-carbon high alloy steel and on basic than on acid steel.

2.4.2.3 The Formation of Non-metallic Inclusions during Steel Making Process:

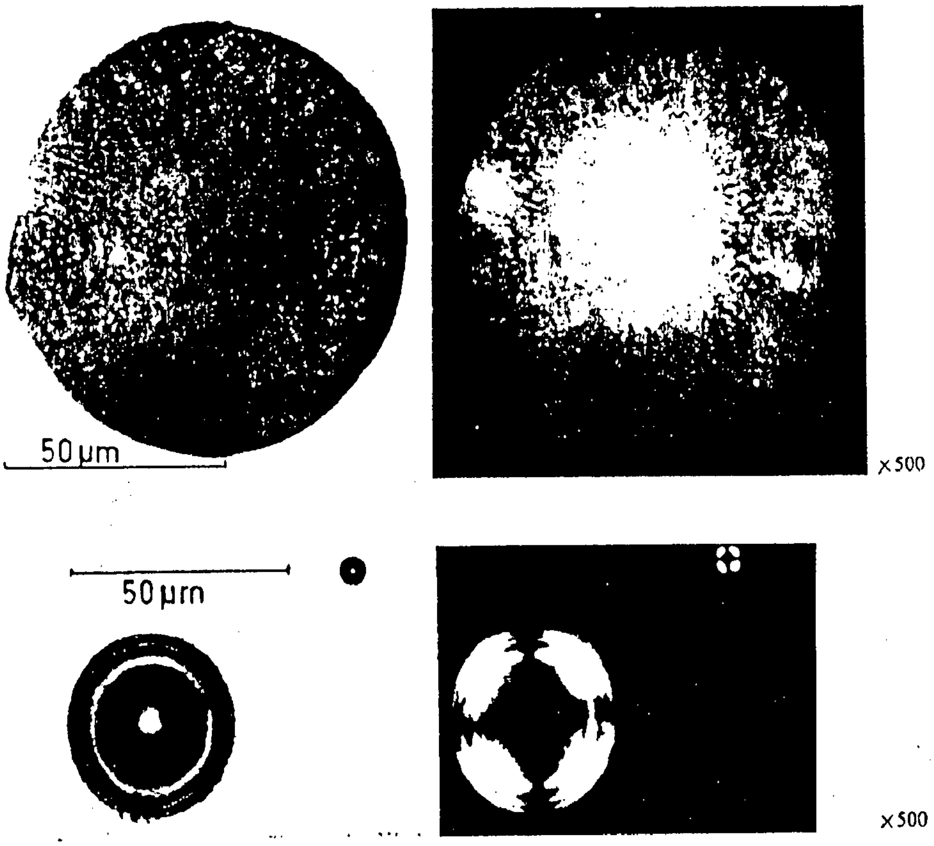
The type, size and composition of the non-metallic inclusions in the molten steel changes at various stages during the steel making process. Small changes in several different operations during steel making may have a great effect on the inclusions resulting in steel. Typical of the steel making parameters of importance are: the boiling time, refractory composition, the deoxidation practice, the composition of deoxidizing alloys and details of the tapping and teeming operations.

Pickering and co-workers [18] made a detailed study of occurrence of non-metallic inclusions in a high carbon steel containing 0.65-0.75%C, 0.5-0.6%Mn and prepared by a 25t. electric arc furnace using double slag practice. Different trials were made with an intention to determine at which stage of the steel making, tapping and teeming processes pick-up of the inclusions occurred. A particular aim was to find the origin of the Ca & Al in the SiO_2



From ref. 53.

Fig 11. The equilibrium diagram for the pseudobinary system FeO–Al_2O_3



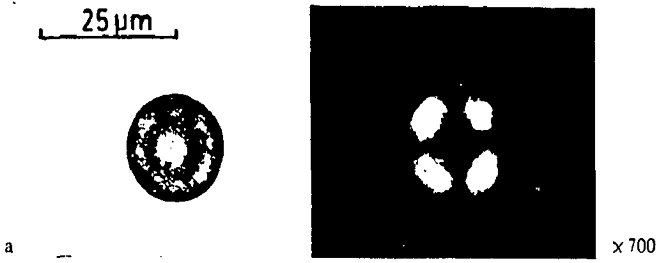
STEEL TYPE Basic Kaldo steel, semi-killed. From ingot

STEEL ANALYSIS, % 0·14 C, 0·07 Si, 1·00 Mn

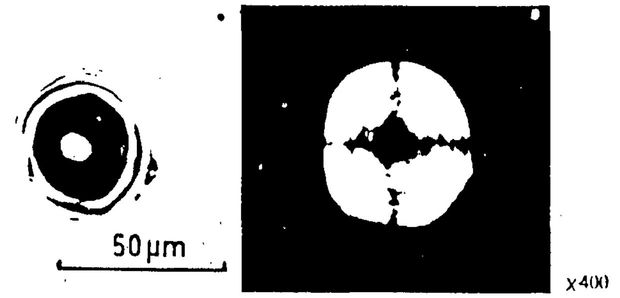
INCLUSIONS 60 MnO, 2 FeO, 37 SiO_2, 2 Al_2O_3, trace of CaO

COMMENT This inclusion type, which is often partly glassy, is sometimes reported as pure silica. It is rather difficult to distinguish between the two phases with the microscope only, but the microhardness of rhodonite is lower than that of silica. Two different inclusions are shown both in ordinary and in polarized light. The larger is crystallized, the smaller is glassy, but both have the rhodonite composition

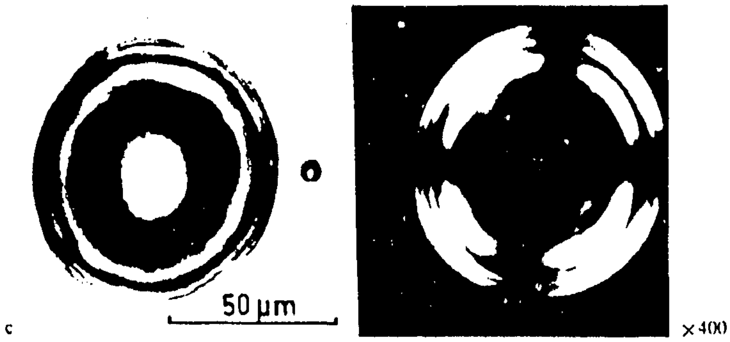
Fig. 12. Oxide inclusion in steel: single-phase rhodonite



Glassy *CS*-phase with only limited CaO-substitution but with a high Al_2O_3 content



Glassy *CS*-phase with MnO partly substituting for CaO



Glassy *CS*-phase with FeO partly substituting for CaO

a STEEL TYPE Austenitic stainless, CaSi-deoxidized. From a scoop sample taken from the mould

STEEL ANALYSIS, % 0·043 C, 0·40 Si, 1·34 Mn, 0·020 P, 0·005 S, 18·5 Cr, 10·1 Ni, 0·50 Mo, 0·029 N

INCLUSIONS, % Glassy CS-phase with 4 MnO, 39 CaO, 3 MgO, 34 SiO_2, 12 Al_2O_3, trace of TiO_2 and Cr_2O_3

COMMENT Electron probe analysis showed the presence of a small amount of MgO. This oxide, according to the authors' opinion, is not present in solid solution in the CS-phase, but as a very fine precipitate of spinel ($MgO{\cdot}Al_2O_3$, F 3) which has clouded the glassy silicate phase

b STEEL TYPE Carbon steel, CaSi-deoxidized

STEEL ANALYSIS, % 0·18 C, 0·27 Si, 0·69 Mn, 0·009 P, 0·021 S, 0·009 N

INCLUSIONS, % Glassy CS-phase with 19 MnO, 23 CaO, 51 SiO_2, 7 Al_2O_3, trace of FeO. Different inclusions showed analysis values 19–22 MnO, 10–23 CaO, 43–51 SiO_2, 7–22 Al_2O_3

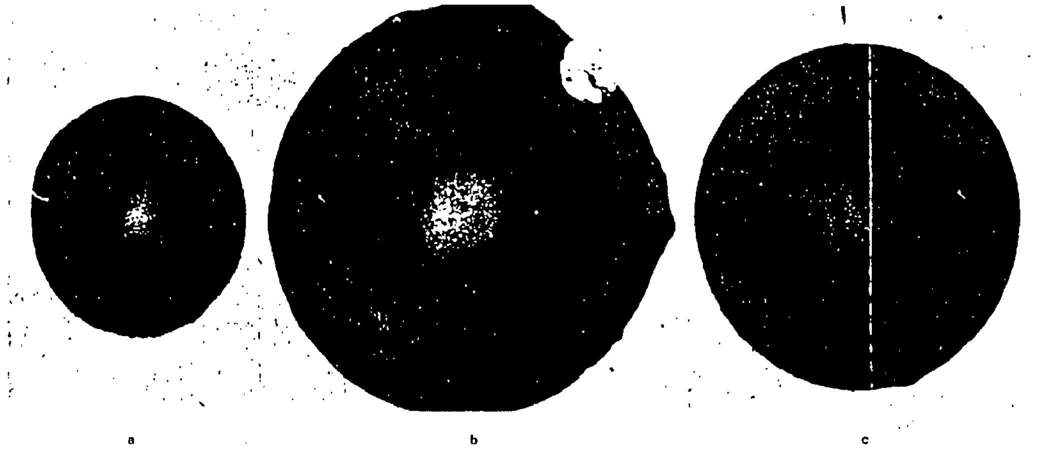
COMMENT Compare rhodonite, $MnO{\cdot}SiO_2$. Fig.40

c STEEL TYPE Scoop sample from Kaldo furnace at a low C-content. The steel was cast into a small sample mould with 5 g CaSi

STEEL ANALYSIS, Unknown

INCLUSION, % Glassy CS-phase with 7 MnO, 30 FeO, 12 CaO, 43 SiO_2. Different inclusions showed analysis values 6–7 MnO, 20–30 FeO, 12–18 CaO, 43–52 SiO_2

Fig·13· Oxide inclusions in steel: glassy calcium silicate of CS-type but with CaO partly substituted by other metal oxides



a manganese–aluminium silicate 35MnO, 9FeO, 28Al_2O_3, 27SiO_2 ×750

b calcium rich silicate 18MnO, 3FeO, 32CaO, 3Al_2O_3, 44SiO_2 ×750

c manganese–aluminium–calcium silicate 35MnO, 8FeO, 7CaO, 17Al_2O_3, 35SiO_2 ×750

Fig.14. Glassy silicates of different composition

inclusions. The following effects were established;

(1) At melt out the oxide inclusions were generally glassy manganese, aluminium silicates resulting from the oxidation of the charge.

(2) During the boil, calcium silicates were picked up from the slag due to the turbulance. The inclusions were still of the glassy silicate type but their CaO content increased rapidly during the boil. Their SiO_2 content showed little change throughout the boil. The MnO content of the inclusions remained reasonably high over the first part of the boil but then decreased to less than 10% at the end. Their Al_2O_3 content decreased rapidly in the early stages of the boil and for most trials, the final Al_2O_3 content of these glassy silicate inclusions at the end of the boil was less than 4%.

(3) During the refining period when deoxidation of the melt was carried out, the inclusion composition quickly reflected the ferro-alloys addition made. At the end of the boil, the inclusions are low in Al_2O_3. They then pick-up Al_2O_3 during refining, but this depends on the deoxidation practice. It is evident that the Al-content of the ferro-alloys (0.7-0.9% in Fe-Si and 1.2-1.7% in Ca-Si) is of great importance for the inclusion content of Al_2O_3. In most trials the inclusions during the refining period were also of the glassy, globular type as shown in Fig.12,13&14 but with changes in composition according to the ferro-alloys addition. The presence of aluminium in the additions caused a marked increase in the Al_2O_3 content of the silicates. There was floatation of inclusions to the slag and a re-entrapment

of more slag inclusions. With increasing time during refining, the Al_2O_3 content decreased, unless it was maintained at a high level by continued additions of aluminium-bearing additions through out refining.

(4) While the CaO in the silicates in part originated from slag entrapment, there was no doubt that the use of calcium silicide as a deoxidant also introduced CaO in the silicates.

(5) The method of reducing Al_2O_3 in the inclusions at the end of refining period were to use only low aluminium additions and to refrain from using such additions immediately before tapping. The CaO in the silicates could also be decreased by not using calcium silicide.

(6) The use of aluminium additions early in refining was effective in converting silicates to alumina etc. which readily floated out. This was very effective in reducing the inclusion content, but some calcium-rich silicates were thereafter picked up from the slag.

(7) During tapping two main phenomena influence the inclusions; namely an increase in CaO-content of the glassy silicates due to CaO pick-up from the slag (slag and metal were poured together) and the appearance of silica rich $MnO-SiO_2-Al_2O_3$ inclusions, often containing cristobalite precipitation. These inclusions were found to be reaction products between liquid steel and the launder refractories (the launder was rammed 'Compo' with about 32% Al_2O_3, 63%SiO_2 and small amounts of CaO, MgO, TiO_2 and Fe_2O_3). The presence of TiO2 in these inclusions was a valuable indications of their origin.

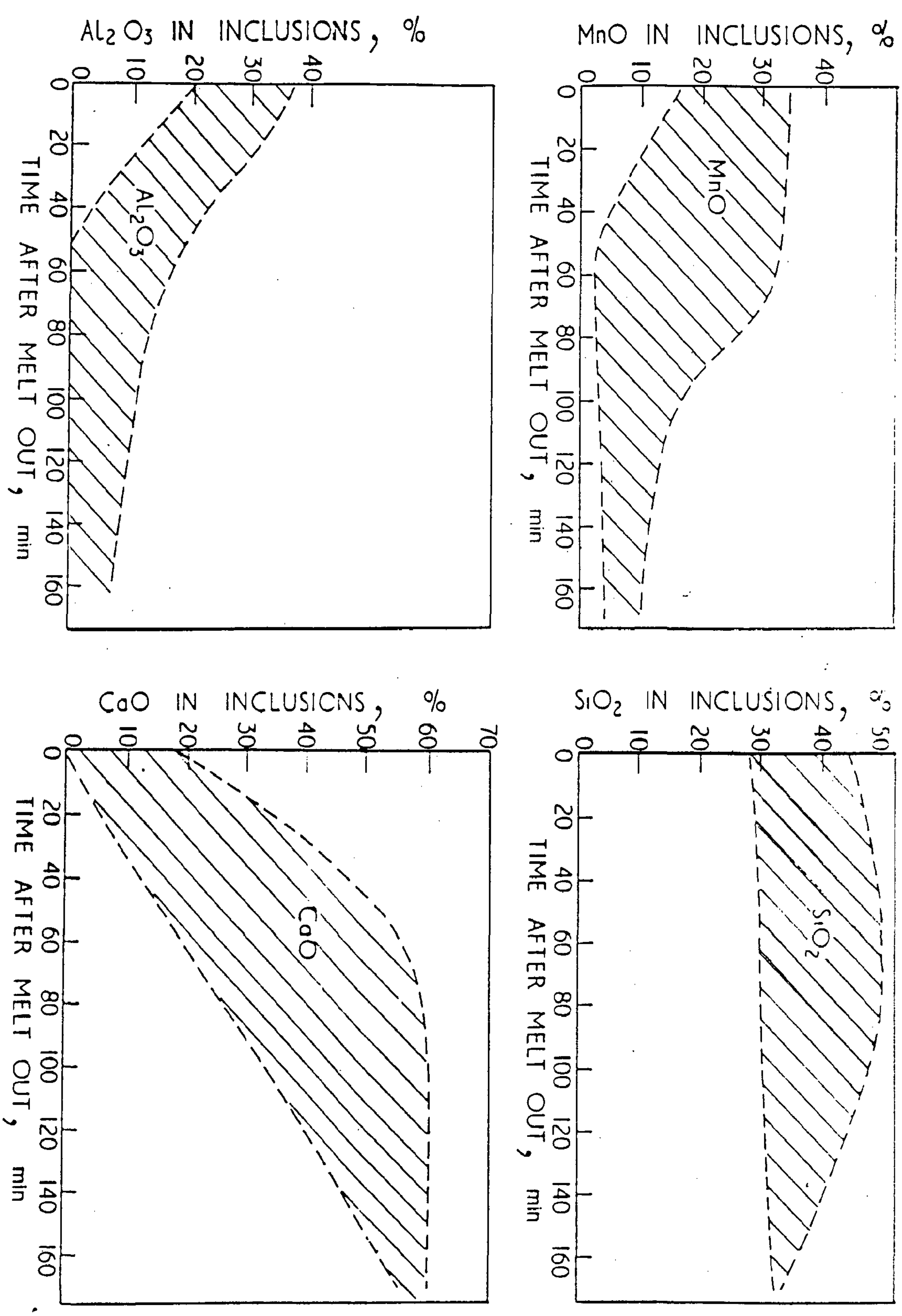
(8) In the ladle large calcarious silicates were entrapped during tapping, but a great part did float out. Therefore the average CaO-content of the inclusions again decreased during the teeming process, whereas the Al_2O_3-content of these inclusions increased if aluminium-bearing ferro-alloys were used in the ladle. A further pick-up of Al_2O_3 by the silicates occurred in the ladle due to ladle refractory erosion, similar to the launder refractory erosion described above (7). In general, the inclusions in the ladle were much larger than those present at the end of the refining period.

(9) In the ingot some floatation can also occur. Due to coalescence and growth by the further precipitation of deoxidation products, the ingot inclusions were always larger than those in ladle stream. It should be noted that ingot scum is a sink as well as a source for inclusions. In top casting, FeO rich inclusions in the steel may originate from the oxide layer formed around the casting stream.

Some of the important results of Pickering [18] are shown in Fig. 15 & 16.

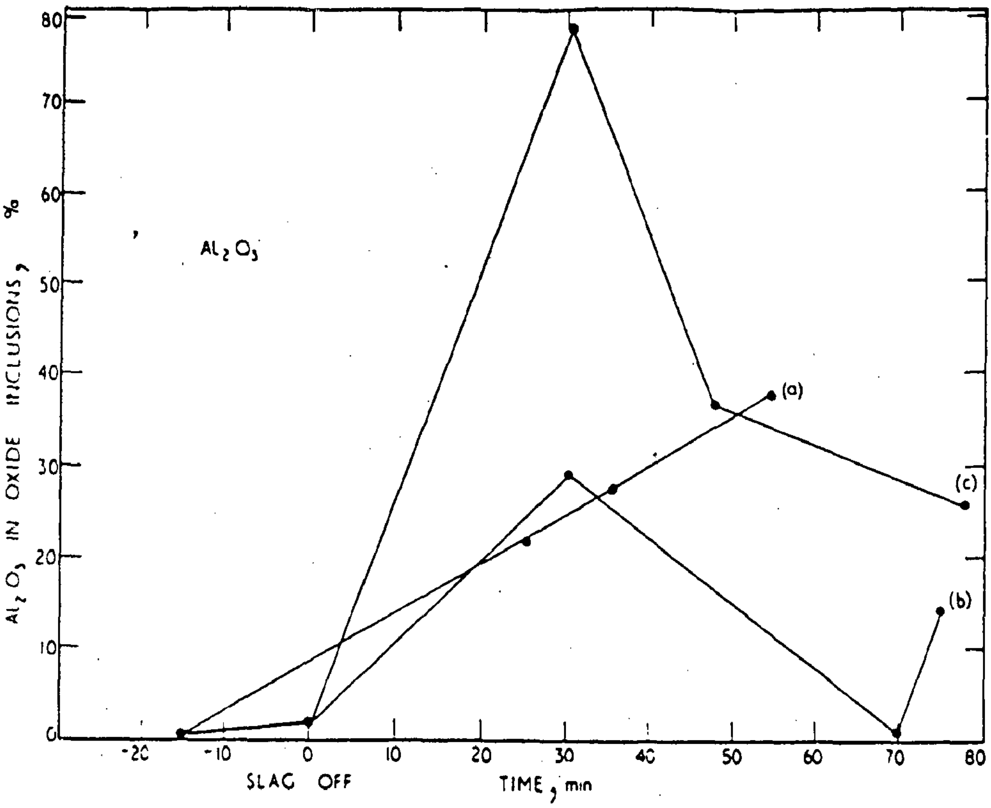
2.4.2.4 Inclusions from Ferro Alloys:

In principle there exists the possibility that inclusions in the ferro-alloys are inherited as inclusions in the steel. The common ferro-alloys are rich in non-metallic inclusions. Due to high concentration of the metal alloyed with iron in these alloys, the inclusion phases are in general rich in the alloying element, for instance Cr in ferro-chromium. The inclusions in ferro-alloys

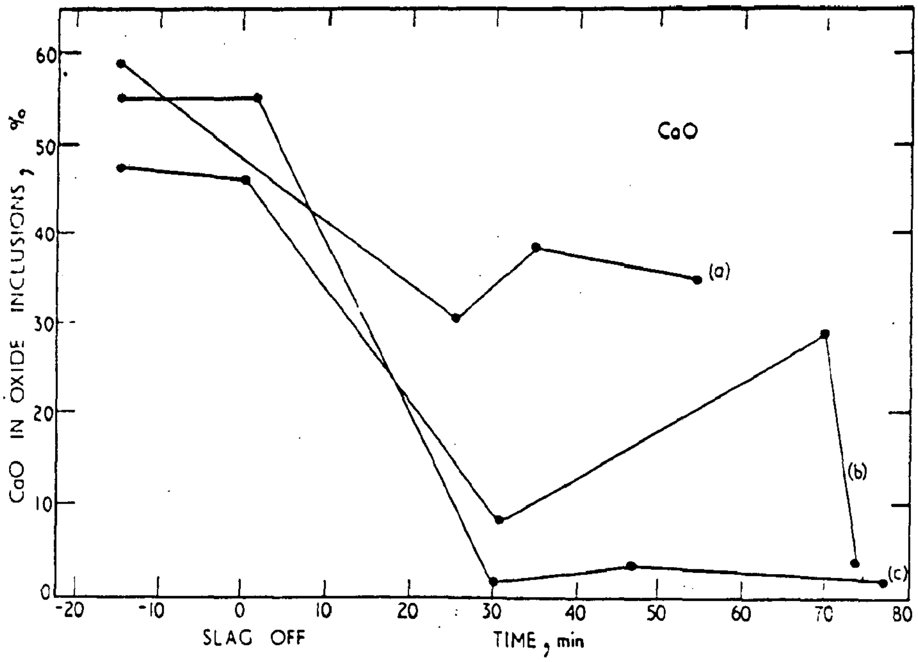


The detailed steel procedure was varied and the areas summarize results from 6 different trials. The variations during the refining period are given in Fig.16. From ref.18

Fig. 15. Variation in the average content of different inclusion components during boil. Basic electric steel, double slag, steel analysis 0·65–0·70%C, 0·5–0·6%Mn, 25 ton furnace



Variation in Al_2O_3 content



Variation in CaO content

Trial a: FeSi and CaSi added at slag off, CaSi also during the whole refining period

Trial b: FeSi added at slag off and 7 minutes after slag off

Trial c: FeSi and Al added at slag off

Fig.16. Variation in the average content of Al_2O_3 and CaO inclusion components during the refining period at different trials. The variation during the boil for the same steel is given in Fig.15. From ref 18

have a characteristic and often complex structure. They therefore usually differ in structure and composition from those in the steel. The work of Schoberl and Straube [19] on inclusions in ferro-chromium and corresponding steels with different Cr-contents, has shown that oxide inclusions in steels normally are not directly inherited from the ferro-chromium. Therefore the use of ferro-chromium alloys very low in inclusions is usually unnecessary. Only if ferro-alloys are added late in the steel process after deoxidation does there seems to be a possibility of direct inheritance, especially for ferro-vanadium high in oxygen [20]. From the standpoint of inclusion formation, it is the aluminium and silicon contents of the ferro-alloys which are more important than their inclusion content. Thus a silicon content higher than about 1% in the ferro-chromium decreases the total amount of oxide inclusions in final steel. The resulting steel inclusions become larger and rounder than if ferro-chromium is low in silicon, when they are sharp and irregular.

Aluminium in the ferro-alloys also has an influence on the steel inclusions. Many ferro-alloys have aluminium contents as high as 1-2%. Therefore the resulting steel may have inclusions either of Al_2O_3 or belonging to the MnO-SiO_2-Al_2O_3 system, even if no aluminium has been added as deoxidant or entered from refractories. Most evidence indicates that the inclusions in the ferro-alloys usually float upto molten steel surface and join the slag or else are dissolved. A direct inheritance of these inclusions seems to occur only accidently.

2.4.2.5 Inclusions from Furnace and Ladle Slags:

Finance slag can be carried over into both the ladle and the ingot and thus be the origin of non-metallic inclusions. Also the ladle slag itself is an important source of non-metallic inclusions. It may be admixed with the molten steel and thus be carried over into the ingot, or it may adhere to the refractory lining of the ladle wall during teeming ('ladle glaze') and contaminate the following steel charge.

In general, the furnace slag will tend to be calcium-rich, to contain only a little alumina and very small amounts of minor refractory additions such as TiO_2 and K_2O. The ladle slag, because it can be contaminated with ladle erosion products, tends to be richer in alumina and to contain more of TiO_2 and K_2O. This has an effect on the composition of the resulting ingot inclusions. Inclusions arising from the slags have the compositions which are usually changed as compared with the slags. This is a result of indigenous precipitation, mainly of MnO and SiO_2 on the slag nuclei.

The presence of MgO and CaO in the inclusions indicates an exogenous source, and the high content of these oxides is a further indication that the exogenous nuclei have a considerable influence on the composition of the inclusions; that is, they are introduced rather late in the steel making process. The most likely sources are slags or refractories.

2.4.2.6 Inclusions from Refractories:

Refractories are an important exogenous source of origin for different non-metallic inclusions. During the whole steel making process molten metal and refractories are in contact and surface reactions between the two phases, as well as erosion effects are possible. It is important to realize that inclusions resulting from refractories are not merely pieces of refractory, which have been accidently eroded from the refractory bricks by the molten steel and then appear embedded in steel matrix. Erosion products act as nuclei for indigenous precipitation from the moment they are included in the molten metal and therefore continuously change their composition as compared with the original refractory. Inclusions formed by surface reactions have a structure which often has no direct relation to the refractory structure and their composition may also be quite different. Components of refractories such as MgO, TiO_2 and K_2O serve as valuable inactive tracers, however, in tracing inclusion origin.

Inclusions from refractories can be of two kinds namely:

(a) Erosion products and,

(b) Reaction products from refractories.

A brief discussion in reaction products from refractories is given below:

Reaction Products from Refractories:

Most of the reactions of refractory origin are not of simple type but are products of surface reactions between refractory materials and the molten metal or molten slags. Most of these phases found in the reacted surface were not present in the original refractory; they were found as reaction product during steel making. The Al_2O_3 pick-up from chamotte is probably the most important among the metal-refractory reactions in common steel making practice. Of special importance are the nozzle and stopper refractories. It has been reported that as much as 30% of the microinclusions originate from these two details if they are made of chamotte. The resulting inclusions are $MnO-SiO_2-Al_2O_3$ particles. The determination of their origin is rather difficult because the same oxides are also the main constituents of indigenous inclusions. Minor additions present in the refractories like TiO_2, ZrO_2 and K_2O are valuable trace elements in establishing a relation between inclusions and refractories.

2.4.2.7 Solubility of Inclusions in Liquid Steel and their Behaviour During Solidification:

Sulphides in the range ordinarily found, are completely dissolved in liquid steel. The size and character of sulphides inclusions are governed largely by three factors, namely, rate of freezing, solubility of the sulphides and quantity present. During freezing, sulphur is concentrated in the molten portion of steel by dendritic segregation, and as soon as saturation is reached, sulphides begin to precipitate and continue to form until solidification is complete. Because they do not start to form until steel is partially solidified, however, they are constrained to locate in the interdendritic channels between the growing crystals.

If the solubility of sulphides is comparatively low, so that precipitation starts early, while the interdendritic channels are wide, there is considerable freedom of location for the first sulphides to form. Further precipitation favours growth of particles already started rather than formation of new nuclei. Under these conditions, large, globular, widely spaced sulphides are formed. The habits of such sulphides is not always readily apparent but is more apparent with higher sulphur and manganese contents [21].

Sometimes the solubility is so high that sulphides are precipitated as one part of sulphide-iron eutectic (Fig. 6 & 7). In such cases, sulphides are restricted to narrow grain boundaries and form thin films or envelopes of minute globules around the primary grains.

As might be expected, composition is the controlling factor in determining the solubility of sulphides, but it is not just the sulphide composition that is effective in this respect; the FeO content of the steel for example, seems to play an important part. In unkilled steels and in most silicon-killed steels, oxides (including silicates) and sulphides tend to precipitate early enough to form large globules. In other words, the presence of iron oxide seems to lower the solubility of (Fe,Mn)S, and saturation is reached at a comparitively early stage in freezing.

When the FeO is reduced practically to the vanishing point by a strong deoxidizer such as aluminium, titanium or zirconium but no appreciable excess of deoxidizer is present, the solubility of (Fe,Mn)S is increased to the extent that it precipitates as a eutectic with the last iron to freeze. When excess of deoxidizer is present, some Al_2S_3, TiS, or ZrS is formed. The sulphides of aluminium and zirconium seem to be appreciably less soluble than

MnS, and when a small excess of aluminium or zirconium is present the sulphides start to precipitate earlier and grow to larger size. Apparently they are crystalline and have irregular outlines. The sulphides of titanium, on the other hand, seems to be very soluble in liquid steel, and with excess titanium, the eutectic sulphide formation is even more pronounced.

If a steel free from exogenous inclusions is frozen very rapidly, as when thrown into water or cast against a chill, the inclusions will be so small that high magnification with the microscope is required to see the larger ones. As the rate of freezing is decreased, the size of largest inclusions will become progressively greater until some size is reached where they tend to float out during freezing. In any case, they grade in size from the largest down to the limit of visibility, and probably there are even smaller ones. This habit is more pronounced with sulphides and the silicate inclusions of silicon-killed steels but is exhibited by other oxides to a lesser degree. Even alumina particles vary in size with the rate of freezing.

This is regarded as evidence that most of these inclusions did not exist in the molten steel but formed during freezing. Whether this growth during freezing is a result of coalescence of sub-microscopic inclusions, precipitation from solution, or a combination of these, has not been definitely established, but the pattern is one that would be predicted on the basis of precipitation. It seems obvious that inclusions of appreciable size do not remain suspended long in liquid steel.

At least part of the formation of silicate inclusions, for example, may be attributed to the fact that the deoxidizing power of silicon increases as the metal cools from pouring temperature to the freezing temperature, which also is accompanied by a decrease in solubility of $\underline{O}$ during freezing, both of which cause the reaction

$$\underline{Si} + 2\underline{O} = SiO_2 \qquad \ldots\ldots\ldots \quad (2.3)$$

to move from left to right, resulting in the formation of silicates.

One result of these characteristics of inclusions is that they are not uniformly distributed in solid steel but are subject to both microsegregation and macrosegregation. In this they follow the law of segregation according to which the crystallization from a metallic melt always tends to be dendritic, and the orientation of the dendrites will be random, although certain directions of growth may be greatly favoured as in the columnar zone of killed and semikilled ingots. The first crystal to form will always be purer than the melt, and the elements other than iron will be concentrated in the adjacent liquid. If this impure liquid is entrapped by rapid freezing, macrosegregation will be slight, while if it is displaced, segregation will be marked. The impure liquid will be displaced by any motion of the liquid along the solidifying wall.

Gas evolution resulting from the reaction between carbon and oxygen will accompany freezing unless the metal is very low in oxygen. Rapid gas evolution will cause motion of the liquid that displaces the impure liquid and greatly increases macrosegregation.

CHAPTER 3.0

PLANT DATA PERTAINING TO THE PRESENT CASE STUDY

3.1 General

The strategy adopted for the present case study was to obtain representative data from nearby Mini Steel Plant on specific grades of steels meant for forgings and castings. For this purpose, detailed processing data for eight different quality heats was obtained from M/S Uttar Pradesh Steels, Muzaffarnagar. Details of these heats are shown in Tables 3.1 to 3.8. These tables show all possible details pertaining to early stages of melting, refining, deoxidation, tapping and teeming. M/S Uttar Pradesh Steels are known for the production of quality steels for castings and forgings and it is for this reason that processing data of various heats was drawn from the above firm for present studies.

The objective of present study is to examine as to how the processing of the heat and subsequent deoxidation practice, tapping and teeming influence the nature and morphology of non-metallic inclusions and thereby the ultimate cleanliness of steels. For this purpose, it is necessary to follow closely the changes taking place in the slag-metal system. In order to fulfill this objective, test specimens were drawn at various stages of the processing of a given heat. Liquid metal samples were taken at the melt out, during boil, during reducing period and from the ladle. Although it is ideal that the liquid metal in the test sample is not killed by Al. as mentioned by Pickering & co-workers [18], some of the test samples for present studies were killed by aluminium wire in the mould.

The present study pertains to an examination of non-metallic inclusions in eight different grades of steels listed below:

(1) Grade no. EN-354, Forging quality steel (Table 3.1)
(2) Grade no. EN-31, Forging quality steel
(3) Grade no. IS:2644 - Foundry grade
(4) Grade no. EN-24, Forging quality steel
(5) Grade no. IS:1030, Foundry grade steel
(6) Grade no. EN-42, Forging quality steel
(7) Grade no. Class IV, IS:1875/71
(8) Grade no. 42 Cr Mo 4 EN-19 foundry grade steel

Apparently all the above heats were prepared using a double slag practice in a 10t direct arc furnace. The data recorded in Tables 3.1 to 3.8 shows all possible processing details pertaining to specific heats.

Test specimens for a detailed study of non-metallic inclusions in individual heats were drawn at following stages:

(a) After melt out
(b) At the end of carbon boil.
(c) At the end of refining period.
(d) In the ladle after ladle addtions and Ar. purging.

The above test specimens were then subjected to a detailed study of non-metallic inclusions. Detailed procedures adopted for this purpose are outlined in the next chapter (Chapter 4.0).

3.2 Process Details of Individual Heats:

From the time the furnace was switched on and the raw materials were charged, complete processing details were noted down and entered in a log sheet. This log sheet shows various additives to the furnace during oxidizing and reducing period and also the spectrometric analysis of various specimens drawn from the melt at different stages. The log sheet further shows alloy additions to the melt/ladle, tapping and ladle temperature and any Argon purging etc. in the ladle.

Table 3.1

PROCESSING DETAILS OF HEAT No.1[EN-354] FORGING QUALITY STEEL

Grade number	:	EN-354
Ingot size	:	18½" x 22½"
Opening Chemistry	:	C=0.62, Mn=0.12, Si=0.05, S=0.032, P=0.058, Cr=0.77, Ni=1.45, Mo=0.14
Final specifications of heat	:	C=0.20 max., Mn=0.50/1.00, Si=0.35 max. S&P=0.045 max. each, Ni=1.50/2.00, Cr=0.75/1.25, Mo=0.10/0.20

Flux Additions (Kgs):

Addition in the charge : Metallurgical coke = 50 kg.

Stage	Oxygen	Iron Ore	Lime Stone	Lime	Flour-spar	CaC_2	Coke	Silica dust
1	2	3	4	5	6	7	8	9
Oxidation	Used	400	600	-	-	-	-	-
Reduction	-	-	250	-	150	-	30	20

Sample Analysis (Spectrometric):

Sl. No.	C	Mn	Si	S	P	Cr	Ni	Mo	V	Cu
1	2	3	4	5	6	7	8	9	10	11
1	0.62	0.12	0.05	0.032	0.058	0.77	1.45	0.14	-	-
2	0.225	0.03	0.02	0.028	0.051	0.30	1.76	0.15	-	-
3	0.10	0.01	0.01	0.029	0.044	0.21	1.84	0.15	-	-
4	0.09	0.03	0.01	0.028	0.032	0.19	1.80	0.15	-	-
5	0.185	0.63	0.24	0.023	0.038	0.85	1.80	0.15	-	-
6	0.180	0.57	0.21	0.022	0.039	0.85	1.78	0.15	-	-
7	0.180	0.56	0.195	0.039	0.032	0.85	1.77	0.145	-	-
8	-	-	-	-	-	-	-	-	-	-

Contd/-

Total charge : 8,100 kg.

Alloy Additions(Kg) :

Fe-Mn			Pure-Mn	Si-Mn	Fe-Si		Fe-Cr			Fe-V	Fe-Mo	Fe-Ni
H.C.	M.C.	L.C.			Dust	High grade	H.C.	M.C.	L.C.			
1	2	3	4	5	6	7	8	9	10	11	12	13
-	-	-	10	70	-	15	80	-	18	-	-	-
-	-	-	-	-	-	10	-	-	-	-	-	-

Grand Total = 203 kg.

Remarks: H.C. = High carbon

M.C. = Medium carbon

L.C. = Low carbon

Tapping temperature = 1654°C

Ladle temperature = 1562°C

Killing with (In the furnace) = Fe-Al. Qty.= 14 kg.

Ladle additions = Calcium-silicide = 3.50 kg.

Power on = 2.00 P.M.

Tapped = 6.40 P.M.

Purging = Ar. Purging, bottom purging

Purging time = 1'30"

Total Ar. Purged = Approx. 1 cu.m.

Shrouding not done.

Table 3.2

PROCESSING DETAILS OF HEAT NO.2 [EN-31] FORGING QUALITY STEEL

Grade number	:	EN-31
Ingot size	:	14" x 16"
Opening Chemistry	:	C=1.18, Mn=0.42, Si=0.29, S=0.06, P=0.042, Cr=0.14
Final specifications of heat	:	C=1.04, Mn=0.36, Si=0.145, P=0.021, S=0.041, Ni=0.05, Cr=1.02, Mo=0.03

Flux Additions (Kgs):

Addition in the charge : Petroleum coke = 100 kg.

Stage	Oxygen	Iron Ore	Lime Stone	Lime	Flour-spar	CaC_2	Coke	Silica dust
1	2	3	4	5	6	7	8	9
Oxidation	Used (n't specified)	150	300	-	12	-	-	-
Reduction		-	250	-	50	-	30	20

Sample Analysis (Spectrometric):

Sl. No.	C	Mn	Si	S	P	Cr	Ni	Mo	V	Cu
1	2	3	4	5	5	7	8	9	10	11
1	1.18	0.42	0.29	0.06	0.042	0.14	-	-	-	-
2	1.10	0.17	0.08	0.06	0.025	0.08	-	-	-	-
3	1.04	0.19	0.07	0.05	0.025	0.09	-	-	-	-
4	1.07	0.49	0.48	0.041	0.030	1.17	-	-	-	-
5	1.10	0.48	0.36	0.036	0.030	1.04	-	-	-	-
6	1.10	0.50	0.33	0.035	0.030	0.99	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-

Total charge : 8191 Kg.

Alloy Additions (Kg) :

Fe-Mn			Pure Mn	Si-Mn	Fe-Si		Fe-Cr			Fe-V	Fe-Mo	Fe-Ni
H.C.	M.C.	L.C.			Dust	High grade	H.C.	M.C.	L.C.			
1	2	3	4	5	6	7	8	9	10	11	12	13
-	-	-	-	30	-	25	116	-	-	-	-	-
-	-	-	-	-	-	-	20	-	-	-	-	-

Grand Total = 191 Kg.

Remarks : H.C. = High carbon

M.C. = Medium carbon

L.C. = Low carbon

Tapping temperature = 1613°C

Ladle temperature = 1545°C

Killing with (In the furnace) = Fe-Al=14 kg.

Ladle additions = Ca-siliside = 4 kg.

Power on = 4.45 p.m.

Tapped = 9.25 p.m.

Purging = Ar + N_2 Purging, Bottom purging

Purging time = 1 min.

Total Ar. purged = 1 cu.m.

Shrouding not done.

Remark: While teeming some iron powder was used along with the stream through the central down sprue.

TABLE 3.3

PROCESSING DETAILS OF HEAT NO.3 [IS:2644] FOUNDRY GRADE

Grade number	:	IS:2644
Ingot size	:	-
Opening Chemistry	:	C=0.34, Mn=0.29, Si=0.02, S=0.040, P=0.030, Cr=0.09, Ni=0.20, Mo=0.07
Final specifications of heat	:	S=0.05 max., P=0.05 max.

Flux Additions (Kgs):

Addition in the charge : 30 kg. Metallurgical coke

Stage	Oxygen	Iron Ore	Lime Stone	Lime	Flour-spar	CaC_2	Coke	Silica dust
1	2	3	4	5	6	7	8	9
Oxidation	Used (n't specified)	150	300	-	-	-	-	-
Reduction	-	-	200	-	50	-	30	20

Samples Analysis(Spectrometric):

Sl. No.	C	Mn	Si	S	P	Cr	Ni	Mo	V	Cu
1	2	3	4	5	6	7	8	9	10	11
1	0.34	0.29	0.02	0.040	0.030	0.09	0.20	0.07	-	-
2	0.19	0.17	0.02	0.036	0.013	0.07	0.57	0.20	-	-
3	0.06	0.08	0.02	0.032	0.011	0.05	0.60	0.20	-	-
4	0.17	1.05	0.24	0.029	0.016	0.50	0.70	0.205	-	-
5	0.17	1.05	0.21	0.028	0.016	0.50	0.65	0.20	-	-
6	0.185	1.07	0.21	0.028	0.017	0.49	0.72	0.21	-	-
7	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-

Total Charge : 4817 kg.

Alloy Additions(Kg) :

Fe-Mn			Pure Mn	Si-Mn	Fe-Si		Fe-Cr			Fe-V	Fe-Mo	Fe-Ni
H.C.	M.C.	L.C.			Dust	High grade	H.C.	M.C.	L.C.			
1	2	3	4	5	6	7	8	9	10	11	12	13
25	-	-	-	50	-	20	35	-	-	-	12	-
25	-	-	-	-	-	25	-	-	-	-	5	-

Grand Total = 197

Remarks : H.C. = High carbon

M.C. = Medium carbon

L.C. = Low carbon

Tapping temperature = 1590°C

Ladle temperature = 1573°C

Killing with (In the furnace) = Fe-Al = 10 kg.

Ladle additions = -

Power on = 11.15 a.m.

Tapped = 2.30 p.m.

Purging = Ar. purging bottom purging

Purging time = 1 min.

Total Ar. purged = 0.75 cu.m. approx.

Shrouding not done

TABLE - 3.4

PROCESSING DETAILS OF HEAT NO.4 [EN-24] FORGING QUALITY STEEL

Grade number	:	EN-24
Ingot size	:	18½" x 22½"
Opening chemistry	:	C=0.77, Mn=0.33, Si=0.180, S=0.050, P=0.039, Cr=2.21, Ni=0.62, Mo=0.12, Cu=0.13
Final specifications of heat	:	C=0.40, Mn=0.59, Si=0.29, P=0.025, S=0.035, Ni=1.43, Cr=1.16, Mo=0.27, Cu=0.15

Flux Additions (Kgs):

Addition in the charge : Nil

Stage	Oxygen	Iron Ore	Lime Stone	Lime	Flour-spar	CaC_2	Coke	Silica dust
1	2	3	4	5	6	7	8	9
Oxidation	Used	500	400	-	-	-	-	-
Reduction	-	-	250	-	100	15	20	30

Sample Analysis(Spectrometric):

Sl. No.	C	Mn	Si	S	P	Cr	Ni	Mo	V	Cu
1	2	3	4	5	6	7	8	9	10	11
1	0.77	0.33	0.18	0.05	0.039	2.21	0.62	0.120	-	-
2	0.55	0.07	0.03	0.046	0.037	1.35	1.28	0.160	-	-
3	0.32	0.03	0.02	0.044	0.025	0.58	1.25	0.180	-	-
4	0.35	0.53	0.21	0.036	0.029	0.97	1.40	0.190	-	-
5	0.355	0.52	0.17	0.039	0.028	0.96	1.42	0.195	-	-
6	0.355	0.47	0.13	0.035	0.027	0.95	1.43	0.190	-	-
7	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-

Total charge: 8731 kg.

Alloy Additions(kg):

Fe-Mn			Pure Mn	Si-Mn	Fe-Si		Fe-Cr			Fe-V	Fe-Mo	Fe-Ni
H.C.	M.C.	L.C.			Dust	High grade	H.C.	M.C.	L.C.			
1	2	3	4	5	6	7	8	9	10	11	12	13
-	-	65	-	-	-	25	35	-	-	-	12	200
-	-	-	-	-	-	15	20	-	-	-	5	50
-	-	-	-	-	-	-	-	-	-	-	4	-

Grand Total = 431 kg.

Remarks : H.C. = High Carbon
M.C. = Medium Carbon
L.C. = Low Carbon

Tapping temperature = 1626°C

Ladle temperature = 1565°C

Killing with (In the furnace): Fe-Al=15 kg.

Ladle additions = Ca-siliside = 4 kg., Graphite coke = 2 kg.

Power on = 5.25 a.m.

Tapped = 11.00 a.m.

Purging = Ar. purging, bottom purging

Purging time = 1 minute

Total Ar. Purged = 0.75 cu.m. approx.

Shrouding not done

TABLE 3.5

PROCESSING DETAILS OF HEAT NO.5 [IS:1030] FOUNDRY GRADE

Grade number : [IS:1030]

Ingot size : -

Opening chemistry : C=0.40, Mn=0.07, Si=0.040, P=0.038, S=0.040

Final specifications of heat : S=0.05 max., P=0.05 max.

Flux Additions (Kgs):

Addition in the charge : Petroleum coke = 30 kg.

Stage	Oxygen	Iron Ore	Lime Stone	Lime	Flour-spar	CaC_2	Coke	Silica Dust
1	2	3	4	5	6	7	8	9
Oxidation	Used	200	500	-	-	-	-	-
Reduction	-	-	250	-	50	20	10	-

Sample Analysis (Spectrometric):

Sl. No.	C	Mn	Si	S	P	Cr	Ni	Mo	V	Cu
1	2	3	4	5	6	7	8	9	10	11
1	0.40	0.07	0.02	0.040	0.038	-	-	-	-	-
2	0.16	0.08	0.03	0.036	0.025	-	-	-	-	-
3	0.14	0.09	0.02	0.040	0.025	0.01	0.36	0.03	0.20	-
4	0.16	1.23	0.38	0.030	0.030	-	-	-	-	-
5	0.18	1.24	0.30	0.028	0.033	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-

Total charge = 7675 kg.

Alloy Additions (kg):

Fe-Mn			Pure-Mn	Si-Mn	Fe-Si		Fe-Cr			Fe-V	Fe-Mo	Fe-Ni
H.C.	M.C.	L.C.			Dust	High grade	H.C.	M.C.	L.C.			
1	2	3	4	5	6	7	8	9	10	11	12	13
-	-	-	5	125	-	25	-	-	-	-	-	-
-	-	-	-	-	-	20	-	-	-	-	-	-

Grand Total = 175 kg.

Remarks : H.C. = High Carbon
M.C. = Medium Carbon
L.C. = Low Carbon

Tapping temperature = 1614°C

Ladle temperature = 1590°C

Killing with (In the furnace) : Fe-Al = 15 kg.

Ladle Additions = Graphite = 1.50 kg.

Power on =

Tapped = 2.40 p.m.

Purging = 6.30 p.m.

N_2 purging

Purging time = 1' 30"

Total N_2 Purged = 1.50 cu.m.

Shrouding not done

TABLE 3.6

PROCESSING DETAILS OF HEAT NO.6 [EN-42] FORGING QUALITY STEEL

Grade number : EN-42

Ingot size : 21"x23"

Opening chemistry : C=0.92, Mn=0.38, Si=0.11, S=0.065, P=0.060, Cr=0.13, Ni=0.10, Mo=0.03, Cu=0.15

Final specifications of heat : C=0.70/0.85, Mn=0.55/0.75, Si=0.10/0.40, S&P=0.05 max. each, Ni=- , Cr= -, Mo= -

Flux additons(kgs):

Addition in the charge : Metallurgical coke = 100 kg.

Stage	Oxygen	Iron Ore	Lime Stone	Lime	Flour-spar	CaC_2	Coke	Silica dust
1	2	3	4	5	6	7	8	9
Oxidation	Used	100	250	-	-	-	-	-
Reduction	-	-	200	-	50	20	-	30

Sample Analysis(Spectrometric):

Sl. No.	C	Mn	Si	S	P	Cr	Ni	Mo	V	Cu
1	2	3	4	5	6	7	8	9	10	11
1	0.920	0.38	0.11	0.065	0.060	0.13	0.10	0.03	-	0.15
2	0.970	0.33	0.07	0.060	0.055	0.14	-	-	-	-
3	0.625	0.10	0.015	0.060	0.021	-	-	-	-	-
4	0.735	0.39	0.22	0.042	0.025	-	-	-	-	-
5	0.780	0.50	0.19	0.035	0.026	-	-	-	-	-
6	0.770	0.50	0.18	0.035	0.026	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-

Total charge = 5995 kg.

Alloy additions(kg):

Fe-Mn H.C.	Fe-Mn M.C.	Fe-Mn L.C.	Pure-Mn	Si-Mn	Fe-Si Dust	Fe-Si High grade	Fe-Cr H.C.	Fe-Cr M.C.	Fe-Cr L.C.	Fe-V	Fe-Mo	Fe-Ni
1	2	3	4	5	6	7	8	9	10	11	12	13
50	-	-	-	-	20	-	-	-	-	-	-	-
10	-	-	-	-	15	-	-	-	-	-	-	-

Grand Total = 95 kg.

Remarks : H.C. = High Carbon

M.C. = Medium Carbon

L.C. = Low Carbon

Tapping temperature = 1591°C

Ladle temperature = 1539°C

Killing with (In the furnace) : Fe-Al+Al = 7+7 = 14 kg.

Ladle additions = Ca-siliside = 3.50 kg. Graphite = 2.50 kg.

Power on = 00.10 a.m.

Tapped = 5.05 a.m.

Purging = Ar purging done, bottom purging

Purging time = 1 min.

Total Ar. purged = 0.75 cu.m. approx.

Shrouding not done.

TABLE 3.7

PROCESSING DETAILS OF HEAT NO.7 [CLASS IV,IS:1875/71] FOUNDRY GRADE

Grade number : Class IV, IS:1875/71

Ingot size : 27"x30"

Opening chemistry : C=0.50, Mn=0.12, Si=0.04, S=0.07, P=0.033

Final specifications of heat : C=0.45, Mn=0.73, Si=0.25, P=0.036, S=0.037, Ni=0.18, Cr=0.14, Mo=0.025, Cu=0.135

Flux additions(kgs):

Addition in the charge : Petroleum coke = 40 kg.

State	Oxygen	Iron Ore	Lime Stone	Lime	Flourspar	CaC_2	Coke	Silica dust
1	2	3	4	5	6	7	8	9
Oxidation	Used	200	450	-	-	-	-	-
Reduction	-	-	250	-	100	15	30	20

Sample analysis (Spectrometric):

Sl. No.	C	Mn	Si	S	P	Cr	Ni	Mo	V	Cu
1	2	3	4	5	6	7	8	9	10	11
1	0.50	0.12	0.04	0.07	0.033	-	-	-	-	-
2	0.46	0.08	0.02	0.061	0.010	-	-	-	-	-
3	0.41	0.11	0.13	0.062	0.018	-	-	-	-	-
4	0.385	0.49	0.15	0.045	0.015	-	-	-	-	-
5	0.370	0.51	0.13	0.044	0.017	-	-	-	-	-
6	0.370	0.50	0.14	0.041	0.019	-	-	-	0.083	-
7	0.415	0.63	0.30	0.034	0.018	-	-	-	0.070	-
8	0.415	0.64	0.43	0.026	0.019	-	-	-	0.095	-
9	0.410	0.72	0.30	0.028	0.019	-	-	-	0.086	-

Total charge = 7400 kg.

Alloy additions(kg.):

Fe-Mn			Pure-Mn	Si-Mn	Fe-Si		Fe-Cr			Fe-V	Fe-Mo	Fe-Ni
H.C.	M.C.	L.C.			Dust	High grade	H.C.	M.C.	L.C.			
1	2	3	4	5	6	7	8	9	10	11	12	13
45	-	-	-	-	20	-	-	-	-	12	-	-
10	-	-	-	-	10	-	-	-	-	3	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-

Grand Total = 110 kg.

Remarks : H.C. = High Carbon

M.C. = Medium Carbon

L.C. = Low Carbon

Tapping temperature = 1595°C

Ladle temperature = 1551°C

Killing with (In the furnace): Fe-Al = 7 kg, Al. shots = 6 kg.

Ladle additions = Ca-siliside = 3.50 kg.

Power on = 5.15 a.m.

Tapped = 10.40 a.m.

Purging = Ar. purging done. Bottom purging

Purging time = 1 min.

Total Ar. Purged = 0.75 cu.m. approx.

Shrouding not done.

TABLE 3.8

PROCESSING DETAILS OF HEAT NO.8 [42 Cr Mo4 EN-19] FOUNDRY GRADE

Grade number : 42Cr.Mo4 EN-19

Ingot size : -

Opening chemistry : C=0.63, Mn=0.14, Si=0.04, S=0.053, P=0.040, Cr=0.15, Mo=0.03

Final specifications of heat : C=0.38/0.45, Mn=0.50/0.80, Si=0.15/0.35 P&S=0.05 max.each, Ni=0.60 max. Cr=0.9/1.20 Mo=0.15/0.25

Flux additions(kgs):

Addition in the charge : Petroleium coke = 40 kg.

Stage	Oxygen	Iron Ore	Lime Stone	Lime	Flourspar	CaC_2	Coke	Silica dust
1	2	3	4	5	6	7	8	9
Oxidation	Used	250	500	-	16	-	-	-
Reduction	-	-	250	-	100	20	30	20

Sample analysis(Spectrometric):

Sl. No.	C	Mn	Si	S	P	Cr	Ni	Mo	V	Cu
1	2	3	4	5	6	7	8	9	10	11
1	0.63	0.14	0.04	0.053	0.04	0.15	-	0.03	-	-
2	0.38	0.14	0.02	0.055	0.018	0.09	-	0.16	-	-
3	0.225	0.16	0.02	0.035	0.009	0.06	-	0.225	-	-
4	0.40	0.99	0.59	0.030	0.018	1.52	-	0.23	-	-
5	0.365	0.97	0.36	0.036	0.018	1.03	-	0.22	-	-
6	0.355	0.90	0.31	0.026	0.018	0.91	-	0.22	-	-
7	0.365	0.89	0.31	0.021	0.018	0.90	-	0.22	-	-
8	-	-	-	-	-	-	-	-	-	-

Total charge : 4872 kg.

Alloy additions(kg) :

Fe-Mn			Pure-Mn	Si-Mn	Fe-Si		Fe-Cr			Fe-V	Fe-Mo	Fe-Ni
H.C.	M.C.	L.C.			Dust	High grade	H.C.	M.C.	L.C.			
1	2	3	4	5	6	7	8	9	10	11	12	13
65	-	-	-	-	-	30	80	-	-	-	20	-
-	-	-	-	-	-	25	10	-	-	-	-	-

Grand total = 230 kg.

Remarks : H.C. = High Carbon

M.C. = Medium Carbon

L.C. = Low Carbon

Tapping temperature = 1611°C

Ladle temperature = 1554°C

Killing with (In the furnace): Fe-Al = 7 kg., Al shots = 7 kg.

Ladle additions = -

Power on = 11.15 a.m.

Tapped = 4.30 p.m.

Purging = No purging done

Purging time = -

Total Ar. purged = -

Shrouding not done.

CHAPTER - 4.0

EXPERIMENTAL PROCEDURE

4.1 General:

The objective of present investigation was (a) To identify the nature, kind and morphology of inclusions and (b) To ascertain the approximate chemical composition of non-metallic inclusions present in different steels under study. For this purpose the cast specimens had to be subjected to qualitative and quantitative metallographic examinations and electron probe micro-analysis. The objective of metallographic examination of polished section was to ascertain the morphology of different inclusions and the quantitative metallography helped to quantify the number of inclusions in a given microsection of a sample. The electron probe micro analyser was planned to be employed to identify the presence of different elements in a specific non-metallic inclusions. At the outset, it was found that the specimen were too hard to be machined as they were water quenched and therefore almost all specimens were required to be annealed over long durations. The subsequent sections deal with the details of actual experimental techniques employed in the present work.

4.2 Annealing of Specimens:

Quenched specimens obtained from the plant were required to be annealed at 950°C for periods ranging from 12 to 18 hrs., for they were too hard to be machined easily. These specimens were originally sliced longitudinally through the centre at the plant itself. Later, after the heat treatment the specimen was cut in a transverse manner using a power hacksaw about 1 cm. away from the top. Thus, two flat surfaces were obtained, one longitudinal and another transverse. Both these surfaces were later prepared for metallographic examination.

4.3 Metallographic Preparation of Specimens:

Starting from rough grinding till final preparation of the polished surface, special precautions were observed throughout. After rough grinding the specimen were taken on the silicon-carbide papers commencing from the rough grades to the finest grades. The specific grades of silicon-carbide papers employed in the present work were:

60,80,100,120,180,300,400,600,800,1000,1200 μm.

In all above cases, wet grinding was followed. At the same time, the polishing was carried out very carefully with a very soft pressure. The polishing was virtually carried out under the weight of the specimen only. Although this practice consumed excessively long period of time but it was considered extremely essential. It is basically because there is always a danger of abrasive particles being embedded into the surface of the specimen and latter being mistaken for a non-metallic inclusion. The above precautions are considered standard precautions in respect of the preparation of metallographic specimens particularly for the examinations of non-metallic inclusions. Similar precautions and procedure have been summarised by Kiessling [6] also.

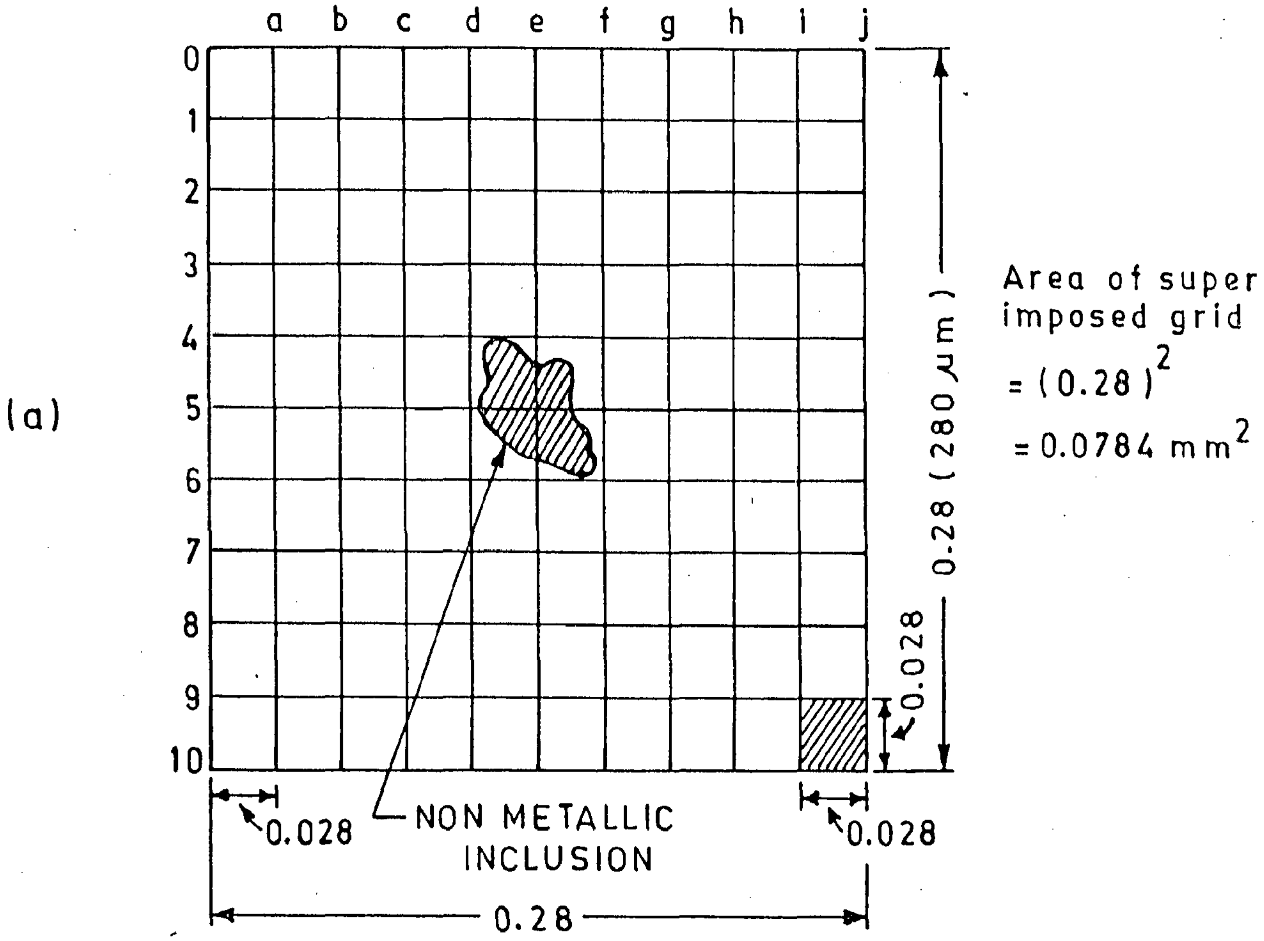
The fine polishing of specimen was carried out on a valvet cloth using diamond paste (grade 0.25 μm). Occasionally, Al_2O_3 suspension of 1.0 μm grade was also employed to obtain mirror polish on the specimen surface completely free of any scratches. Considerable time was spent in perfecting this practice of obtaining a mirror polish in each case.

No etching practice was followed in present studies as it was planned to identify the composition of individual non-metallic inclusions using the EPMA technique.

4.4 Quantitative Metallography:[33]

The objective of this study was to quantify the number and average size of inclusions present in a given micro-section. For this purpose, a standard magnifaction of X190 was employed throughout the entire set of measurements. A systematic study was carried out to obtain reliable data in this respect.

A superimposed grid was introduced in eye piece, the size of which was accurately measured using a standard scale (A glass strip having 1mm divided into 100 equal divisions, the least count of this scale being 0.01mm). This standard scale was placed on to the objective and was focused against the superimposed grid fixed into the eye piece. After the scale was sharply focused on to the superimposed grid in the eye piece, the accurate size of one edge of the square grid could be precisely measured. Using this procedure, it was found that one side of the square of the superimposed grid fixed into the eye piece was equal to 0.28 mm (280 um). This grid was further sub-divided into ten equal parts. Therefore, the length of one small part was equal to 0.028 mm (28 um). Since the grid introduced in the eye piece was of square configuration, apparently a micro area of 0.28 x 0.28 = 0.0784 mm^2 would be covered by this grid on the specimen. Details of grid dimensions and the dimensions of a single small square within this grid are shown in Fig.17(a).This figure also shows details pertaining to the standard strip scale (1 mm divided into 100 parts,



SUPER IMPOSED GRID (X 190)

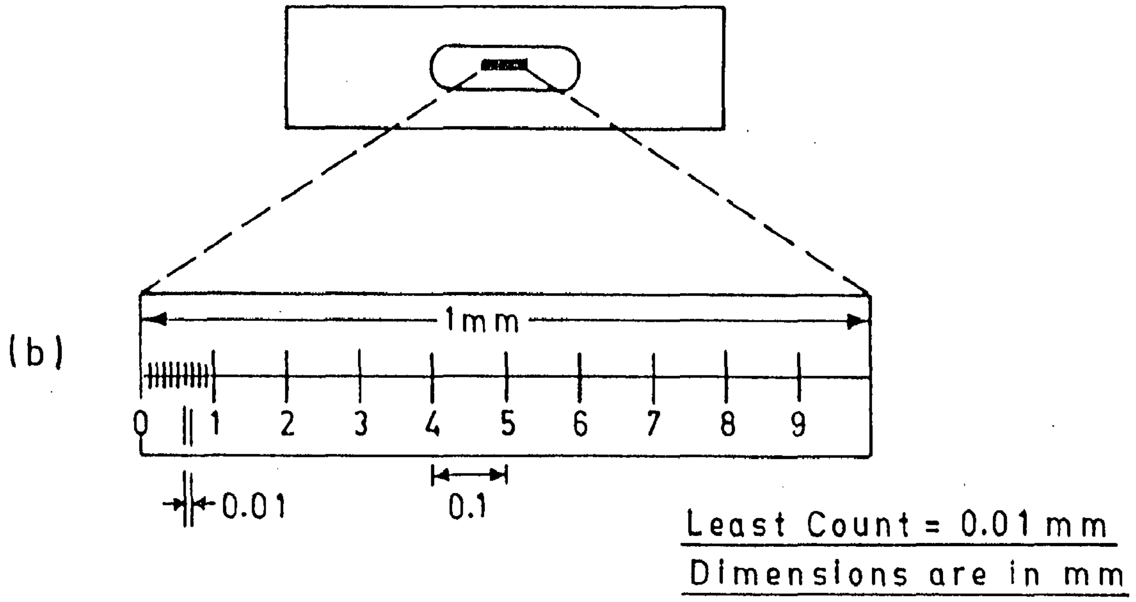


Fig.17(a&b)

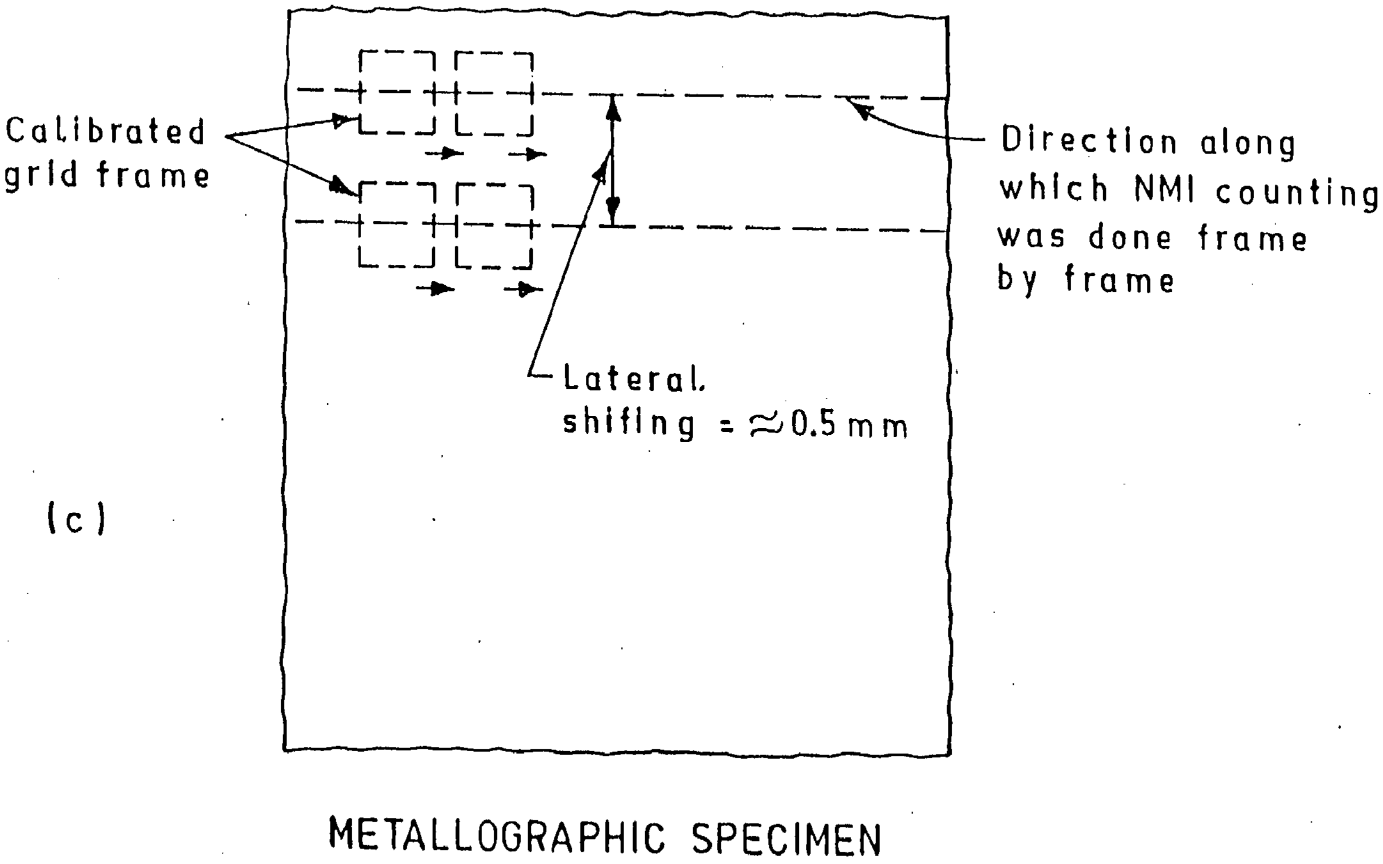


Fig.17(c)

Fig.17. Quantitative Metallographic examination of NMIs in steel specimens using superimposed grid frame and calibrated glass strip (least count 0.01 mm).

(a) Details and dimensions of superimposed grid.
(b) Details of calibrated glass strip.
(c) Method of examination of steel specimen frame by frame.

least count = 0.01 mm). (Fig.17-b).

Once the dimensions of the grid were fixed as above, the quantitative metallographic observations were commenced. A systematic procedure was followed to observe the number and size of inclusions on different steel specimens. The methodology adopted for this purpose is shown schematically in Fig.17(c). The entire polished surface of the specimen was scanned thoroughly one grid frame after the other. After one linear length was completed, a lateral shift of about 0.5 mm was made on the specimen surface and then the entire length was again examined in the same manner frame after frame. It must be mentioned that both the longitudinal as well as transverse surfaces of every specimen were examined thoroughly.

In a given frame covered by the superimposed grid, the number of inclusions occurring in this area were counted. This practice was followed in all other subsequent frames and the observations recorded systematically. Occasionally the dimensions of comparitively larger inclusions were also measured. This practice would result in very large number of observations from which reasonably accurate statistical mean can be determined. Besides this, this system of scanning the entire surface of specimen thoroughly would not allow any features of non-metallic inclusions to escape from direct observations. Although this practice is extremely laborious but still this procedure was strictly adhered to throughout the observations. From these observations, a statistical mean and standard deviation were determined in each case. The number of NMI determined by the above procedure were found in terms of NMI/0.0784 mm^2 area on the specimen surface. This data was later converted to NMI/mm^2 and then finally to NMI/mm^3 using Schwartz-Saltykvo equation [22,23].

$$Nv = 2.38 \times Na^{1.6} \qquad .... (4.1)$$

where,

Nv = No. of NMI/mm^3

Na = No.of NMI/mm^2

The final results are therefore recorded in terms of NMI/mm^3.

4.5 Optical Microscopy:

The general distribution of NMI in different specimens was first observed at lower magnification (X47), and also photographed. Some typical inclusions were also observed at higher magnifications and also photographed. This examination helped greatly to ascertain the morphological features of different inclusions. It should be mentioned that all the photomicrographs were taken in an unetched condition. It is because the objective of this study was not to ascertain the minerological constituents present in the inclusions but only determine their morphological features. For this reason, even the polarized light was not employed. Reichert-Jung optical Microscope, model MeF3, was employed for above studies.

4.6 EPMA Examination of Non-metallic Inclusions:

The objective of this study was to determine the presence of various elements in non-metallic inclusions with a view to ascertain their approximate chemical nature. For this purpose, JEOL Superprobe Micro-analyser Model JXA8600M was employed extensively. Almost in all cases an excitation voltage of 25 KV was found adequate. The instrument was capable of focusing the electron beam down to a diameter of 1 µm on the specimen. For this reason, even very fine inclusions could be easily analysed effectively for their constituents. JEOL EPMA instrument being highly sophisticated, several other facilities were also attached with the instrument. For example, the steel specimen loaded into the chamber could be observed from outside with the help of an optical microscope. The steel specimen could easily be moved in all directions and the exact location on the specimen could be fixed under the cross wires for examination. With this instrument was also attached the SEM facility, using which the exact location of NMI could be fixed on the cross wire and simultaneously viewed on the fluorescent screen. Using this facility, the precipitate of NMI could be viewed at any magnification ranging from X80 to X80,000. In the present work however magnification levels in the range of X250 to $\simeq$ X3000 were employed. Another facility attached with the JEOL instrument was the computer system for recording and processing the data and printing out the results of point or line analysis. In the present work mostly spot analysis was carried out to determine the presence of various elements in the non-metallic inclusions. The chemical analysis results were obtained in the form of histograms in the present work. This form of analysis obtained in the present work is therefore basically qualitative in nature. This analysis is very valuable in the sense that the presence of specific elements in the NMI can help to approximately identify the possible combination of minerals that can be present in the inclusions. Simultaneously, it is possible to take the SEM pictures of these inclusions at any appropriate magnification to reveal their morphological details.

A general study of the kind and morphology of inclusions using optical examination revealed that there were only some typical kinds of inclusions present in all the eight different steels investigated in the present work. It is for this reason that only four typical samples were selected for EPMA study. These four samples exhibited all the common types of inclusions observed in all the eight different quality steel under investigation. Usually only the inclusions present on the longitudinal section of the specimen were examined by the EPMA because larger number of inclusions were observed to occur along this section. Only in one case, both the longitudinal as well as the transverse surface of the specimen was examined by the EPMA. When the inclusions were very small, the picture could be magnified suitably and a spot well with in the inclusion selected for point analysis. The spot analysis was carried out at several locations with in a given inclusion to obtain an over all picture of chemical composition of the inclusion. Every effort was made to cover many such locations on a given specimen for spot chemical analysis. In case of complex morphologies and comparatively larger inclusions every effort was made to examine the analysis of inclusion at several locations with in the inclusion. But printouts for chemical analysis were recorded only in typical cases. For example, when the analysis of another inclusion was found to be the same as the previous case, only one print out referring to the previous composition only was taken to avoid duplication of results.

The specimens examined by the EPMA are marked by two star in Table 5.1 [Next Chapter].

CHAPTER 5.0

RESULTS AND DISCUSSIONS

5.1 General:

The total results of present study are classified in three different sections. The first section deals with optical examination of non-metallic inclusions in five typical cases. The objective of this study is to examine the morphology of typical inclusions present in different steels. The second section deals with the quantitative metallographic examination of NMIs. The objective of this study is to quantify the average number of inclusions present in eight different steels examined in the present work. For any given quality of steel, four different specimens were drawn in a definite sequence: After melt out, after refining, after reducing period and from the ladle. The results of this study are reported in terms of number of NMI.mm^{-3}. Both the longitudinal and transverse sections of the cast specimen were examined for this purpose. The third section of the present investigation deals with EPMA. examination of non-metallic inclusions. The objective of this study was to make a microanalysis of inclusions at different locations in situ.

5.2 Optical Examination of Nonmetallic Inclusions:

The optical pictures pertaining to different heats are presented in the following order: (Sequence of heats shown in Table 5.1)

(1) Heat at serial no.1 (Table 5.1), EN-354 (a) specimen drawn at stage D (from the ladle) Transverse Section - Fig.18, (b) Specimen drawn at stage B, Longitudinal Section, Fig.19.

(2) Heat at Serial No.3 (Table 5.1), IS:2644, specimen drawn at stage B (After refining), Longitudinal Section, Fig.20.

(3) Heat at Serial No.4 (Table 5.1), EN-24, specimen drawn at stage C (After reducing period), Transverse Section - Fig.21

(4) Heat at Serial No.5(Table 5.1), IS:1030, specimen drawn at stage A (After melt out), (a) Transverse section shown in Fig.22 & 23, (b) Longitudinal section shown in Fig.24.

(5) Heat at Serial No.7 (Table 5.1), IS:1875/71, class IV, specimen drawn at stage B (After refining), (a) Transverse section shown in Fig.25, (b) Longitudinal section shown in Fig.26.

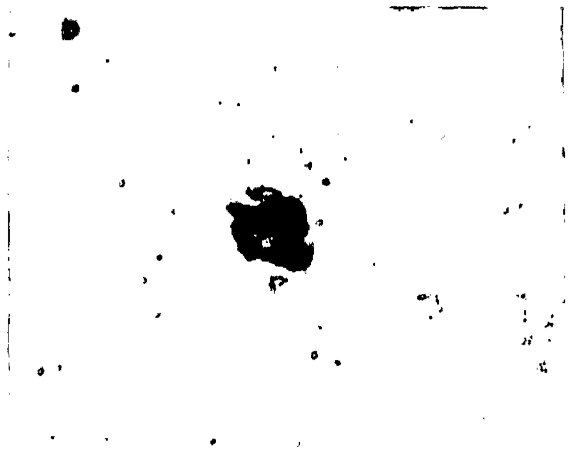
All the above photo micrographs are shown in a sequence in nine different plates one after the other.Special features pertaining to the non-metallic inclusions shown in the above photmicrographs are discussed thereafter.

18(1) X190

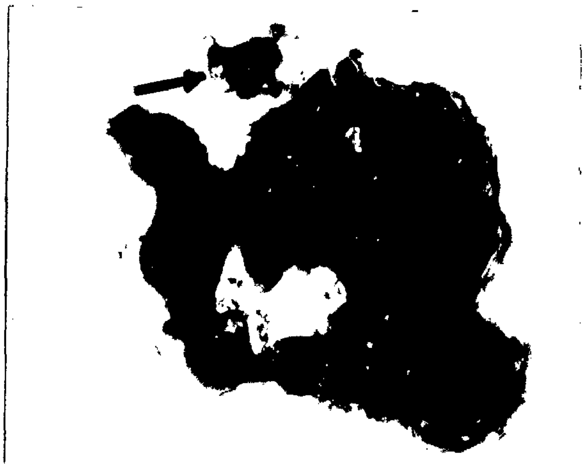
18(2) X947

18(3) X190

18(4) X947



18(5) X190

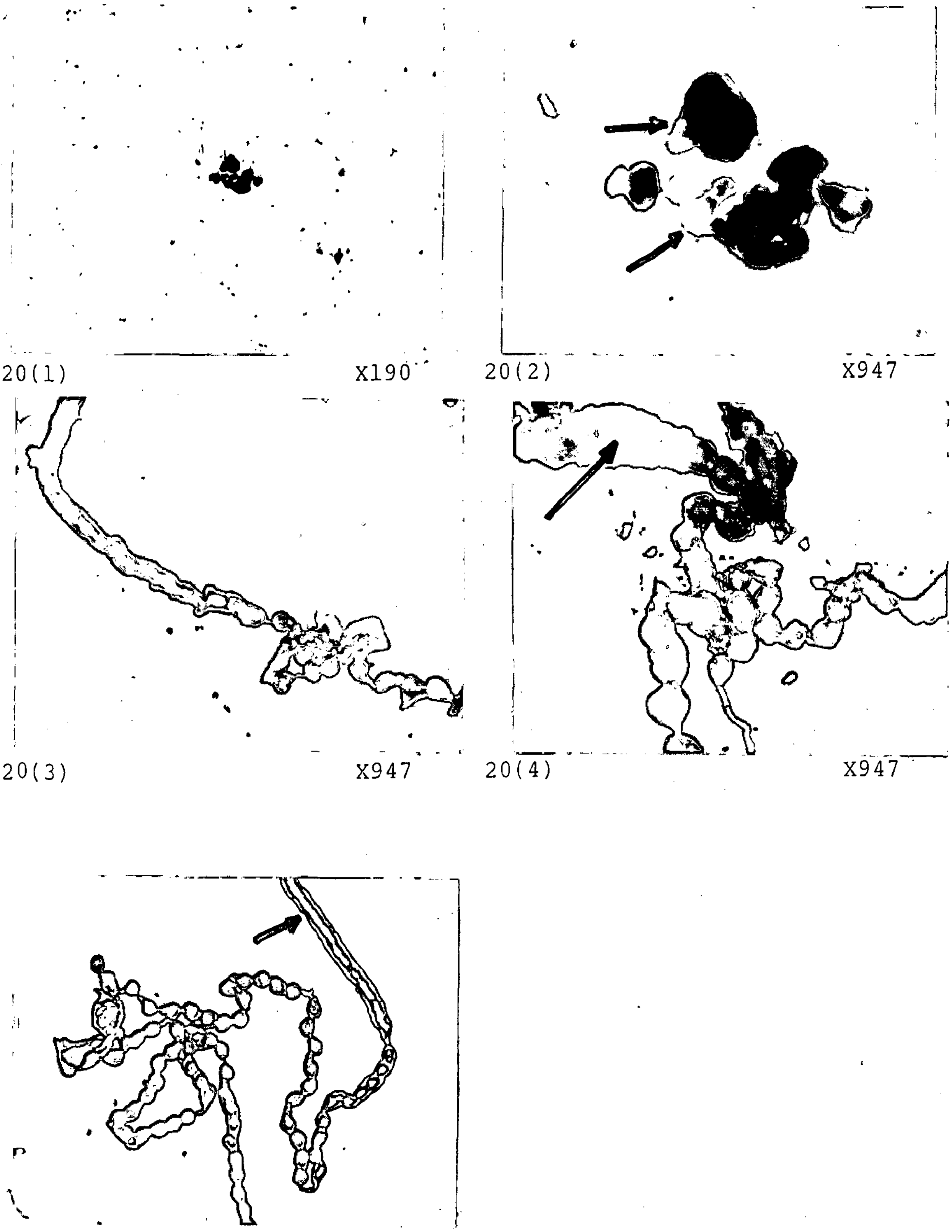


18(6) X947

Fig.18. Optical pictures showing the morphology of Non-metallic inclusions in steel. Specimen drawn from Heat No.1 (EN-354, forging quality) at stage D (from the ladle). Transverse-section of the specimen examined optically.

19(1) X506 19(2) X947

Fig.19. Optical pictures showing the morphology of Non-metallic inclusions in steel. Specimen drawn from Heat No.1 (EN -354, forging quality) at stage D (from the ladle). Longitudinal-Section of the specimen examined optically.

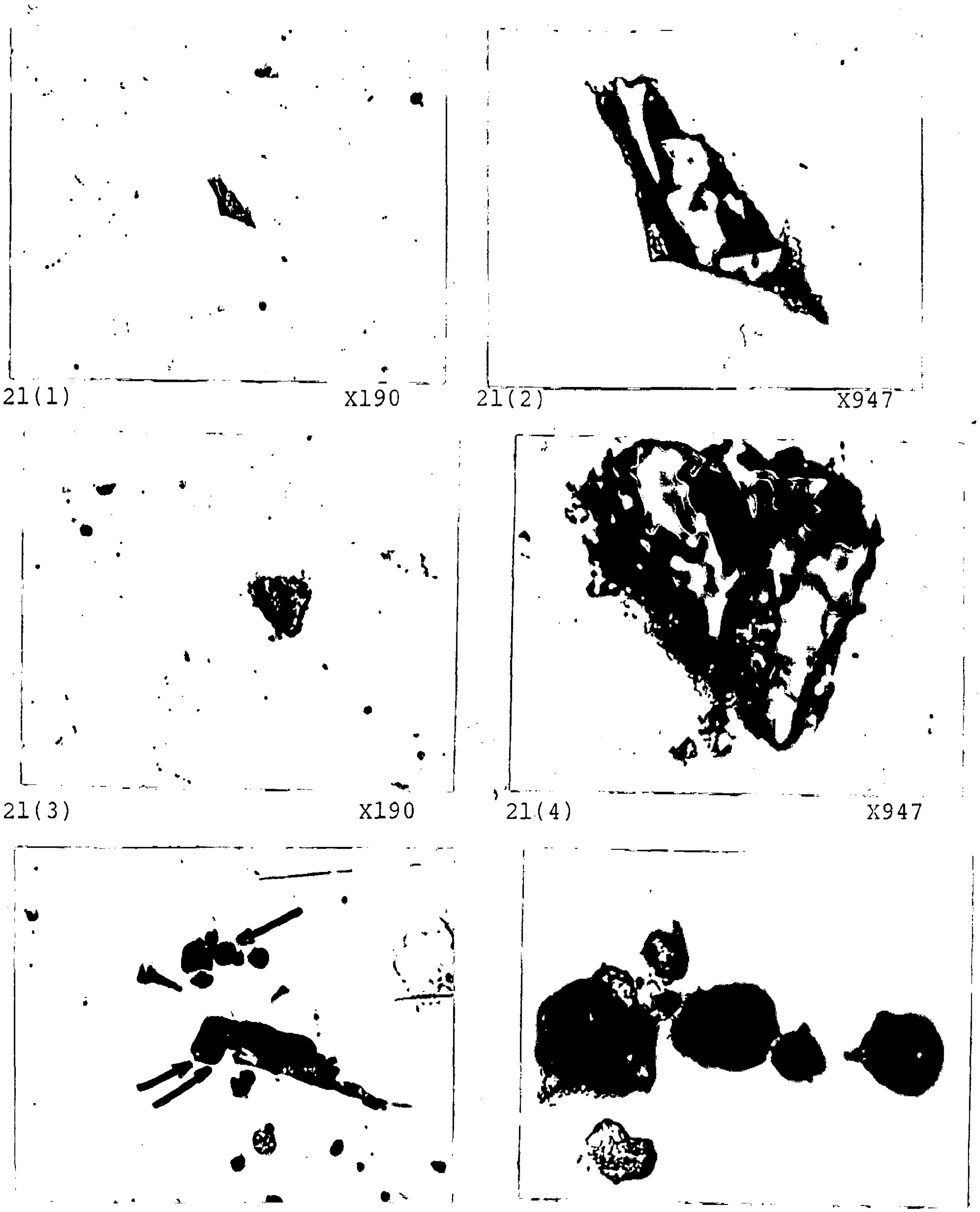


20(1) X190 20(2) X947

20(3) X947 20(4) X947

20(5) X947

Fig.20. Optical pictures showing typical morphology of inclusions found in Heat No.3 (IS:2644, foundry grade), specimen drawn at stage B (after refining), Longitudinal Section. Note typical tendency of inclusion bits to coagulate. Also note typical pearl-necklace morphology of inclusions.



21(1) X190

21(2) X947

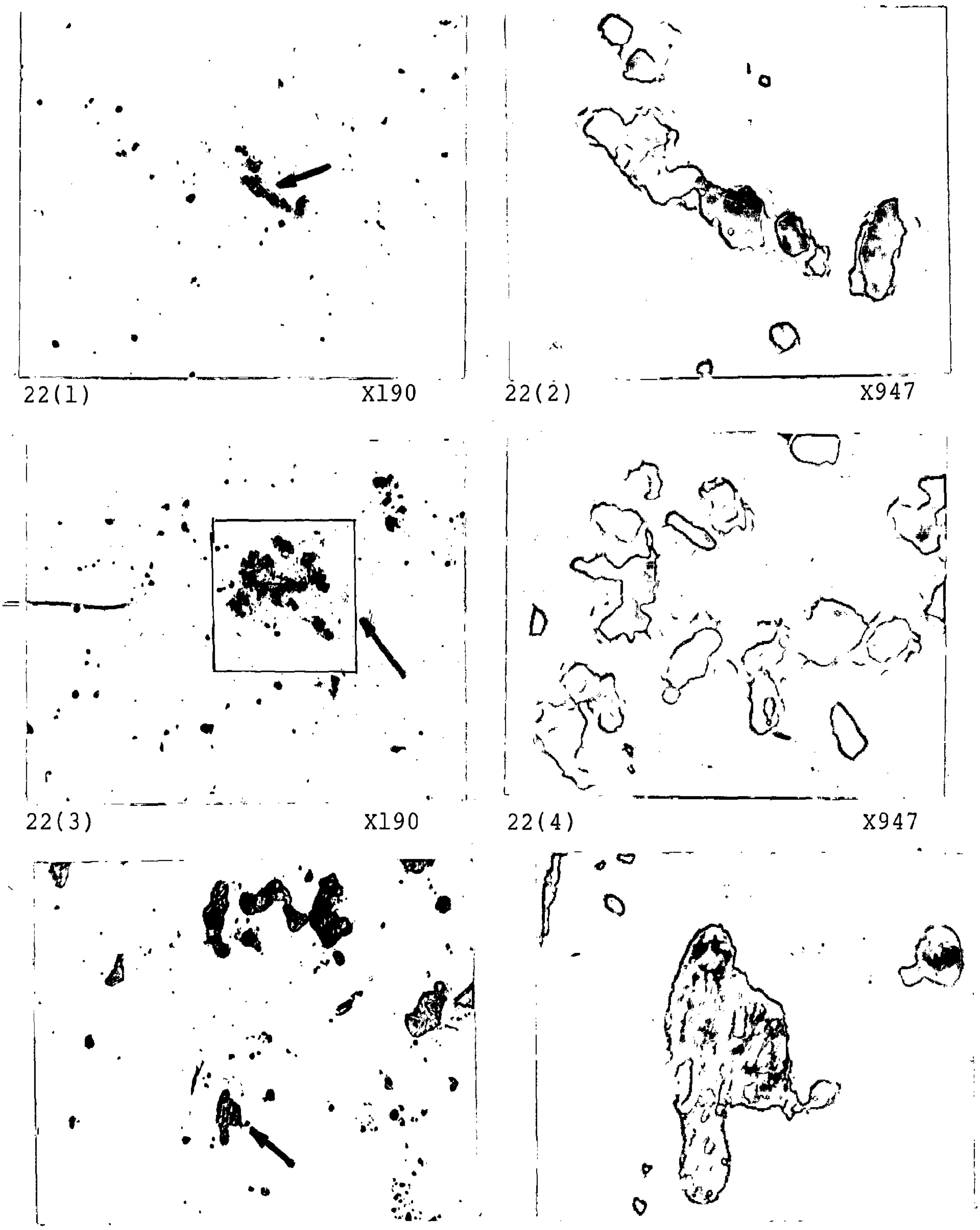
21(3) X190

21(4) X947

21(5) X190

21(6) X947

Fig.21. Optical pictures showing typical kinds of inclusions observed in Heat No.4 (EN-24, forging quality) at stage C (after reducing period). Transverse Section. Note typical exogenous refractory inclusions in Fig.(1 to 4) in a partially reacted state. Also note globular deoxidation products tending to coalesce (5 and 6).



22(1) X190

22(2) X947

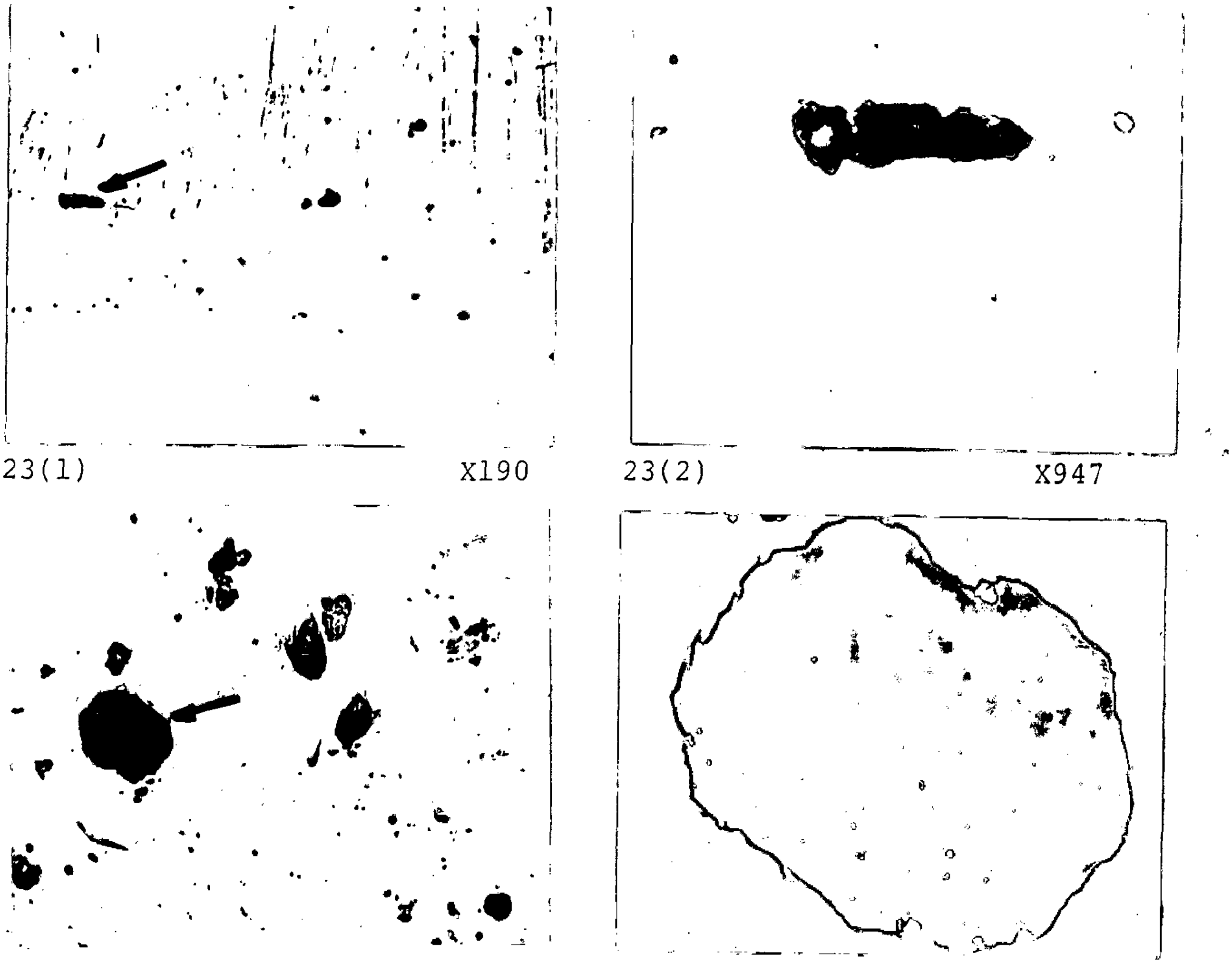
22(3) X190

22(4) X947

22(5) X190

22(6) X947

Fig.22. Optical pictures showing the morphology of Non-metallic inclusions observed in Heat No.5 (grade IS:1030, foundry grade) at stage A (after melt out), Transverse Section. Inclusions shown at 190X in the pictures to the left. Specific locations magnified at 947X. Mostly globular FeO inclusions.



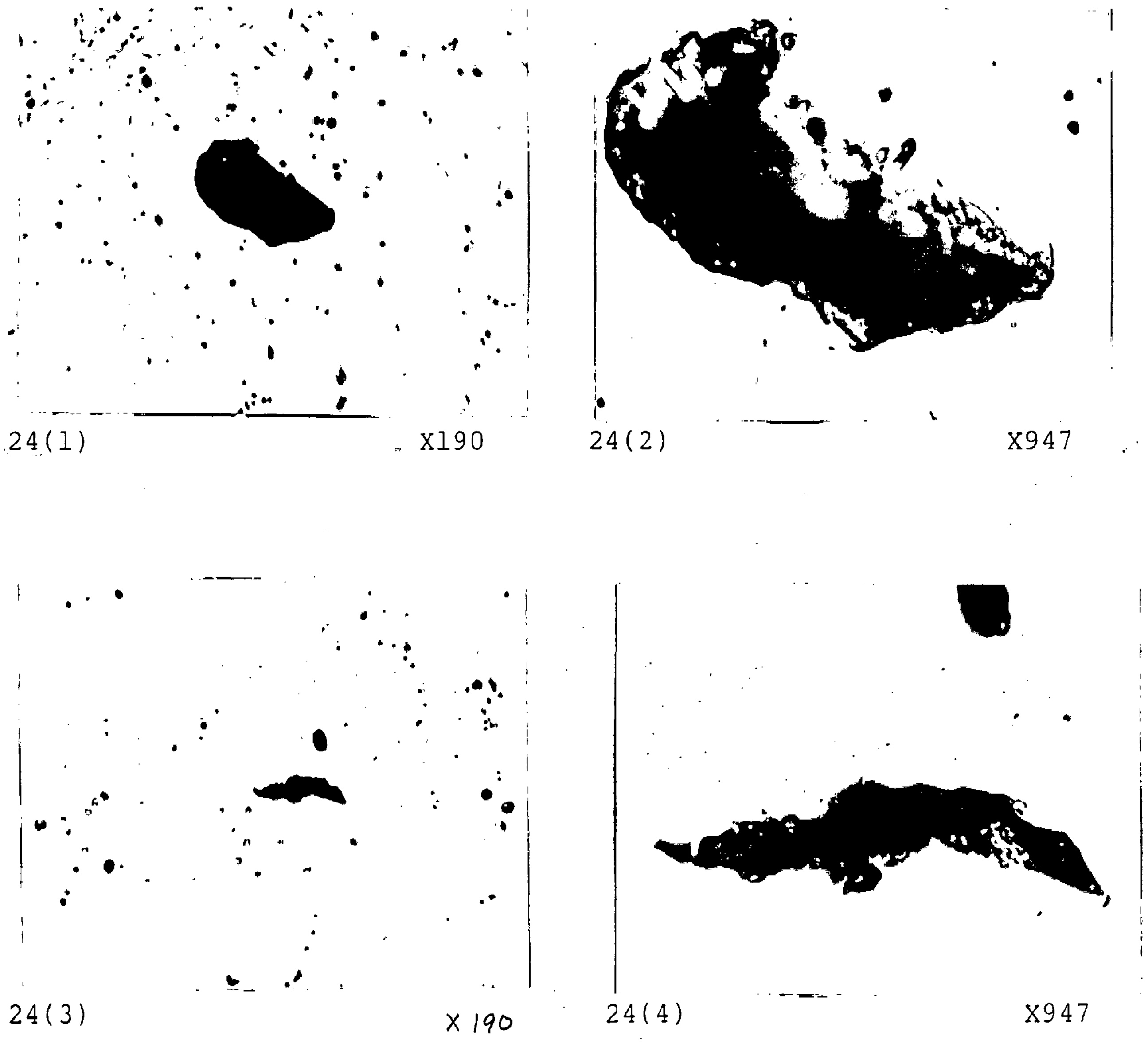
23(1) X190

23(2) X947

23(3) X190

23(4) X947

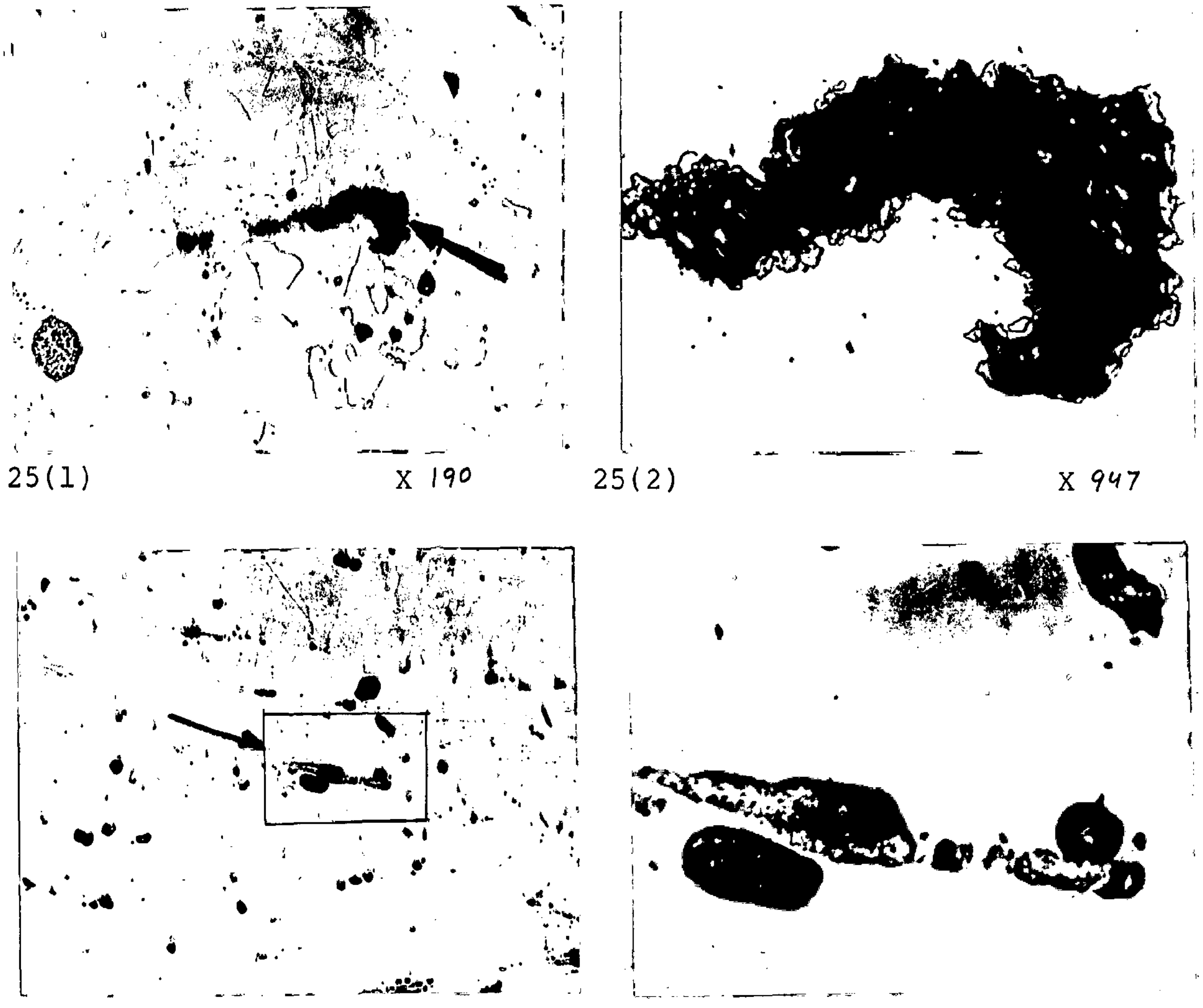
Fig.23. Optical pictures showing the morphology of Non-metallic inclusions in steel. Specimen drawn from Heat No.1 (EN - 354, forging quality) at stage D (from the ladle). Transverse-Section of the specimen examined optically.



24(1) X190 24(2) X947

24(3) X 190 24(4) X947

Fig.24. Longitudinal Section of the specimen drawn from Heat No.5 (grade IS : 1030, foundry grade) at stage A (after melt out). Note a big FeO-MnO inclusion in Fig.24(1) and 24(2), which may be an exogenous inclusion. Inclusion shown in Fig.24(3) & (4) could be FeO-MnO-SiO_2 reaction product.



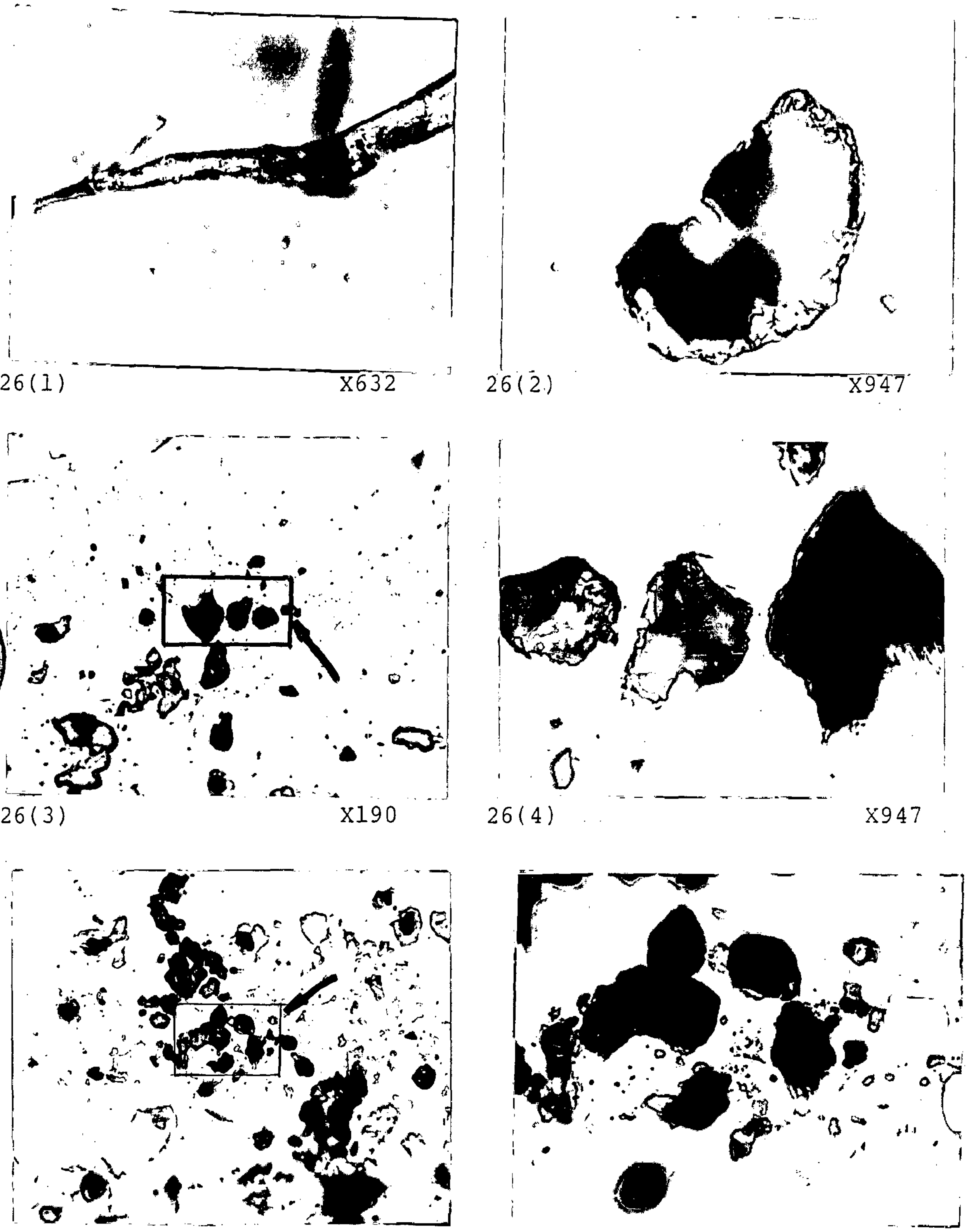
25(1) X 190

25(2) X 947

25(3) X 190

25(4) X 947

Fig.25. NMIs observed in Heat No.7 (IS:1875:71, foundry grade, class IV) at stage B (after refining) of the processing of heat, Transverse Section. Inclusions shown in Fig.25(1) & (2) are likely to be a slag inclusion of the type $CaO-Al_2O_3-SiO_2-FeO$. Inclusions shown in Fig.25(3) and (4) are likely be reaction products involving $FeO-MnO-Al_2O_3$.



26(1) X632

26(2) X947

26(3) X190

26(4) X947

26(5) X190

26(6) X632

Fig.26. Longitudinal Section of the heat detailed in Fig.25. Also, the reaction products are detailed in Fig.25.

(1) Fig.18 and 19:

Fig.18 shows photomicrographs of typical non-metallic inclusions taken at various locations of transverse section of specimen drawn from the ladle. On the left side of this plate the optical picture is taken at lower magnification(X190), which are again photographed at higher magnification also (X 947), inorder to reveal the morphological features of the inclusions. Another advantage of examining the inclusions at higher magnification is that the presence of various constituents with in the inclusion also become clearly apparent and visible. It can be seen from all the pictures at higher magnification that the inclusion is aggregate of several minerological constituents. This is apparent because the colour of different minerals present in the inclusion under ordinary light display different shades. It could be possible to identify different minerals present in the inclusion using polarized light according to the practices developed earlier [1]. This however was not attempted in the present work basically because it was planned to identify these different minerals and their approximate composition using the EPMA technique which is considered to be more accurate and sophisticated compared to the optical techniques referred to above. Since the inclusions shown in Fig.18 pertain to stage D (from the ladle), the NMI observed must be by and large deoxidation products. Apparently, these deoxidation products have not been able to float out of the liquid melt during the holding period of the ladle. On a closer examination of the pictures at higher magnification it can be seen that several smaller deoxidation products are trying to coagulate and form a larger aggregate. This tendency of coagulation where all the particles have yet not fully joined together are shown by an arrow in Fig.18(2). This tendency is also visible in Fig.18(6).

Optical pictures shown in Fig.19 which pertain to stage B, (after oxidation period) display interesting morphologies of non-metallic inclusions. Fig.19(1) for instance shows a chunky mass of non-metallic inclusion which appears to be a complex combination of minerals. On the other hand the pearl necklace morphology of non-metallic inclusion Fig.19(2) is quite typical and also reported by other workers[30]. As suggested by Golikov [30], this kind of inclusions are likely to be an exogenous inclusion of iron and manganese oxides in the process of solution in a molten steel. The kind of inclusion as shown in Fig.19(1) has been reported by a number of other workers [31,6] also. As suggested by J.C.C. Leach [31], this globular inclusion is a duplex calcium-aluminate in sheet form. A similar inclusion quoted by Kiessling [6] shows a glassy calcium-aluminate matrix with spinel.

(2) Fig.20:

Optical pictures shown in Fig.20 pertain to Heat at serial no.3 and stage B (after refining). Optical pictures shown at serial no.1 and 2 show an aggregate of tiny spherical non-metallic inclusions. It can be seen that it is just a cluster of NMI particles and that all the particles have not joined together properly (this is shown by an arrow). Other photomicrographs shown in Fig.20(3,4&5) display typical pearl necklace morphology of NMI particles. This aspect has been discussed in the previous section.

It should be mentioned that the above pearl necklace morphology was observed in the previous case also after the end of refining stage. On a closer examination of this morphology at higher magnification (Fig.20/4, X947) it was apparent that tiny globular particles have joined together in a linear fashion giving rise to the above typical shape of non-metallic inclusions. On one end, it appears that these globular particles have fused or merged together losing their individual identity (this location is marked by an arrow in Fig.20/4 and Fig.20/5).

(3) <u>Fig.21</u>:

Optical pictures shown in Fig.21 pertain to heat at serial no.4 and stage C (after reducing period). The inclusion shown in Fig.21(1) at lower magnification and 21(2) at higher magnification does not appear to be a deoxidation product as the morphology of inclusion shows sharp features. It is apparent from Fig.21(2) that the inclusion is a complex mineral. The original mineral must have undergone reaction with the surrounding steel, dissolved oxygen and deoxidizers added and as a result it must have undergone several changes in its original composition. This is apparent from different shades of colours displayed by the inclusion under ordinary light. The same appears to be true of the inclusion shown in Fig.21(3) and 21(4). The set of NMIs shown in Fig.21(5) and 21(6) show distinctly different morphological features. These are apparently the reaction products of deoxidation process. It is because the individual particles display almost globular morphology. The set of NMI particles shown in Fig.21(5) and marked by an arrow have been magnified and shown in Fig.21(6). From this picture it can be seen that the individual particles are globular in nature. Another particle marked by double arrows in Fig.21(5) shows a fused mass in which apparently several particles have coagulated together. These are all obvious reaction products of the process of deoxidation whenever many such particles would coagulate together and forma comparatively much larger particle, there would be fairly good chances of its floating to the surface and joining the slag. In this way, the steel can be rendered relatively free of non-metallic inclusions. But for this purpose, two conditions must be fulfilled. The first condition is that the deoxidation product muct be fluid at the steel making temperature so that they may coalesce together easily. The second condition is that the steel in the ladle must be given adequate holding time so that the inclusions may get time to float out.

(4) Fig.22, 23 and 24:

Optical pictures shown in Fig.22 and Fig.23 pertain to heat at serial no.5 and stage A (after melt out), transverse section. The particular inclusion or aggregate of inclusions which have been magnified and shown alongside in the micrograph are marked by an arrow in Fig.22. The common features observed in these photomicrographs are almost similar to the ones discussed in the previous paragraph (Fig.21). The NMI particles observed are all reaction products formed at the melt out stage. These particles are likely to be FeO inclusions as the oxygen potential of the bath at the end of meltout is fairly high. Some of these NMI particles show a usual tendency for coagulation. The NMI particles shown in

Fig.22(6) has undergone some chemical changes but basically this appears to be a FeO indigenous inclusion. Referring to the NMI particles shown in Fig.23, it can be seen that all the particles are the result of chemical reactions with in the melt. One such large FeO inclusion can be seen in Fig.23(3), marked by an arrow at Fig.23(4). The inclusions shown in Fig.23(2) are the result of coagulation of smaller FeO reaction products in a longitudinal fashion. In this case, almost all the smaller particles have fused together and formed an elongated inclusion.

Some comparatively larger inclusions observed in the longitudinal section of the above grade of steel (Heat at serial no.5) are shown in Fig.24. From Fig.24(1) and 24(3), it can be seen that the inclusion photographed is much larger compared to other smaller inclusions present in the matrix. It is probable that the above inclusions are primarily FeO/MnO reaction products. It appears that many smaller FeO/MnO reaction products in the form of tiny globules have coalesce together to give rise to the shape shown in Fig.24(3) and 24(4). It may be possible that the inclusion shown in Fig.21(1&2) was originally an exogenous inclusion which was transformed later during the course of steel making process. On a closer examination it can be seen that the outer boundary of this inclusion is very sharp while the inner portion of this piece is being eaten up by the surrounding material. Like this particularly the interior portion of this inclusion can be seen to be undergoing transformation through chemical reaction.

(5) Fig.25 and 26:

Optical pictures shown in Fig.25 and 26 pertain to heat at serial no.7 and stage B (after refining). Fig.25 pertains to transverse section while Fig.26 pertains to longitudinal section of the steel specimen.

Micrographs shown in Fig.25(1 to 4) appear to be the result of reactions during the process of refining operation. The area enclosed by marked frame in Fig.25(3) has been magnified and shown in Fig.25(4). The morphology of inclusion observed in the two cases are different. The inclusions shown in Fig.25(3&4) display globular morphology while inclusion shown in Fig.25(2) displays quite a different morphology. As suggested by M. Ichinoe, H. Mori, H. Kajioka, and I. Kokubo [32] these inclusions could contain mainly Al_2O_3, CaO and some SiO_2 and FeO. The origin of these inclusions is thought to be due to intimate contact of slag with the liquid metal during the refining operation.

The kind of inclusions observed in the longitudinal section of the same heat are shown in Fig.26(1 to 6). It can be seen that a variety of morphologies and small and big inclusions both are found in this case. It is apparent from Fig.26(2) that the original inclusion is in the process of dissolution and the interior portion of this inclusion has already been eaten up considerably. Other morphologies shown in Fig.26(3&5), the enclosed frames of which have been magnified and shown in the adjoining pictures, display usual morphologies of NMIs and their tendency to coagulate whenever possible. On a closer examination of Fig.26(4), it can be seen that some inclusions are in an altered state. At few locations such as shown in Fig.26(5), the density of occurrence of inclusions is fairly high compared to other cases. This can be entirely attributed to the specific steel making practice followed in a given plant. In any section of the finished steel when the order of density of inclusions is as high as shown in Fig.26(5), it would be expected to deteriorate the quality of steel seriously. It is because these NMIs represent a serious amount of discontinuity in the cast structure.

It should be mentioned that most of the non-metallic inclusions present in all the eight different grades of steel examined in the present work fall in one or the other category of inclusions discussed in the above paragraphs and pictures (Fig.18 to 26). A detailed examination of five different Heats discussed above was therefore considered adequate to cover all the eight grades studied in the present work.

5.3 Quantitative Metallography:

Results pertaining to this study are summarised in Table 5.1. In this study, the occurrence of NMIs in different steel specimens drawn at various stages of the processing of individual heats have been quantified in terms of number of NMIs.mm^{-3}. This data has been determined in both longitudinal as well as transverse section of individual specimens. In effect, this data shows volume fraction (V_f) of non-metallic inclusions occurring in different specimens. In all eight different heats and four different stages of the processing of individual heats have been covered by this study. The objective of this study was to ascertain as to how the volume fraction (V_f) of NMIs varies in different specimens and as to how the processing details influence this parameter. The processing details of individual heats are shown in Tables 3.1 to 3.8. It can also be seen from Table 5.1 that all the eight heats investigated in the present work are of different quality and therefore have different targeted compositions. For this reason, the processing details are also slightly different from each other.

From the present observation certain general inferences can be drawn:

(1) The number of non-metallic inclusions observed at the melt out stage are usually on the higher side. Upon refining (carbon-boil stage) the amount of NMIs would tend to decrease. It is because during carbon boil, the inclusions would tend to join the slag phase.

(2) Upon refining the non-metallic inclusions would tend to decrease further because they will get adequate time to

Table - 5.1

Quantitative Metallography Results pertaining to the No. of NMI/mm^3 in different grades of steels at different stages of processing of individual heats.

Sl. No.	Steel Grade No.	Stage when specimen was drawn	Non-Metallic Inclusions			
			Longitudinal Section		Transverse Section	
			No.of NMI.mm^{-3}	Standard deviation	No.of NMI.mm^{-3}	Standard deviation
1	2	3	4	5	6	7
1.	EN-354 (FQ)	A	4650	4.63	1799	1.23
		B	8403	8.02	3893	5.05
		C	3893	5.01	3893	3.75
		D**	2430	3.03	1799	1.66
2.	EN-31 (FQ)	A	4650	4.88	1283	1.59
		B	3893	3.25	1283	1.85
		C	2430	2.90	3130	4.14
		D	2430	2.87	2430	3.70
3.	IS:2644 (FOU)	A	3130	4.24	2430	4.29
		B	2430	4.99	1799	2.20
		C	1283	1.73	1283	1.14
		D	2430	2.05	1283	2.38
4.	EN:24 (FQ)	A	3130	2.61	1283	6.33
		B	4650	5.69	9489	4.14
		C**	2430	1.61	1283	0.96
		D	1283	3.52	1283	4.59
5.	IS:1030 (FOU)	A**	802	1.85	802	1.46
		B	5529	4.82	7449	4.63
		C	3130	3.21	2430	5.50
		D	1799	1.79	3130	1.07
6.	EN-42 (FQ)	A	1283	1.36	1799	1.86
		B	5529	5.43	6462	4.67
		C	1799	2.49	1799	1.56
		D	3130	3.86	1283	4.21
7.	Class-IV IS:1875/ 71(FOU)	A	7448	34.80	2430	2.57
		B**	4650	8.73	7448	3.39
		C	3130	2.71	3893	3.70
		D	802	3.72	1799	2.32
8.	42CrMo4 ≃ EN-19 (FOU)	A	1283	1.61	1283	1.12
		B	4650	4.63	1799	1.23
		C	4650	9.04	2430	2.53
		D	802	1.47	2430	3.38

Contd/-

Remark*: A = After melt out
B = After oxidation
C = After reducing period
D = After tapping (from ladle)
FQ = Forging quality
FOU = Foundry grade

** - Specimens also examined by the JEOL superprobe micro-analyser Model JXA 8600M.

float out and join the slag.

(3) In some instances where further additions are not made in the ladle, the non-metallic inclusions would have a tendency to decrease. But on the other hand if some additions are made the NMIs in the finished steel may show an upward trend in their occurrence.

(4) The volume fraction (V_f) of non-metallic inclusions observed in longitudinal sections of different grades is generally on the higher side compared to the volume fraction of non-metallic inclusions in the transverse section.

Besides the above general conclusions, the results of present study don't lead to any specific trend or conclusion. It is primarily because as many as eight different grades are involved in the study in which the alloy additions and processing details are slightly different from each other. Perhaps a more rewarding and meaningful strategy would be to select only one or two grades of steels and examine their subsequent eight or ten heats for the occurrence of non-metallic inclusions. Using this strategy, it would then be possible to improve the cleanliness ratings of finished steels.

During quantitative metallographic observations it was found that non-metallic inclusions show a tendency for preferential segregation in specific locations. In the present study it was observed that inclusions show a tendency for segregation along the corners and the edges of the steel specimen. In the rest of the cross-section upto the centre the distribution of inclusions was found otherwise normal. It is for this reason that the standard deviation (σ) found in few cases is exceptionally high. This tendency of segregation of inclusions of different kinds has been observed by other workers also [34]. For example oxide, sulphide, silicate and other kinds of inclusions show preferential locations for their segregation in the cast steel. Compared to smaller size test samples, this tendency would be more predominent in larger ingots. This tendency of segregation of inclusions can be attributed to (a) The solidification pattern of the ingot and (b) The stage when the non-metallic inclusion is formed or precipitated from the liquid steel.

It can be seen from the results presented in Table 5.1 that in some cases, for instance in Heat No.3 and 6, the non-metallic inclusions tend to increase from stage C to stage D which is in fact undesirable. It might be because adequate time might not have been provided for the NMIs to float out in the ladle. Usually otherwise, if adequate time is provided before teeming, the non-metallic inclusions entrained in the liquid metal would be able to float out and join the top scum. In a normal case, the volume fraction of NMIs would drop down considerably as can be seen in Heat No.7 and 8. An examination of the data in Table 5.1 ultimately reveals that standard steel making practices have not been faithfully adhered to by the melters of M/S Uttar Pradesh Steels. It need not be over emphasized that a strict adherence to standard steel making practices is very vital in the production of clean steels.

5.4 EPMA Examination of Non-metallic Inclusions:

5.4.1 General:

Results pertaining to the EPMA examination of four different specimens pertaining to Heat No.1,4,5 and 7 are presented in this section. These specimens were drawn at different stages of steel making practice. For example the specimen of Heat No.1 pertains to stage D (from the ladle). Similarly specimen of Heat No.4 was drawn corresponding to stage C (after reducing stage). The specimens from Heat No.5 and 7 were drawn at stage A (after melt out) and stage B (after refining) respectively. From a given specimen a number of non-metallic inclusions occurring at different locations were examined by the EPMA. The NMIs at that location was also photographed using the SEM facility attached with the JEOL EPMA instrument. Simultaneously the microanalysis of this NMI was also carried out and recorded in the form of histograms. The facility of microcomputer and print out was attached with the JEOL EPMA instrument. Analysis results recorded in the present section pertain to only spot or point analysis. The histograms therefore present a comparative data of the amount of different elements present in the inclusion. The objective of spot analysis was not to analyse or identify the presence of different phases or minerals in the inclusions. The presence of different elements to varying degrees in the histograms nevertheless indicates what different minerals or a combination of minerals are likely to be present in the inclusion. The kinds of inclusions present in the four typical specimens mentioned above will generally cover the usual kind of inclusions present in all the eight grades of steels examined in the present work.

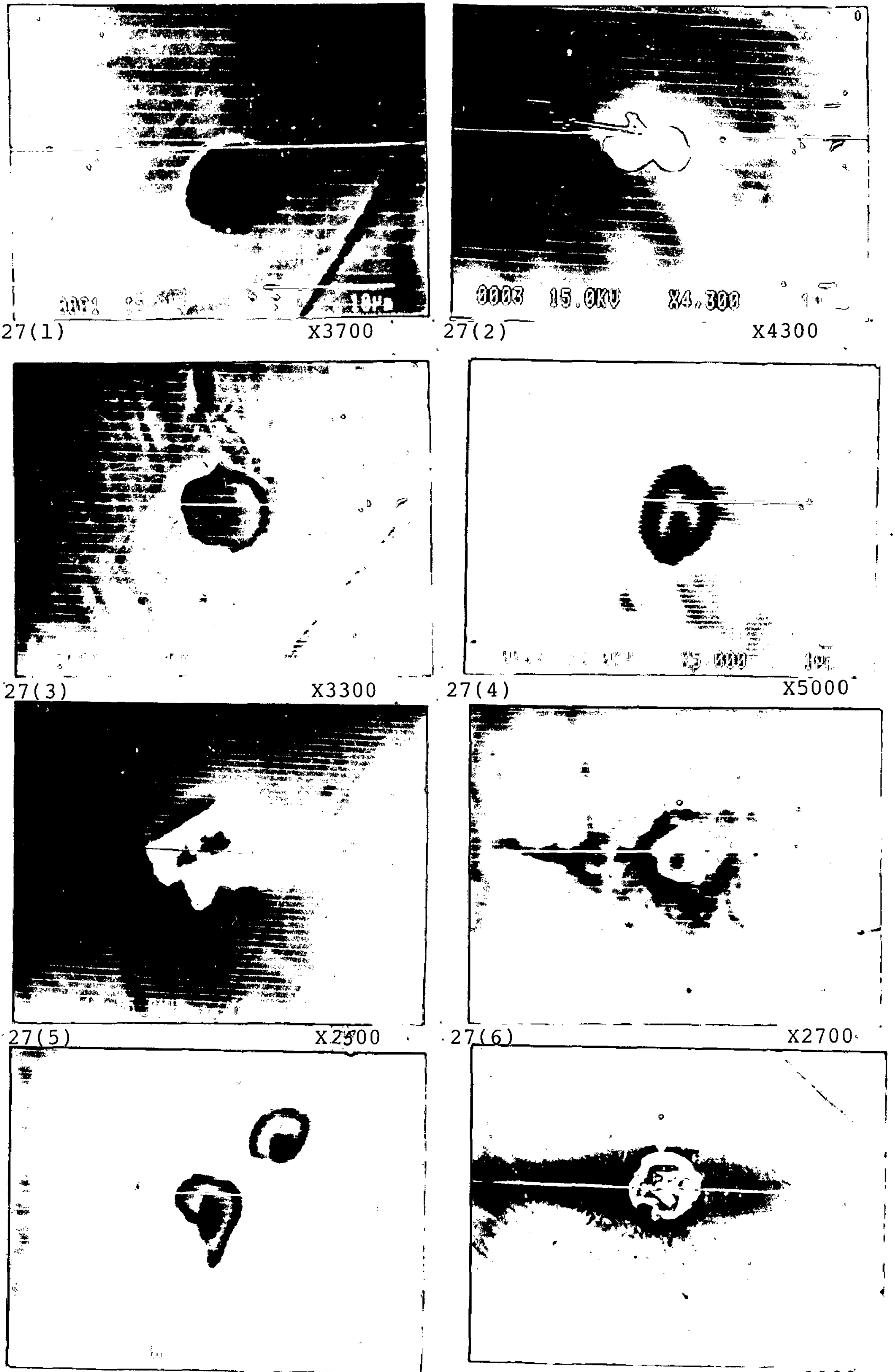
5.4.2 Heat No.1, Stage D (From the Ladle):

Inclusions examined in this case are shown in Fig.27. These are all the SEM pictures taken by the JEOL EPMA. Corresponding histograms showing spot analysis results are given in Figs.28 to 36.

Fig.27/1 shows a globular inclusion the analysis of which is recorded in Fig.28. This SEM picture was taken at X3700 and the marker recording shows that the size of inclusion observed is about 6 µm in diameter. The analysis of this inclusion recorded in Fig.28 shows that it is a complex inclusion containing sulphides of aluminium, calcium, manganese, iron and titanium. The presence of Al, Ca and Mn, must be from the deoxidizers employed and the presence of Ti could be attributed to small amount of titanium present in the charge.

The average size of inclusion observed in the SEM picture shown in Fig.27/2 is approximately 5 µm. As it is evident from the spot analysis results shown in Fig.29, the inclusion contains sulphides of Fe and Zn and some amount of SiO_2. It is strange as to how Zn has come in the analysis of this particular inclusion. In fact at this stage it is difficult to ascertain the precise source of this element in the inclusion. Analysis of another inclusion shown in Fig.30 indicates that it is a silicate of iron and manganese containing some amount of Al_2O_3 and traces of calcium. The composition of this inclusion therefore should belong to Fe-Mn-Si-Al-O system.

An examination of the inclusion shown in SEM picture 27/3 indicates that it is again a globular inclusion of approx.6-7 µm in diameter. Results of spot analysis of this inclusion shown in Fig.31



27(1) X3700

27(2) X4300

27(3) X3300

27(4) X5000

27(5) X2500

27(6) X2700

27(7) X3300

27(8) X1100

Fig.27. SEM pictures of inclusions taken by JEOL superprobe microanalyser. Heat No.1, Stage D, (from the ladle).

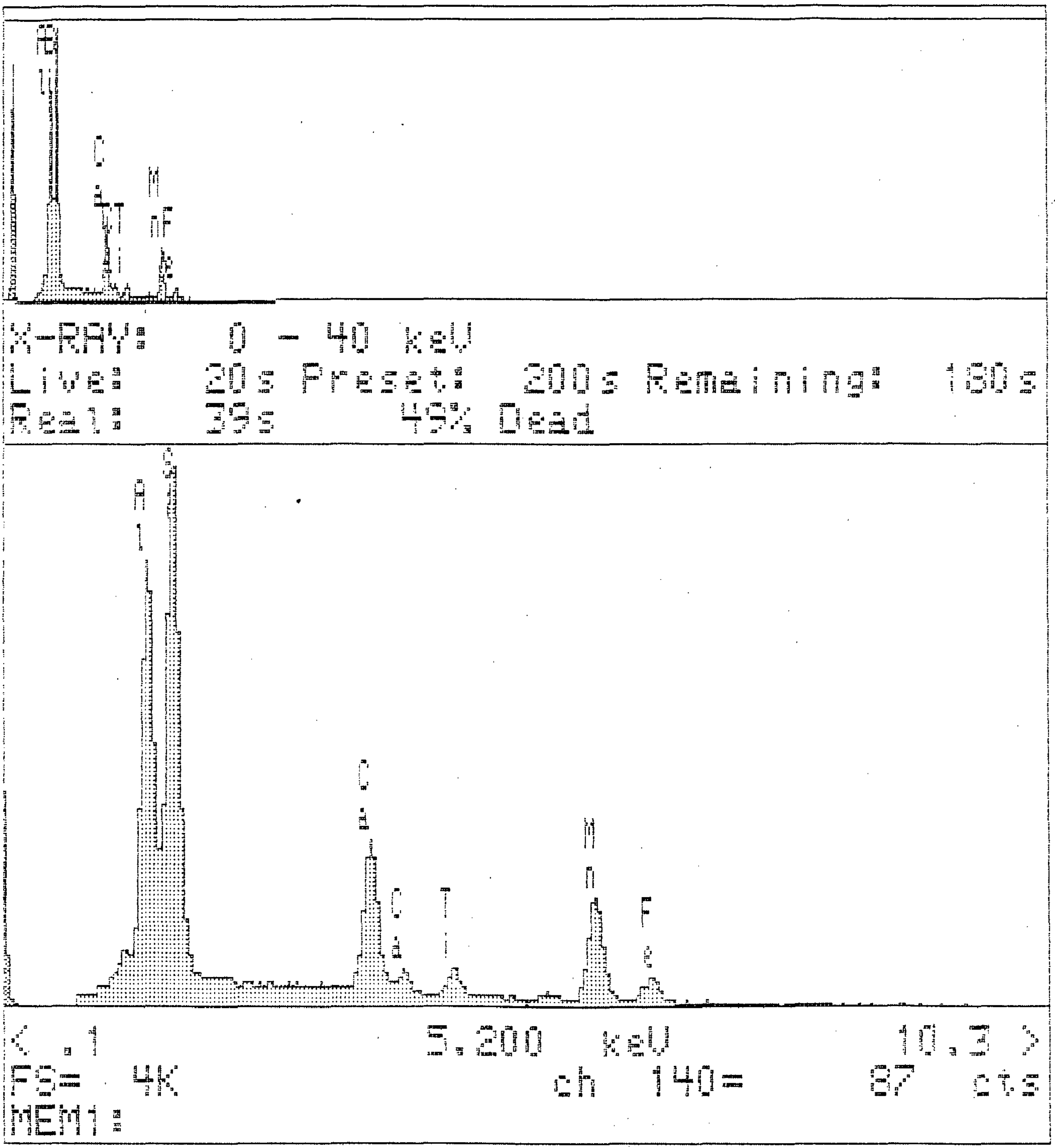
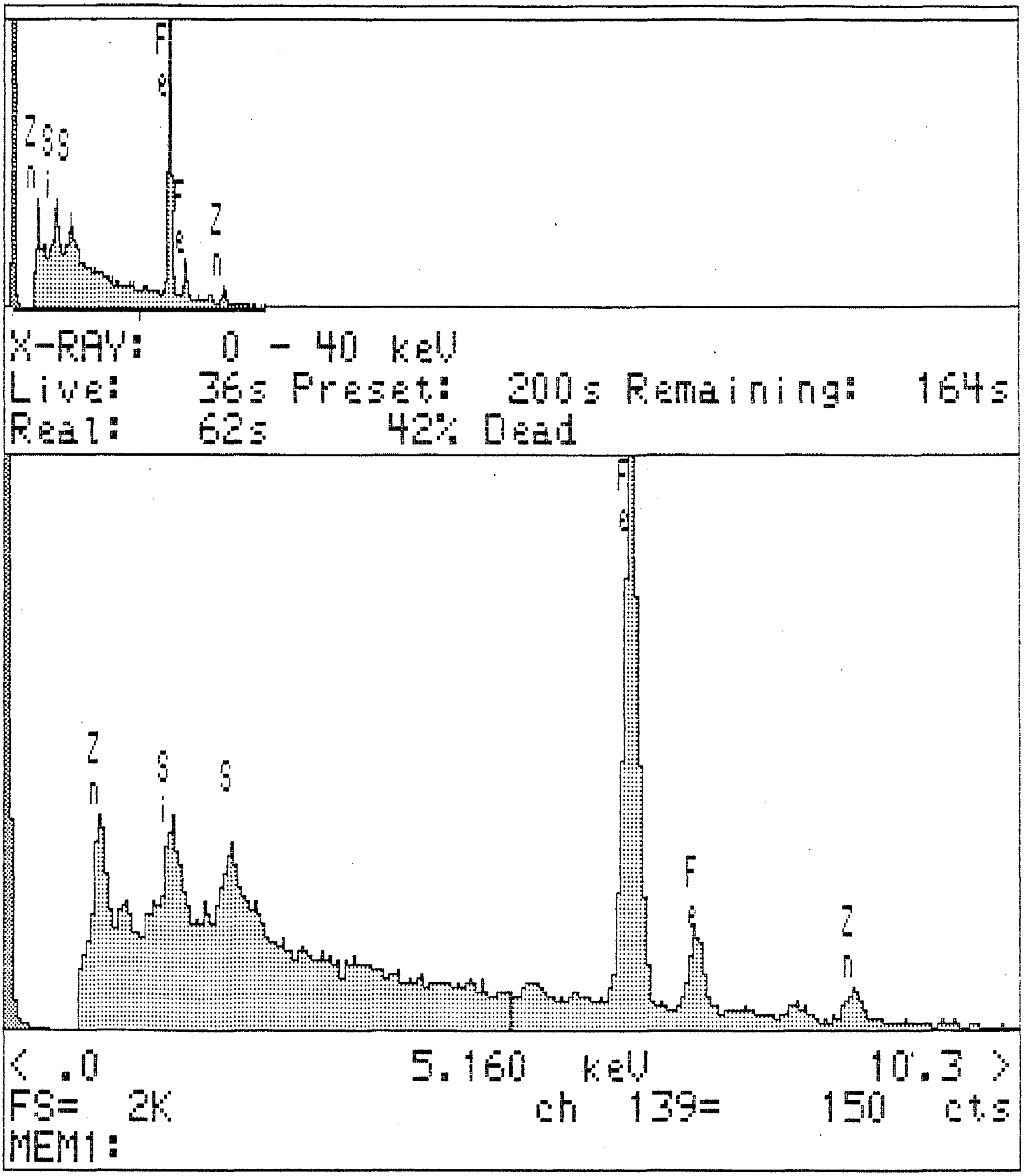


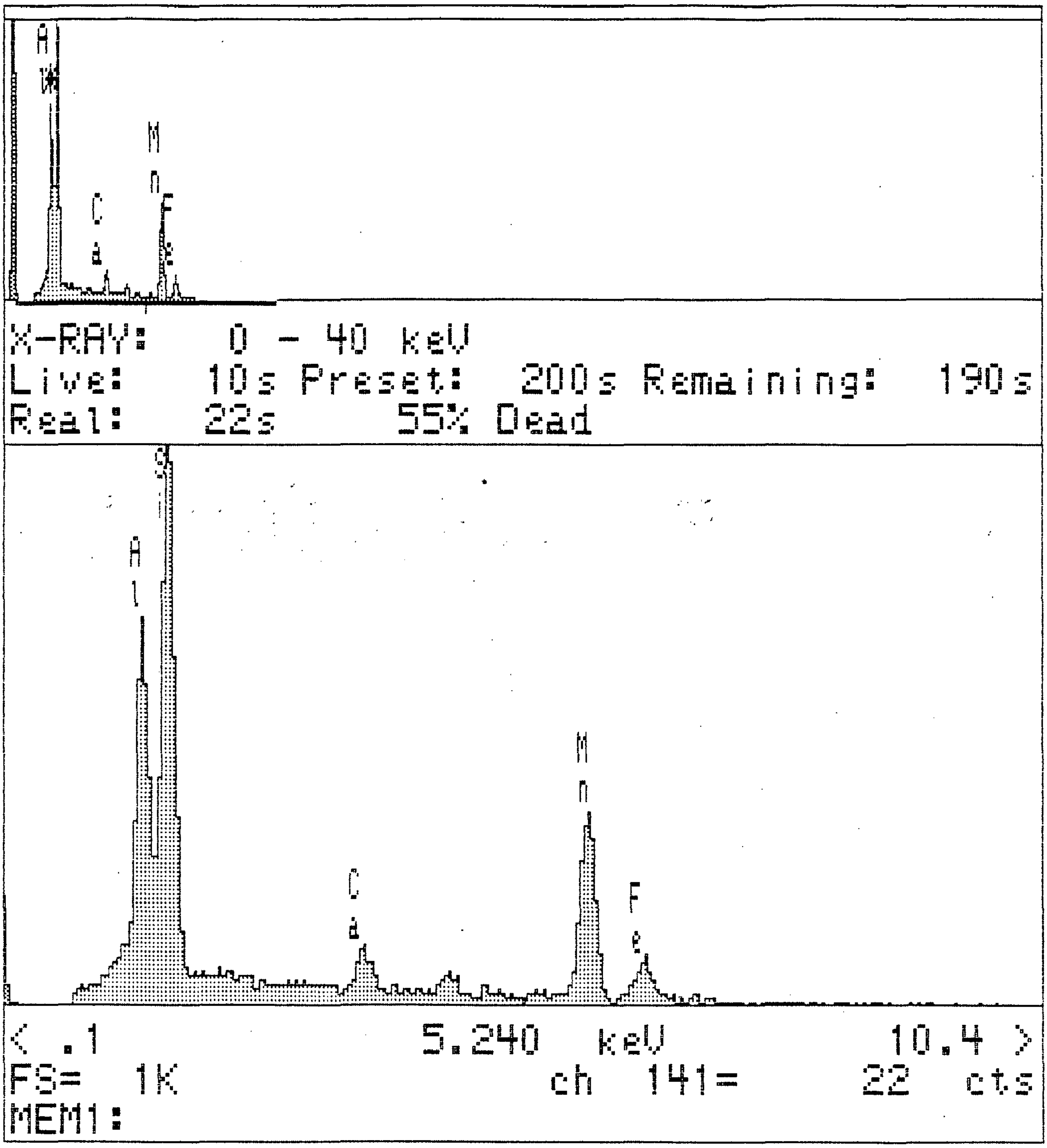
Fig.28. Spot/Point analysis of inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle). Using JEOL superprobe Micro analyser model JXA-8600M.



```
X-RAY:    0 - 40 keV
Live:    36s Preset:   200s Remaining:   164s
Real:    62s      42% Dead
```

```
< .0               5.160  keV          10.3 >
FS=  2K                 ch  139=     150  cts
MEM1:
```

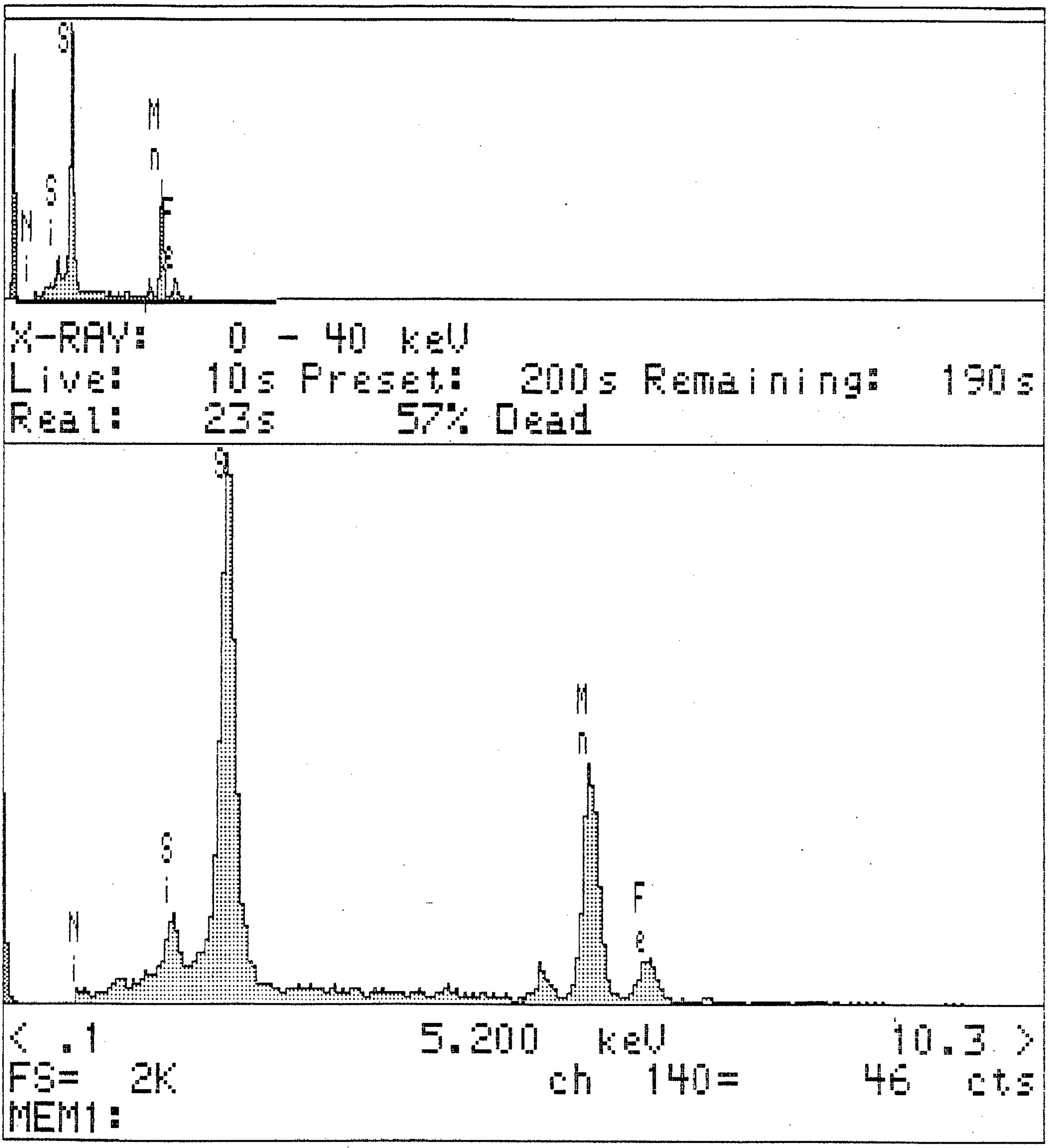
Fig.29. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle).



```
X-RAY:    0 - 40 keV
Live:    10s Preset:  200s Remaining:  190s
Real:    22s      55% Dead
```

```
< .1                 5.240  keV           10.4 >
FS=  1K                    ch  141=       22  cts
MEM1:
```

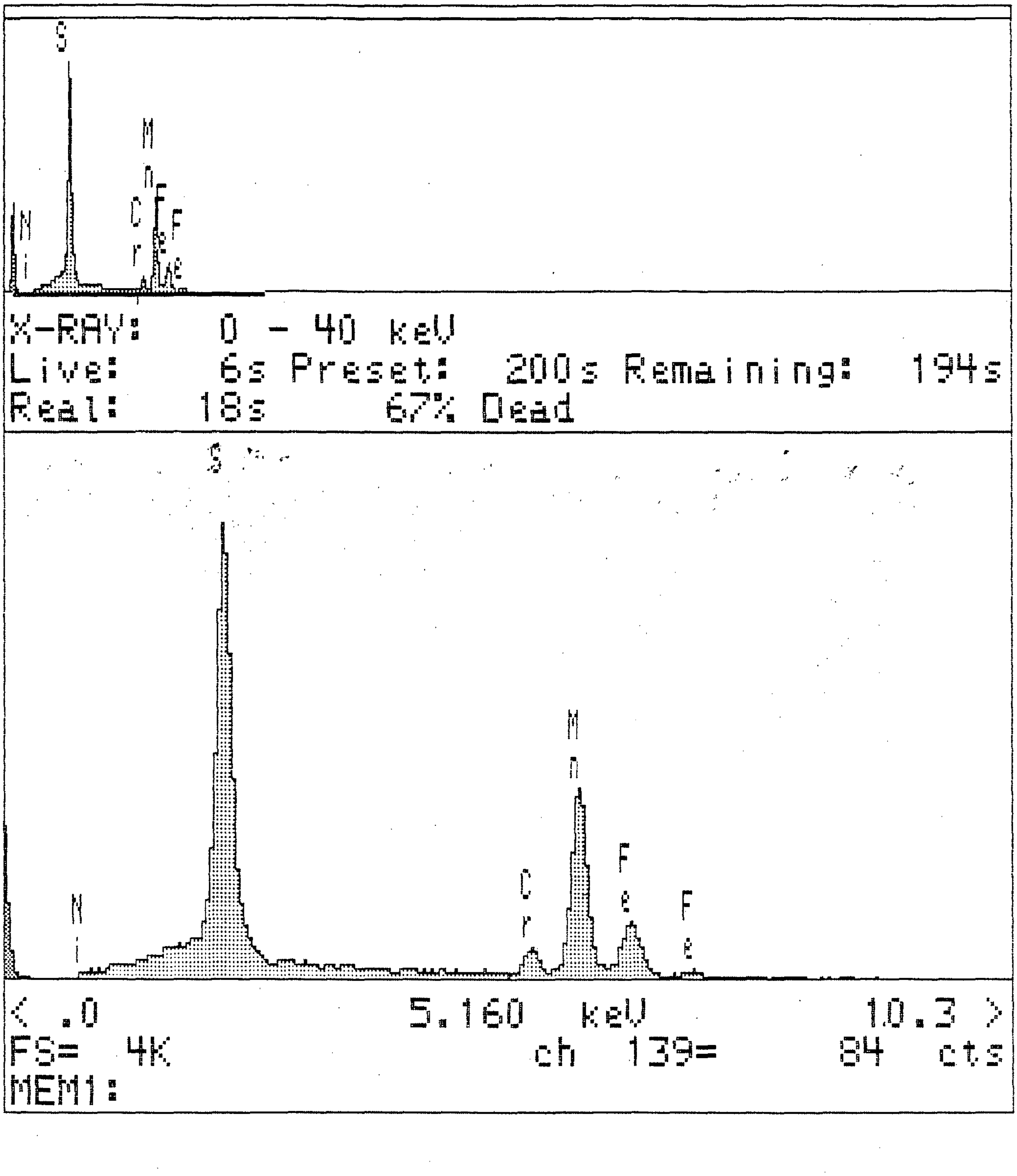
Fig.30. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle).



```
X-RAY:    0 - 40 keV
Live:    10s Preset:   200s Remaining:   190s
Real:    23s       57% Dead
```

```
< .1                5.200   keV             10.3 >
FS=  2K                  ch  140=        46  cts
MEM1:
```

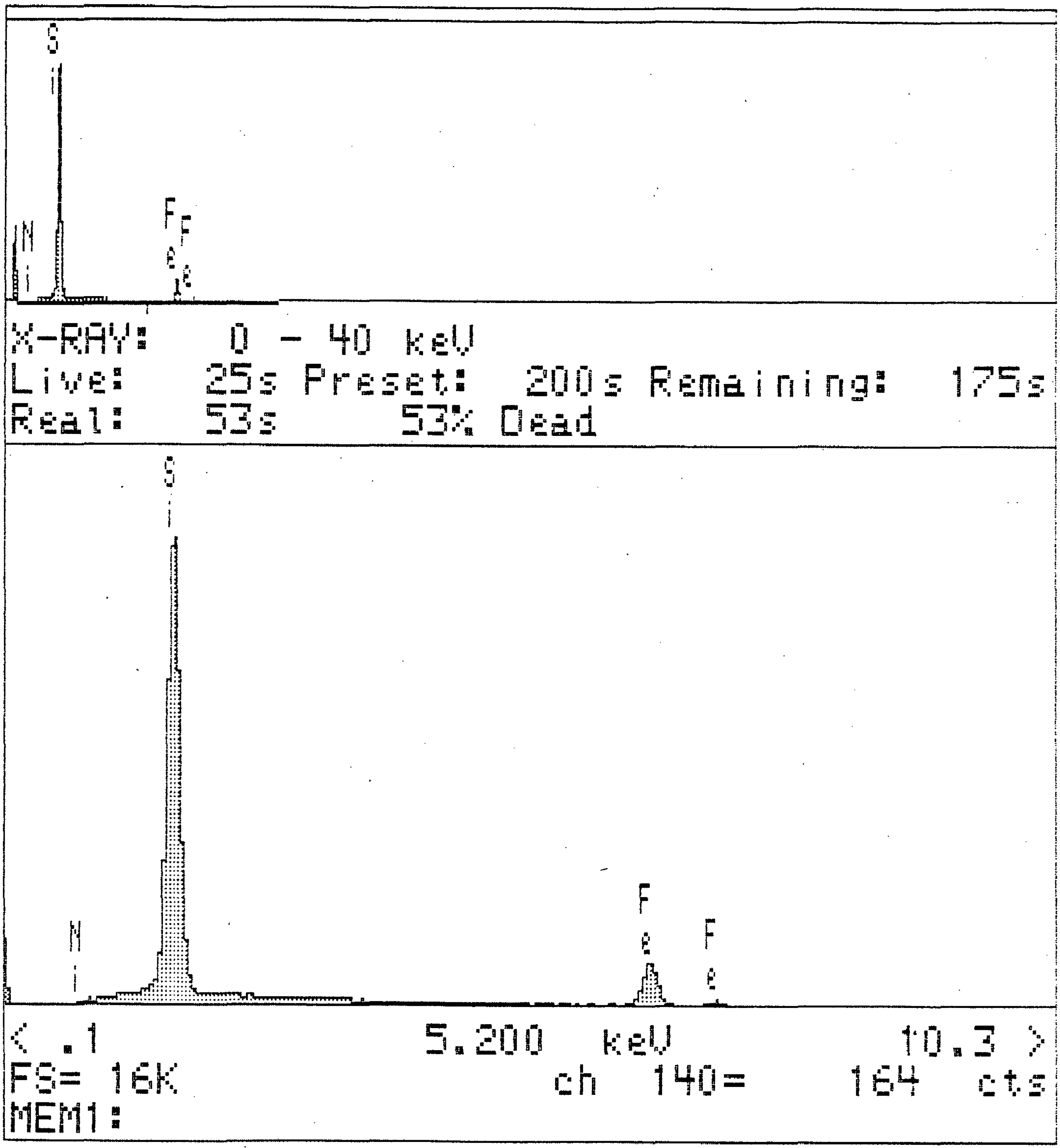
Fig.31. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle).



```
X-RAY:    0 - 40 keV
Live:     6s Preset:  200s Remaining:  194s
Real:    18s      67% Dead
```

```
< .0              5.160  keV           10.3 >
FS= 4K                 ch 139=       84  cts
MEM1:
```

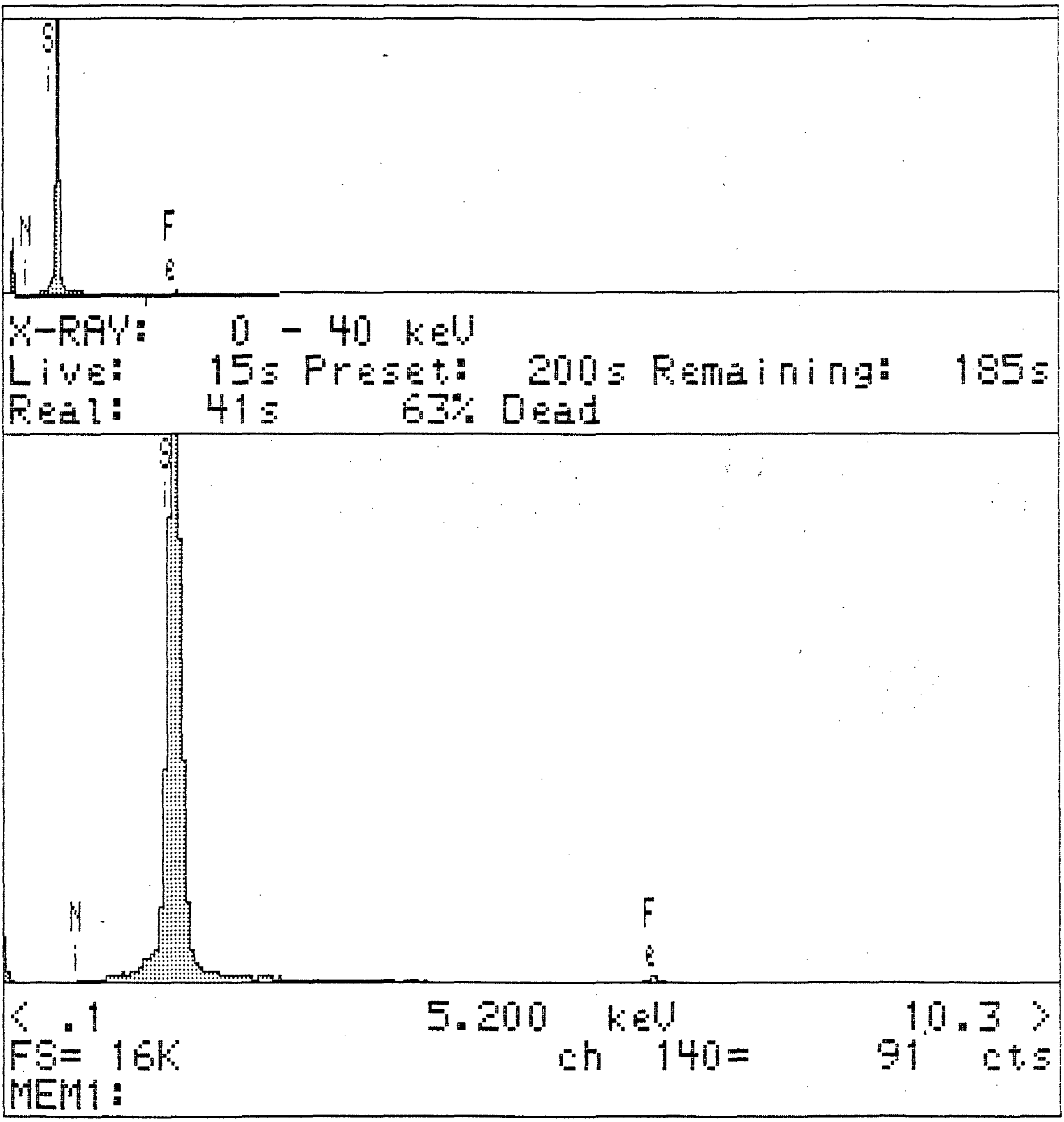
Fig.32. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle).



```
X-RAY:    0 - 40 keV
Live:    25s Preset:  200s Remaining:  175s
Real:    53s      53% Dead
```

```
< .1              5.200   keV          10.3 >
FS= 16K                ch  140=     164   cts
MEM1:
```

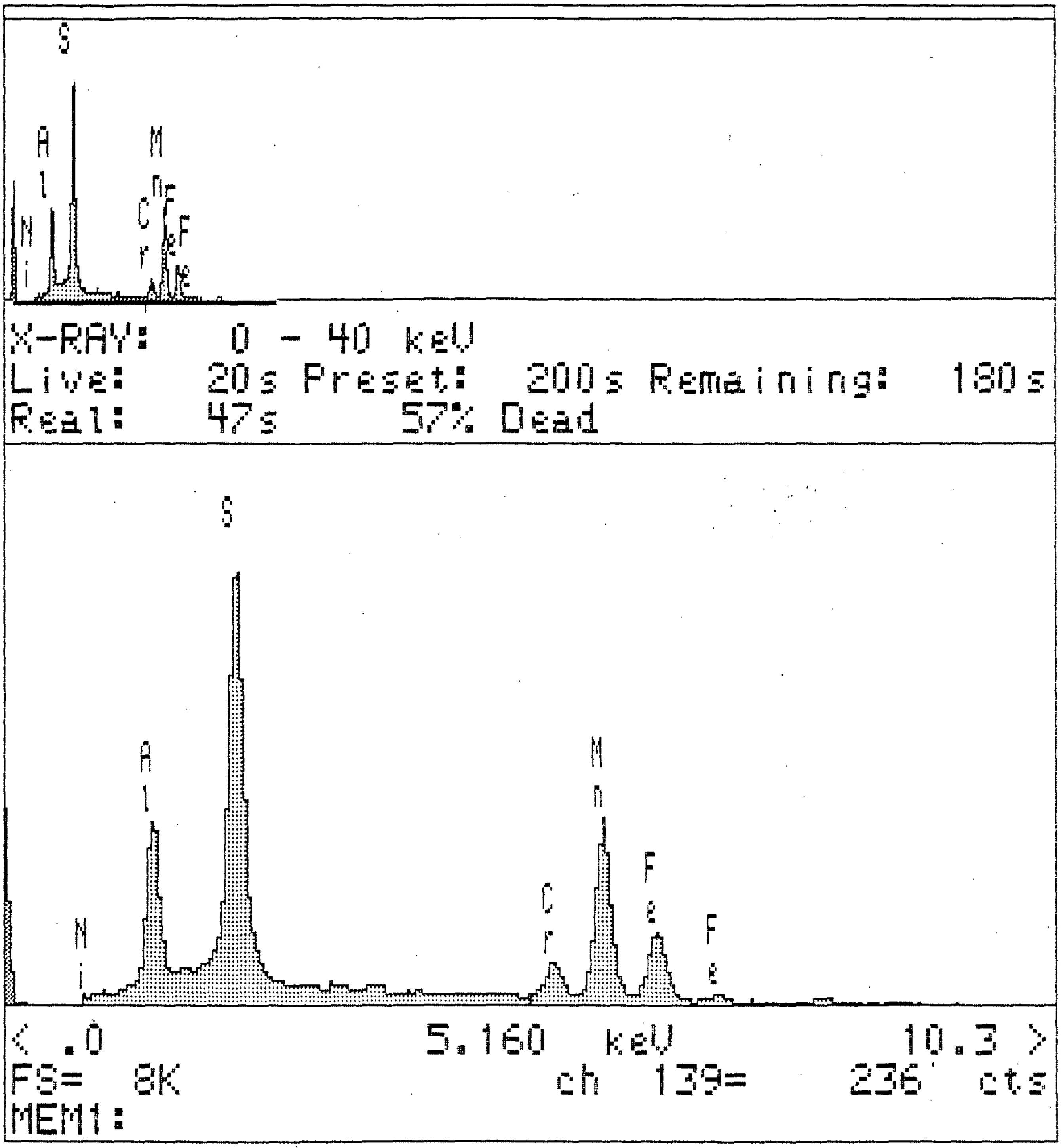
Fig.33. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle).



```
X-RAY:    0 - 40 keV
Live:    15s Preset:   200s Remaining:   185s
Real:    41s      63% Dead
```

```
< .1              5.200  keV          10.3 >
FS= 16K                ch  140=       91  cts
MEM1:
```

Fig.34. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle).



```
X-RAY:    0 - 40 keV
Live:    20s Preset:   200s Remaining:   180s
Real:    47s      57% Dead
```

```
< .0              5.160  keV            10.3 >
FS=  8K                ch  139=      236  cts
MEM1:
```

Fig.35. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle).

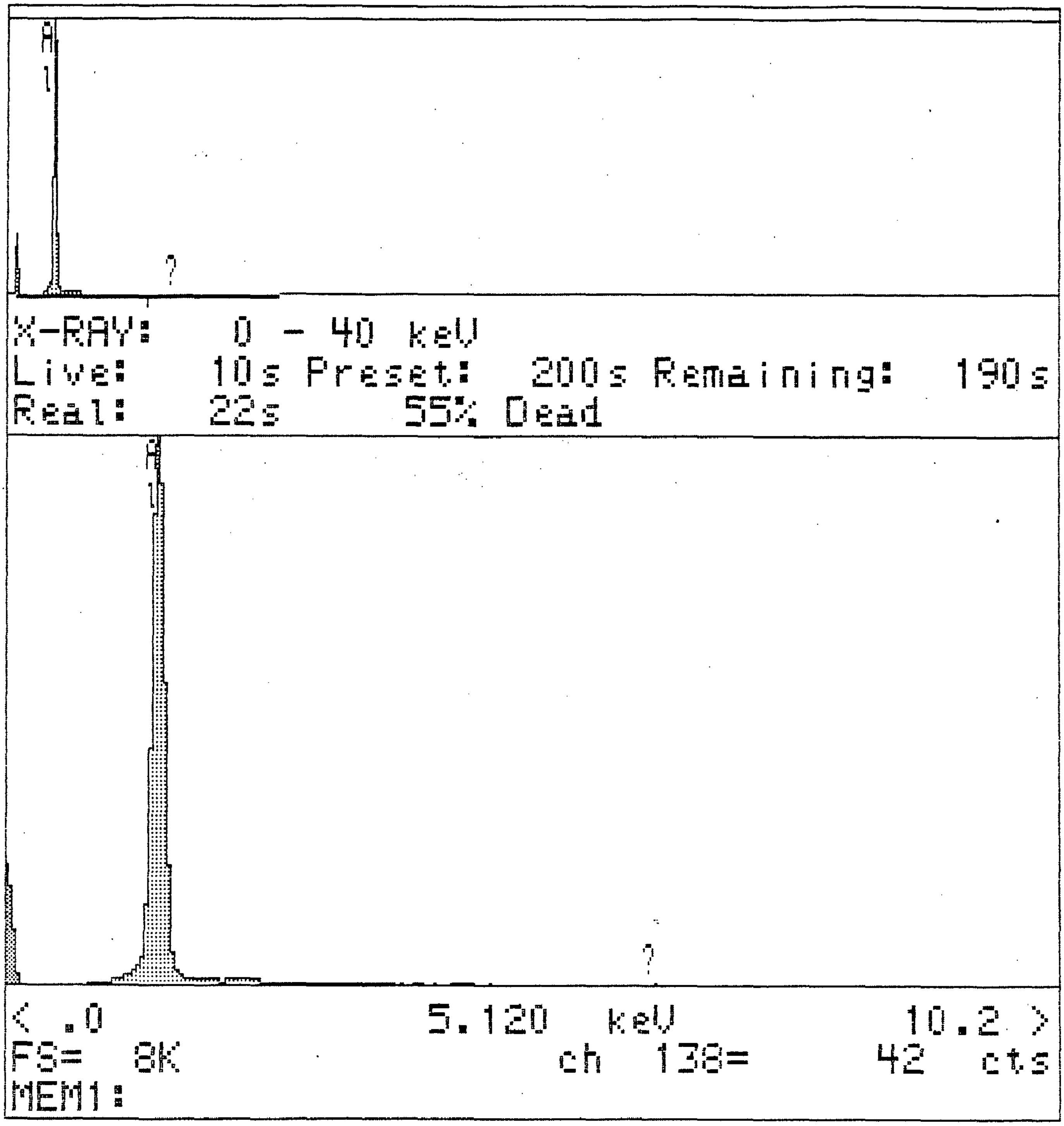


Fig.36. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.1 at stage D. (From the ladle).

indicate that it is also a sulphide of Fe and Mn containing very small amount of SiO_2 also. These are all the products of deoxidation and therefore indigenous in nature. The shape of this inclusion is something ideal and what is aimed at during practical steel making. In case such globules are able to coalesce and form larger droplets of the size of approx. 20 to 40 µm, they may even be able to float out of the liquid steel and join the top scum.

The composition of next inclusion shown in Fig.27/4 also appears to be a sulphide of Mn and Fe containing very small traces of Cr. The size of this inclusion can be seen to be approx. 5 µm. The results of spot analysis of this inclusion by the EPMA are shown in Fig.32. It can be seen that sulphur when present in combination with Fe and Mn forms globular inclusions which is indeed most desirable.

The shape of another inclusion examined is shown in Fig.27/5 and its microanalysis is reported in Fig.33. It is apparent from the microanalysis and the shape of inclusion that it is an exogenous inclusion of $FeO-SiO_2$ nature. Such inclusions can be formed as a result of the erosion of spout and ladle refractories. The inclusion appears to be basically a silicate refractory piece which has been partially altered as a result of the reaction of this refractory piece with the liquid steel. The inclusion shown in Fig.27/6 displays similar features upon microanalysis, the results of which are given in Fig.34. Since the size of inclusions observed in Fig.27/5 and 27/6 are nearly 12 µm and 8 um respectively they are most likely erosion products of the refractories.

The inclusion shown in Fig.27/7 appears to be a complex one. The microanalysis of this inclusion is reported in Fig.35, which indicates that it is a sulphide of iron, manganese and chromium plus some oxides of aluminium. The shape of this inclusion again appears to be globular but it appears it contains several minerals with in the inclusion. This inclusion appears to be more complex than what was observed in Fig.27/1, 3 and 4.

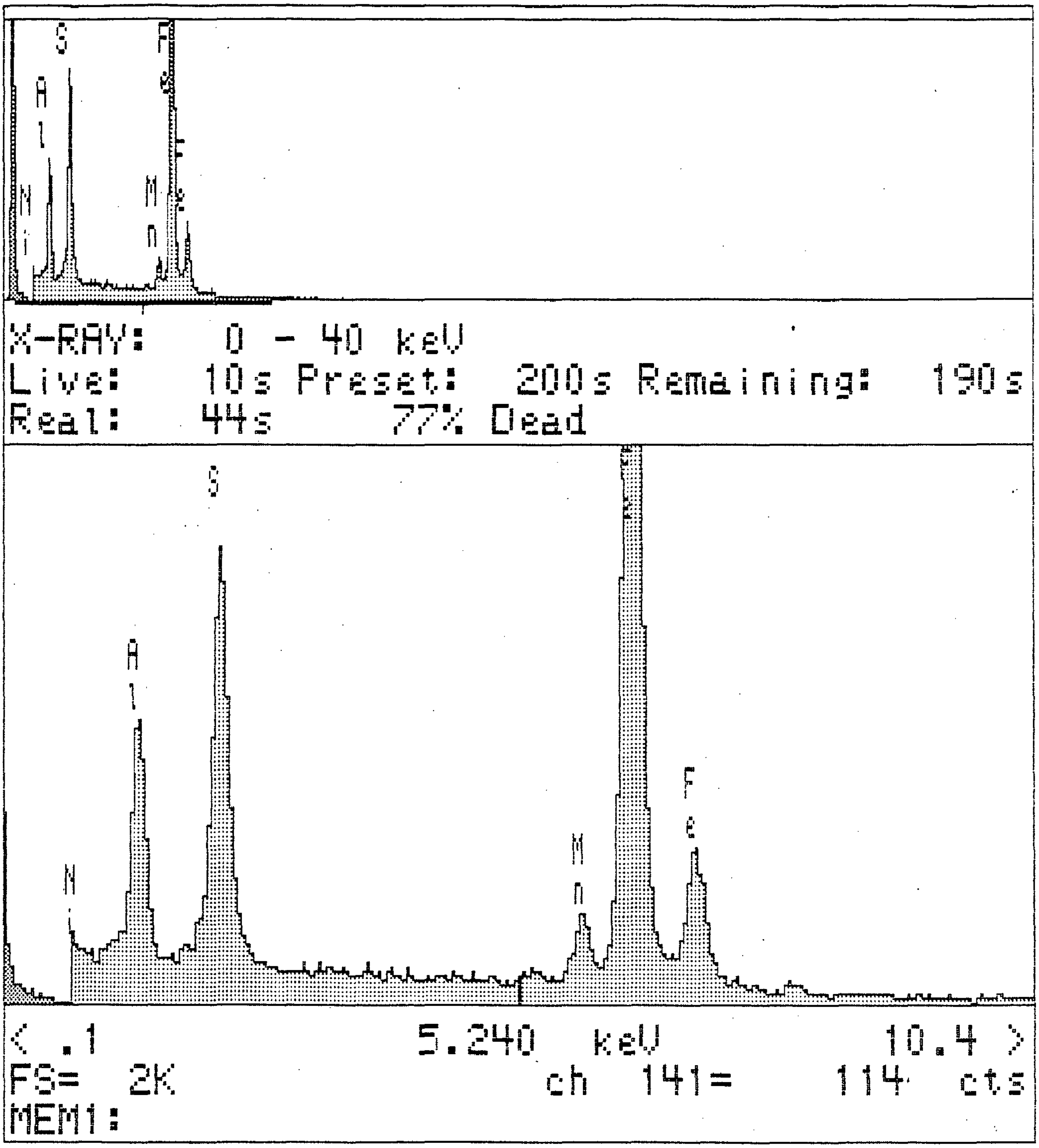
The last inclusion observed in this specimen is shown in Fig.27/8. The microanalysis of this inclusion recorded in Fig.36 shows that it is only Al_2O_3. This inclusion must have been formed as a result of the deoxidation of the liquid steel by aluminium or Al-shots. This inclusion through globular appears crystalline in its morphology. The average size of this inclusion can be seen to be about 20 μm.

5.4.3 Heat No.4, Stage C (After Reducing Period):

Results pertaining to this particular heat are recorded in Fig.37 to 40. In the same manner a number of locations of this specimen were investigated by the EPMA for the microanalysis of the inclusion. Since this particular specimen belongs to stage C, the bath was held under reducing slag for fairly long time. During the reducing period a number of alloying elements e.g. Fe-Si, Fe-Cr, Fe-Mo, Fe-Ni and some Fe-Al were introduced in the bath. The exact amount of individual alloy additions can be seen in Table 3.4. At the same time the steel bath during this period is quiet as the carbon-boil was terminated and bath killed with about 15 kg. Fe-Al before commencing the reducing period. Also as a matter of routine practice the bath is covered throughout by a strong reducing slag. As such any inclusions formed during this stage would be expected to contain mainly Mn,Fe,S,Al,Si and Ca. This is what is precisely observed in the present case.

The probe analysis results presented in Fig.37 indicate that the inclusions are basically sulphides of Iron and Manganese containing some amount of Al_2O_3. These sulphide inclusions are present in the steel basically because some sulphur is always present in the finished steel. It can be seen from the data recorded in Table 3.5 that though the starting sulphur was approx. 0.050 in the opening chemistry but it was reduced down to 0.035 and corresponding to this specimen the Mn in this specimen was 0.47%. It is for this reason that the sulphide inclusions are a combination of Fe and Mn sulphides. There is some Al_2O_3 in the inclusion because the bath was killed in the furnace using about 15 kg. Fe-Al. Since affinity of Al for dissolved oxygen is extremely high the dissolved oxygen of the bath will be engaged by Al immediately. Part of the Al_2O_3 inclusion may be in a position to coalesce and float out of the bath and join the slag. But part of the Al_2O_3 inclusions may still stay in the bath. The results of inclusion analysis shown in Fig.39 indicates that inclusion has nearly the same analysis as discussed above. The only thing is that the Al_2O_3 content of this inclusion is slightly on the higher side compared to the previous one (Fig.37).

The analysis of inclusions recorded in Fig.38 and 40 appears to be a complex one. Besides Fe, the inclusion contains Ca and Si (Fig.38). This inclusion therefore appears to be belonging to the system $FeO-CaO-SiO_2$. This inclusion therefore appears to be a slag



```
X-RAY:     0 - 40 keV
Live:    10s Preset:   200s Remaining:   190s
Real:    44s      77% Dead
```

```
< .1                5.240  keV          10.4 >
FS=  2K                ch  141=      114  cts
MEM1:
```

Fig.37. Spot/Point analysis of inclusion observed in the steel specimen drawn from heat No.4 at stage C. (After reducing period). Using JEOL superprobe Micro-analyser Model JXA-8600M.

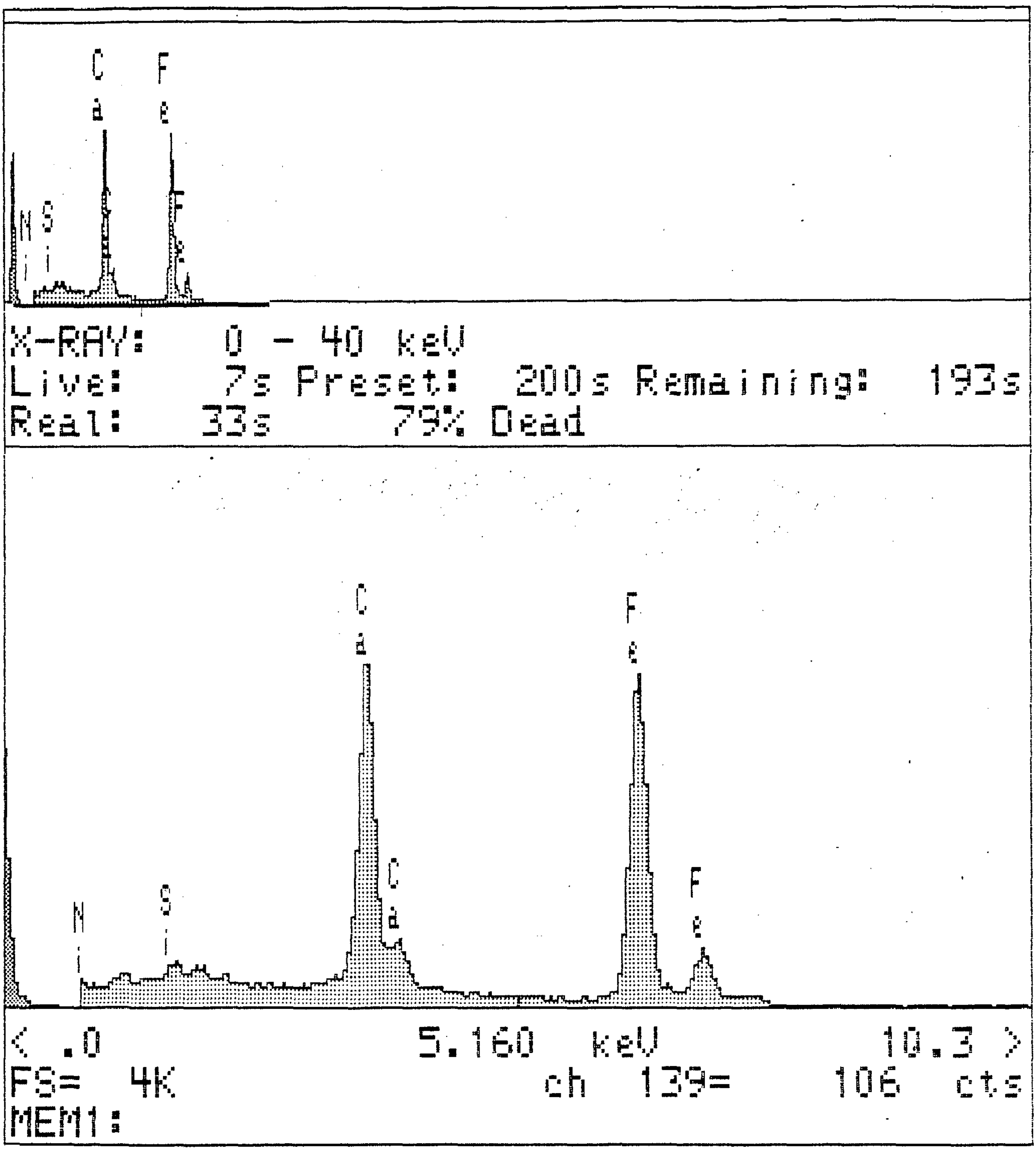
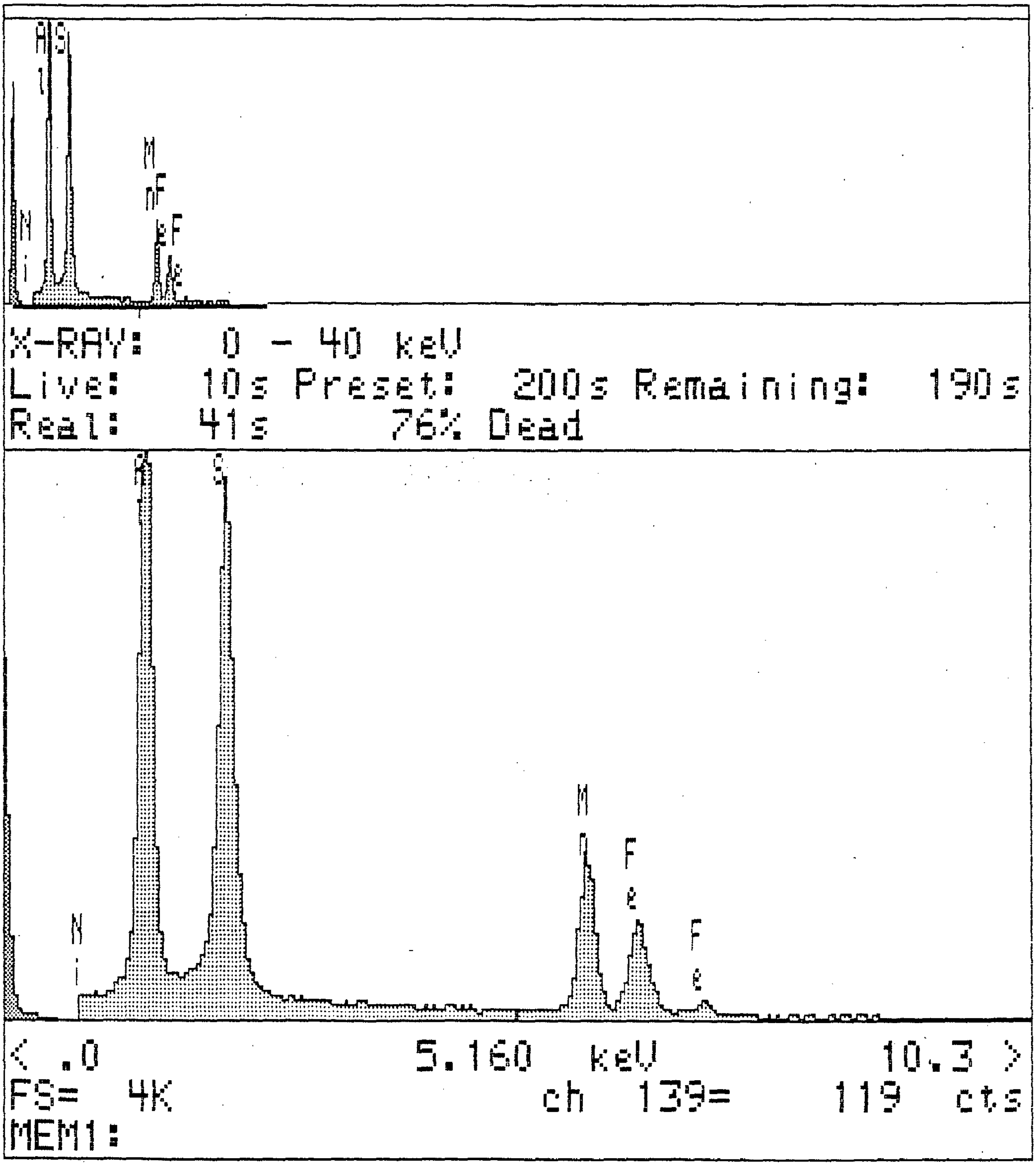


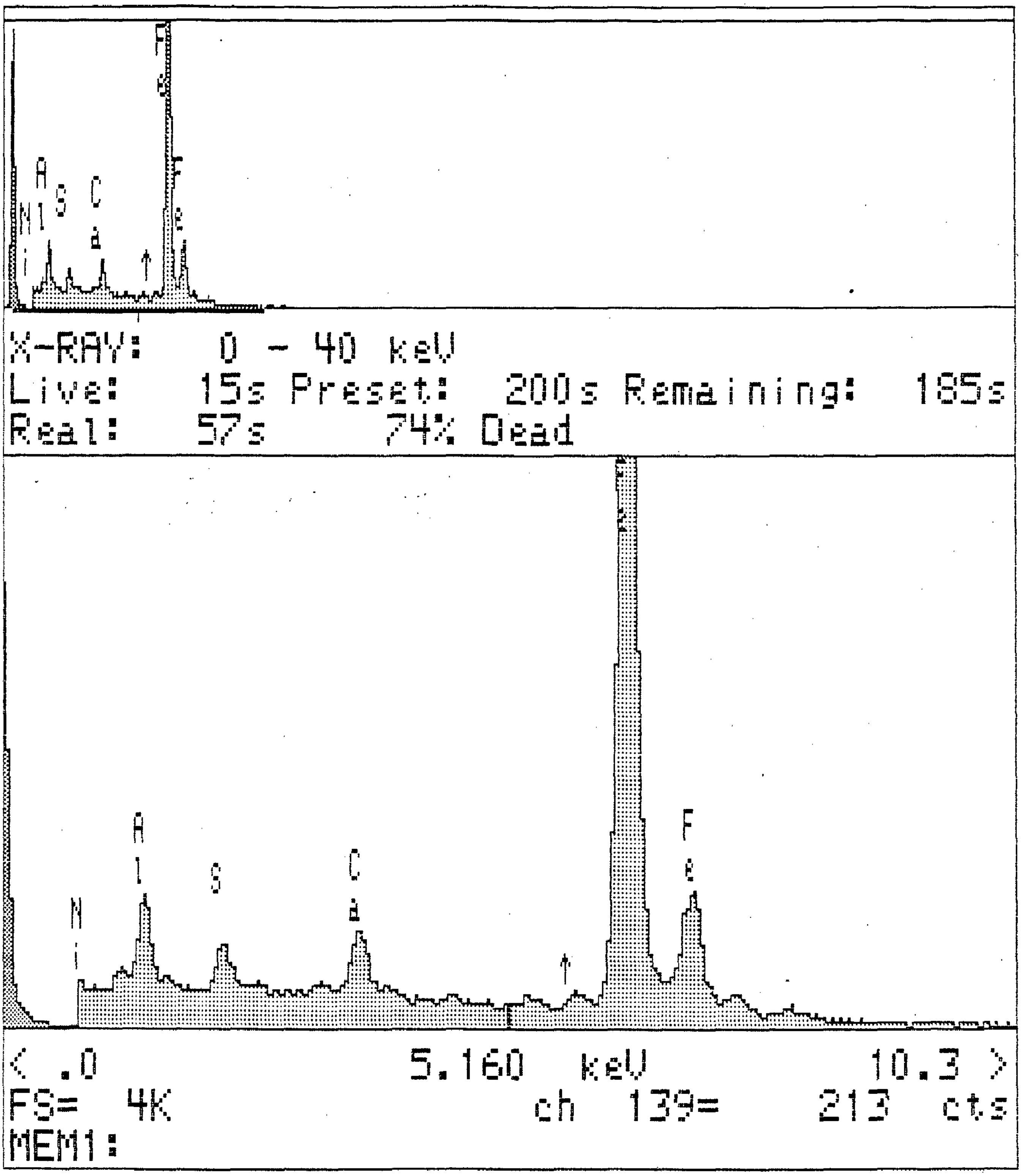
Fig.38. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.4 at stage C. (After reducing period).



```
X-RAY:    0 - 40 keV
Live:    10s Preset:  200s Remaining:  190s
Real:    41s      76% Dead
```

```
< .0                5.160  keV            10.3 >
FS=  4K                 ch  139=      119  cts
MEM1:
```

Fig.39. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.4 at stage C. (After reducing period).



```
X-RAY:    0 - 40 keV
Live:    15s Preset:  200s Remaining:  185s
Real:    57s      74% Dead
```

```
< .0                5.160  keV           10.3 >
FS=  4K                 ch  139=    213  cts
MEM1:
```

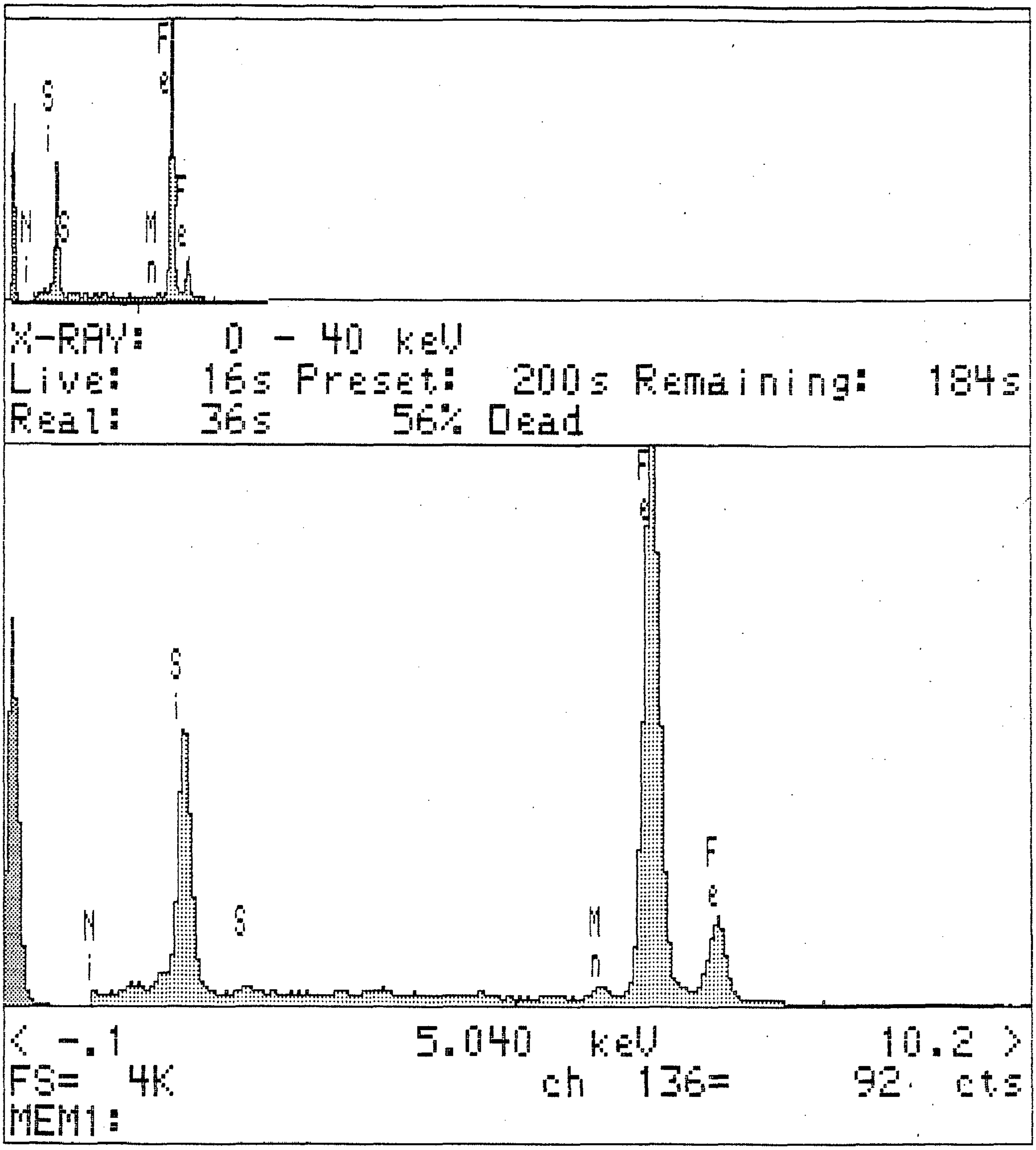
Fig.40. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.4 at stage C. (After reducing period).

inclusion rather than being a deoxidation product. During the stage when carbidic slag is in the process of being prepared, the SiO_2 dust and lime stone added would tend to fuse together and form a slag. Under the action of direct are and coke the CaC_2 is produced. But the production of CaC_2 under the action of the arc takes time. If the sample is with drawn in between and if proper case is not taken to separate the slag fully it is possible that some slag inclusion might get entrained in the liquid metal. The entrained slag would be expected to contain FeO, SiO_2 and some CaO. These kinds of inclusions therefore should be treated as exogenous inclusions. The analysis results recorded in Fig.40 indicate that this inclusion is also a complex one. The inclusion predominantly contains Iron and very small amounts of S and Ca. Similarly the inclusion contains a measurable quantity of Al. It is likely therefore that the inclusion contains predominantly FeO and some amount of Al_2O_3 and some CaS. This inclusion does not show the presence of any manganese. As such the inclusion could be a part of slag phase entrained in the liquid metal.

5.4.4 Heat No.5, Stage A (After Melt Out):

The practice of manufacture of Heat No.5 is nearly the same as that of Heat No.4. The starting sulphur in the opening chemistry was 0.04 which was reduced down to 0.028%. At this final stage, the steel contained 1.24% Mn. For killing this steel again 15 kg. Fe-Al was employed in the furnace before starting the reducing period. The nature of inclusions observed in this case would therefore be expected to be nearly the same as found in Heat No.4.

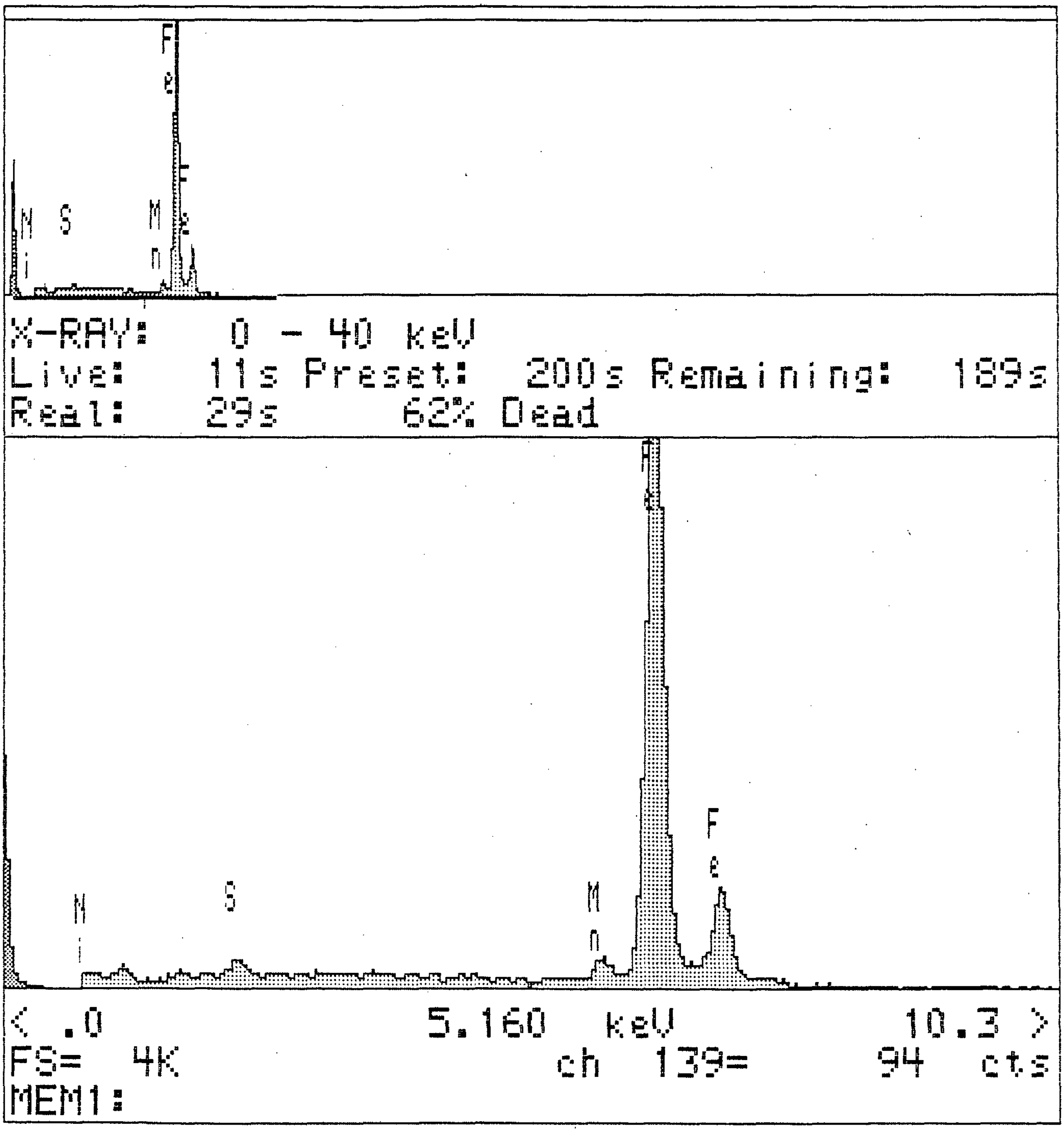
Results pertaining to the microanalysis of a number of inclusions in specimen 5(A) are recorded in Figs.41 to 47. It can be seen from the results recorded in Fig.41 that the inclusions are basically $FeO-SiO_2$ type in which some MnO is also present. These inclusions give a dark blackish appearance under the SEM. Same is the conclusion that can be drawn from Fig.42. The inclusion analysis recorded in Fig.43 shows that it is basically SiO_2 with small amount of FeO in it. Results of analysis shown in Fig.44 lead to the conclusion that it is a complex inclusion. The inclusion contains $FeO-MnO-Al_2O_3-CaO$. It is possible that the calcium present in the inclusion may be in the form of CaS, meaning thereby that some sulphur in the melt has combined with CaO resulting in the formation of CaS. During meltout stage, the molten steel keeps trickling over the lime pieces already sandwitched with the steel scrap. This might lead to the formation of some CaS at the interface. Also at the melt out stage there is not a complete and clear cut separation of slag from the molten steel. At the same time, the slag is also not in a fully digested condition. As such, it is possible that some CaS may be trapped in the liquid melt. The results shown in Fig.45 clearly indicate that the inclusion is of FeS-MnS type which is a common occurrence in steel. Results of analysis shown in Fig.46 indicate that the concerned inclusion is just FeO. The results of last inclusion examined in this case are recorded in Fig.47. It can be seen that it is a complex inclusion of the type $FeO-MnO-SiO_2-Al_2O_3$.



```
X-RAY:    0 - 40 keV
Live:    16s Preset:   200s Remaining:   184s
Real:    36s      56% Dead
```

```
< -.1            5.040  keV          10.2 >
FS= 4K                  ch  136=      92  cts
MEM1:
```

Fig.41. Spot/Point analysis of inclusion observed in the steel specimen drawn from heat No.5 at stage A.(After melt out). Using JEOL superprobe Micro-analyser model JXA-8600M.



```
X-RAY:    0 - 40 keV
Live:    11s Preset:  200s Remaining:  189s
Real:    29s      62% Dead
```

```
< .0               5.160  keV          10.3 >
FS=  4K                ch  139=       94  cts
MEM1:
```

Fig.42. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.5 at stage A. (After melt out).

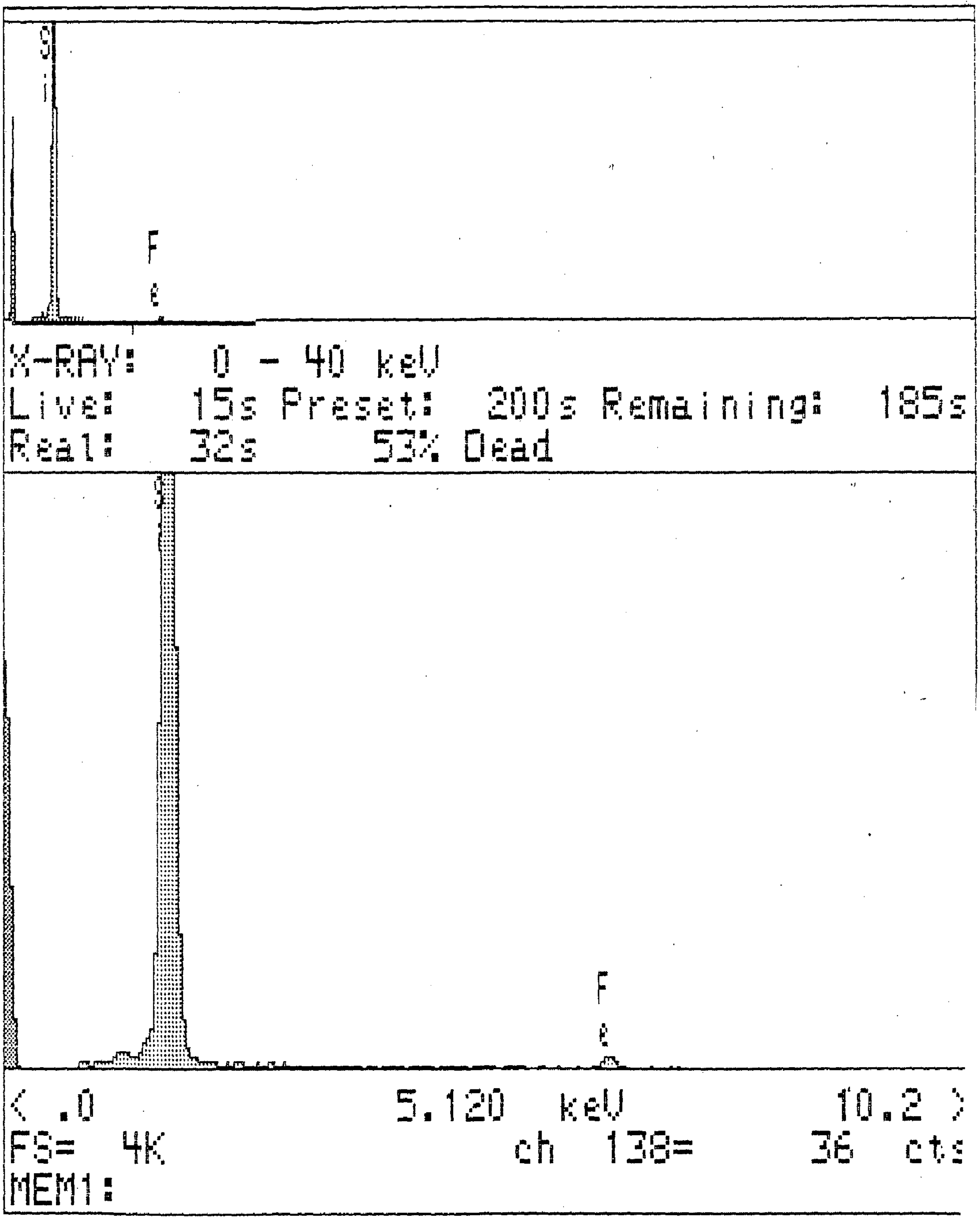
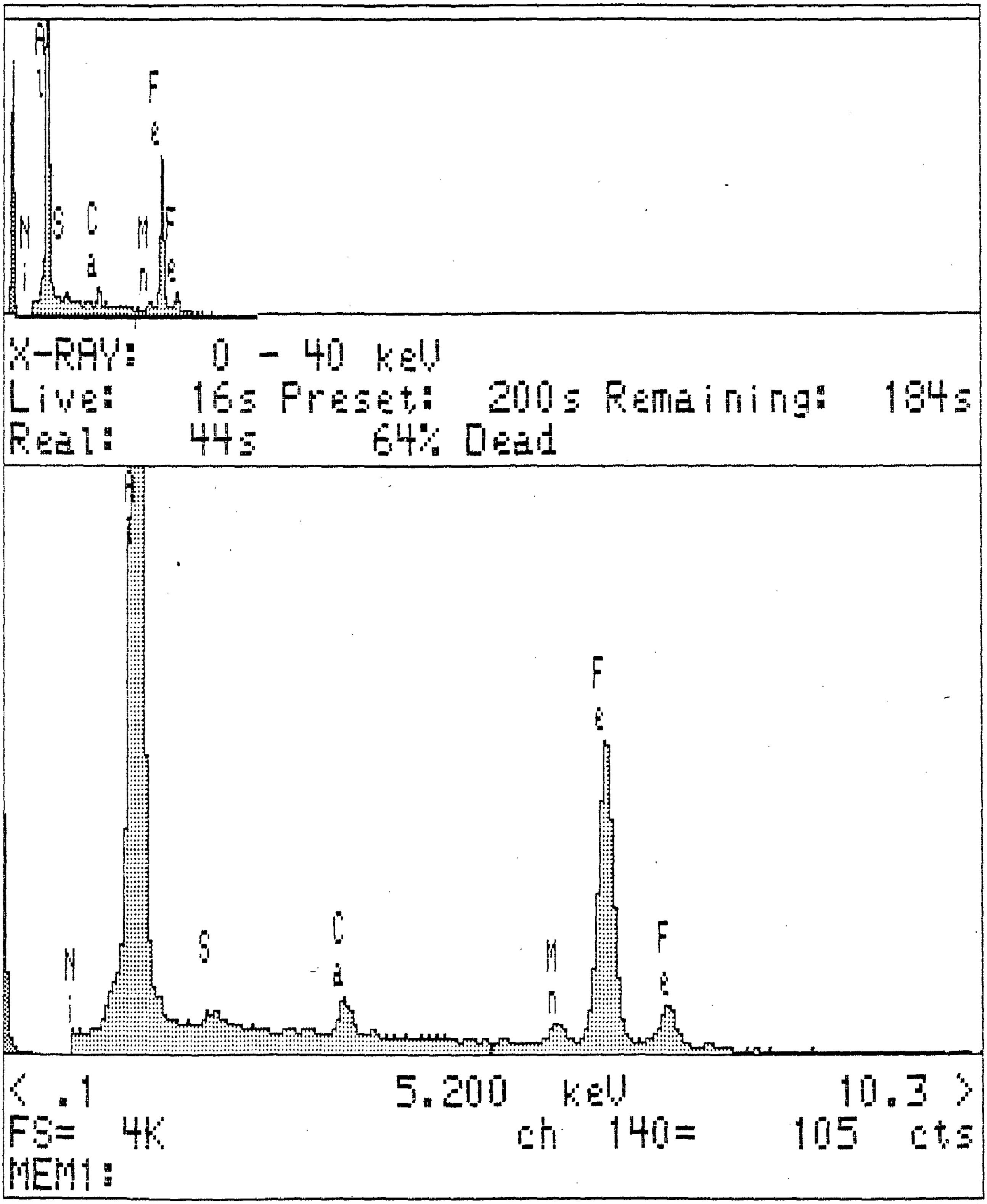


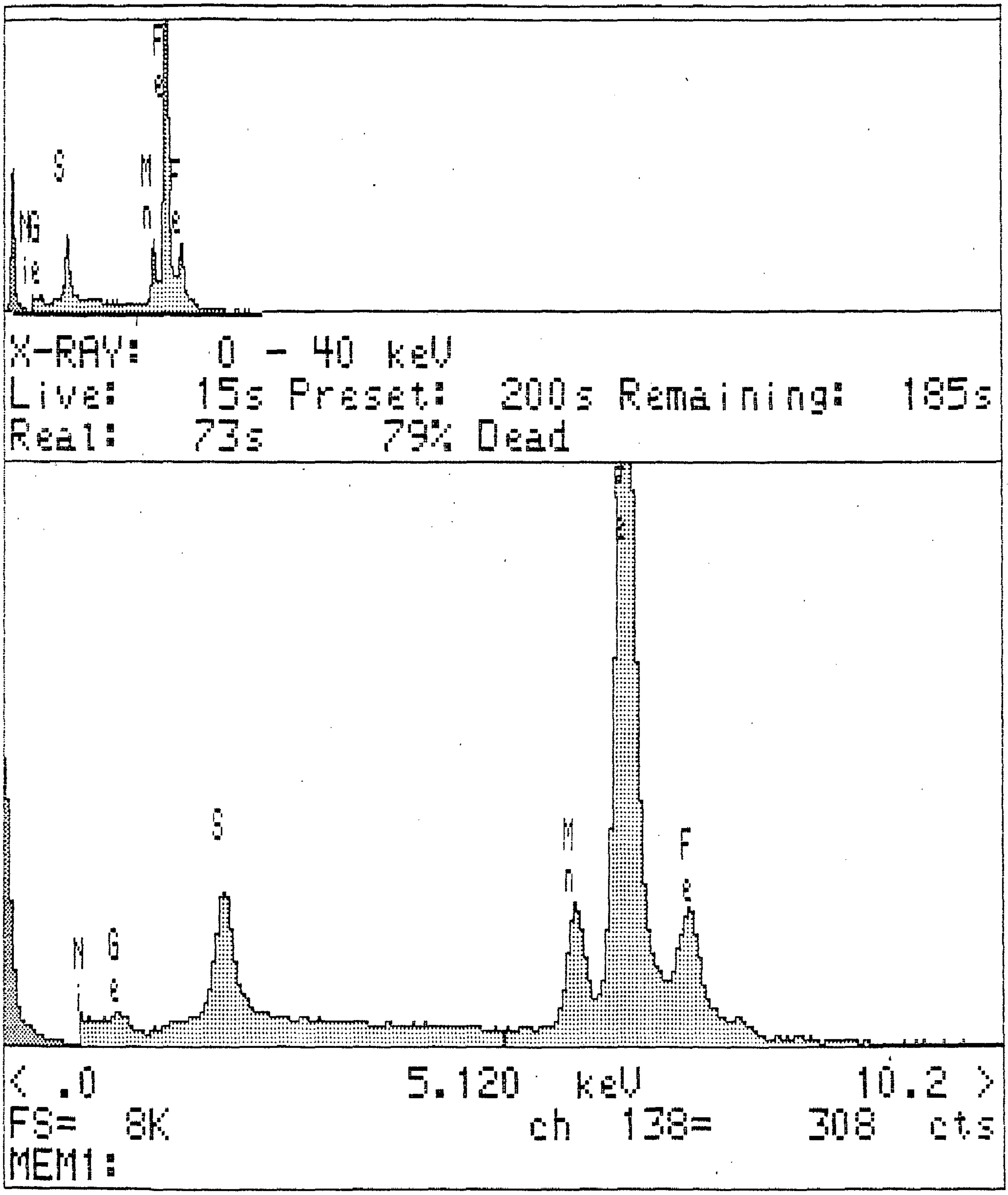
Fig.43. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.5 at stage A. (After melt out).



```
X-RAY:    0 - 40 keV
Live:    16s Preset:  200s Remaining:  184s
Real:   44s      64% Dead
```

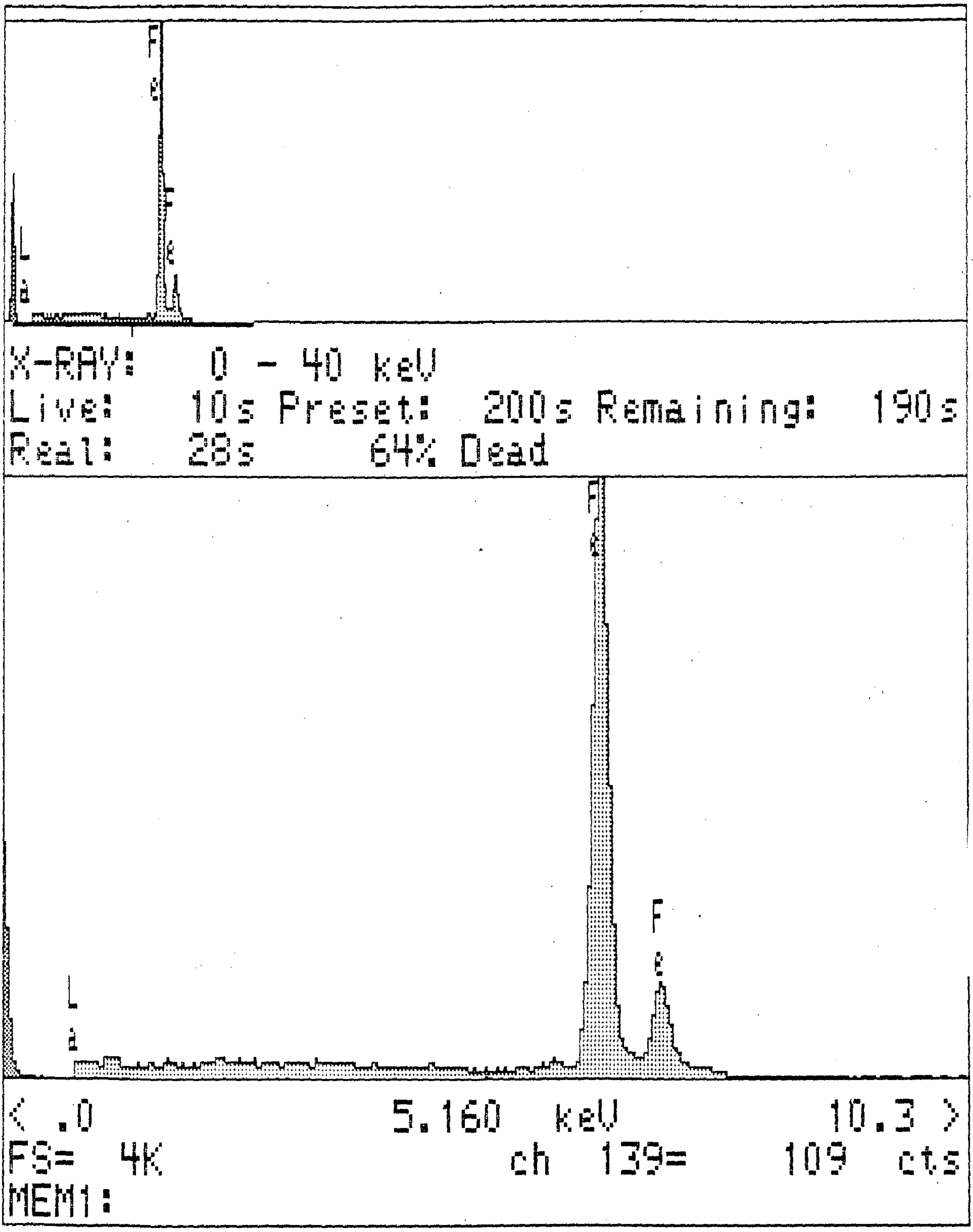
```
< .1                5.200  keV           10.3 >
FS=  4K                   ch  140=     105  cts
MEM1:
```

Fig.44. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.5 at stage A. (After melt out).



```
X-RAY:   0 - 40 keV
Live:   15s Preset:  200s Remaining:  185s
Real:   73s     79% Dead
< .0             5.120  keV          10.2 >
FS=  8K               ch  138=     308  cts
MEM1:
```

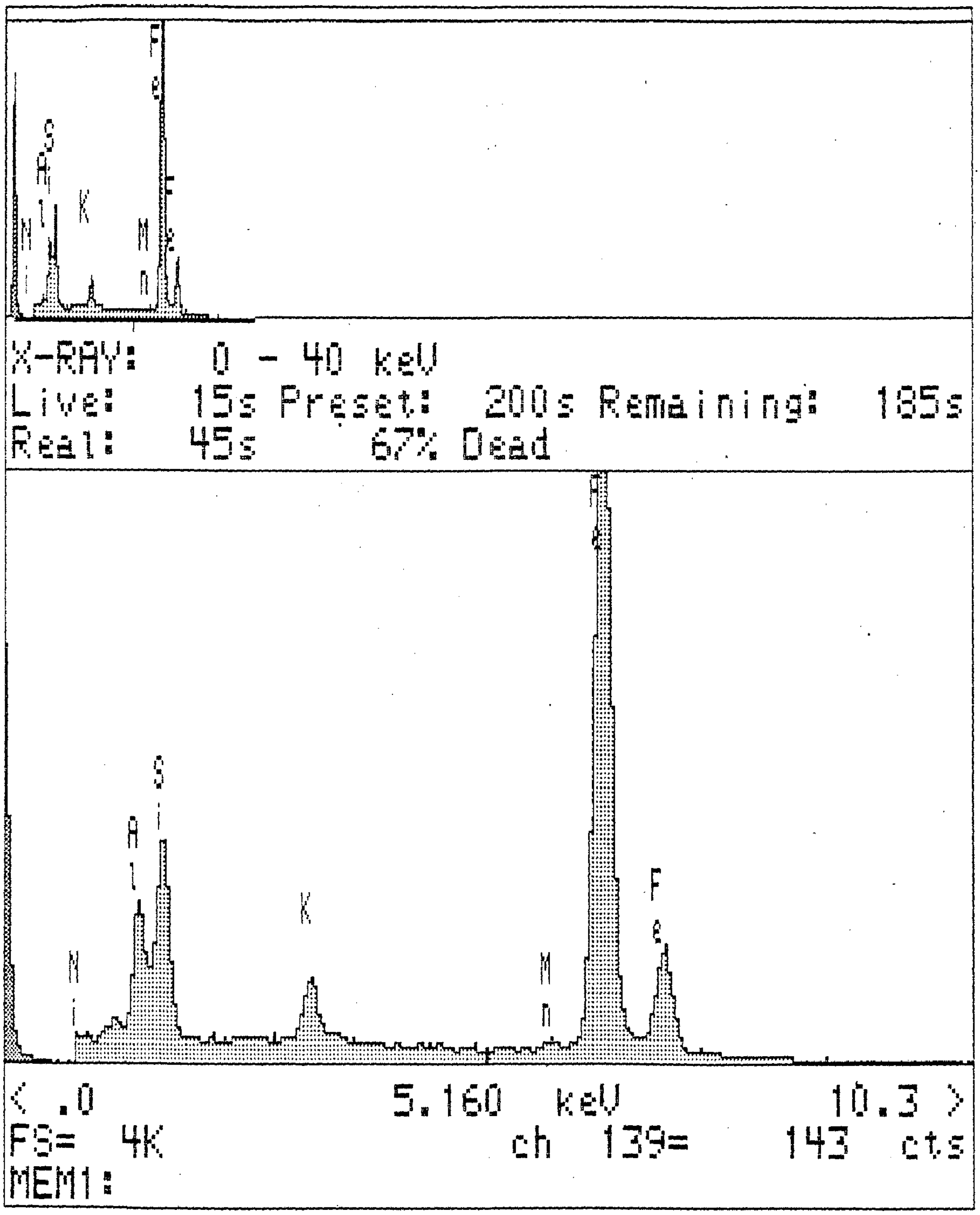
Fig.45. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.5 at stage A. (After melt out).



```
X-RAY:    0 - 40 keV
Live:    10s Preset:  200s Remaining:   190s
Real:    28s      64% Dead
```

```
< .0             5.160  keV          10.3 >
FS=  4K               ch  139=     109  cts
MEM1:
```

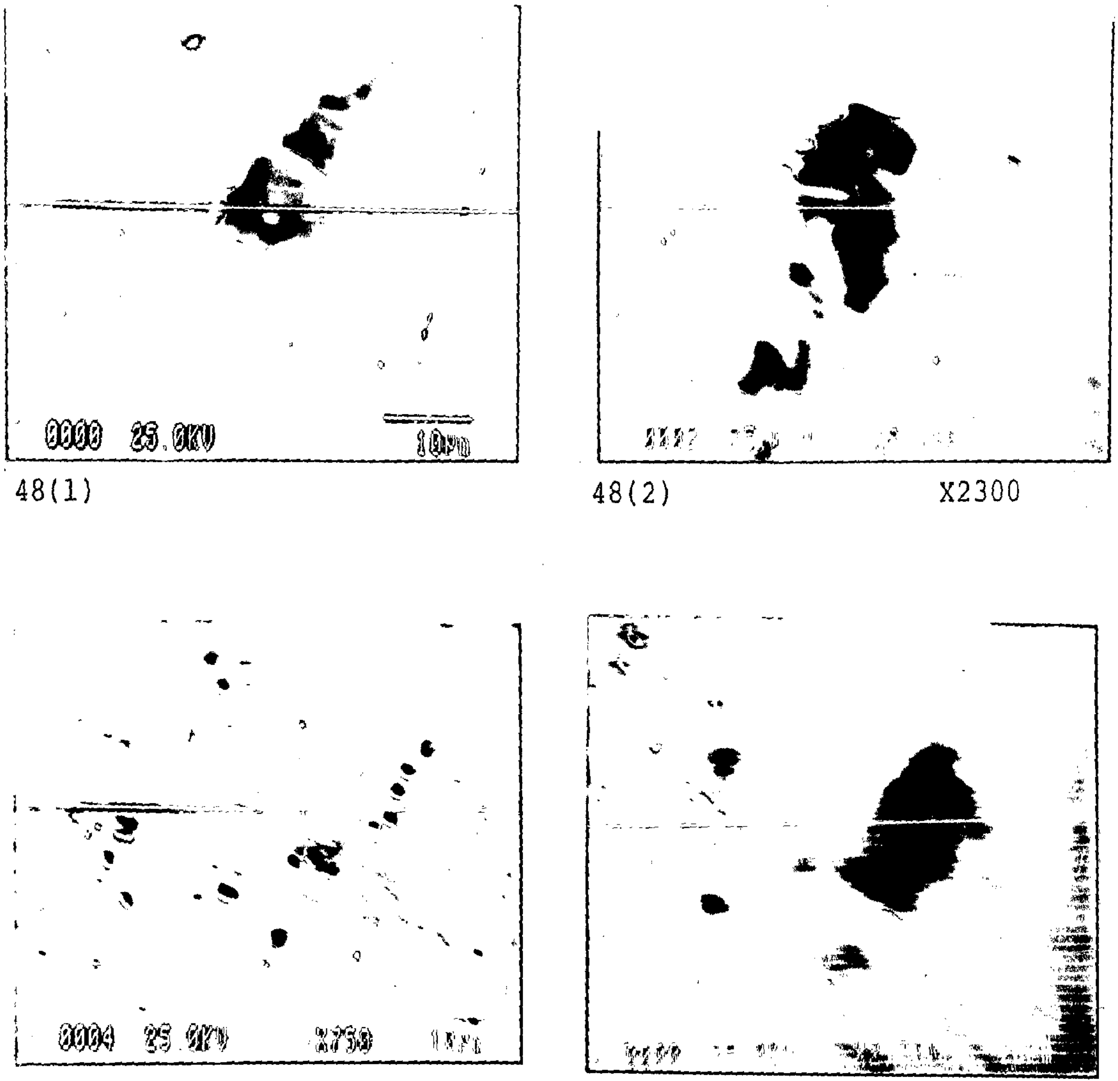
Fig.46. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.5 at stage A. (After melt out).



```
X-RAY:    0 - 40 keV
Live:    15s Preset:   200s Remaining:   185s
Real:    45s     67% Dead
```

```
< .0              5.160  keV          10.3 >
FS=  4K               ch  139=      143  cts
MEM1:
```

Fig.47. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.5 at stage A. (After melt out).



48(1)

48(2) X2300

48(3) X750

48(4) X2700

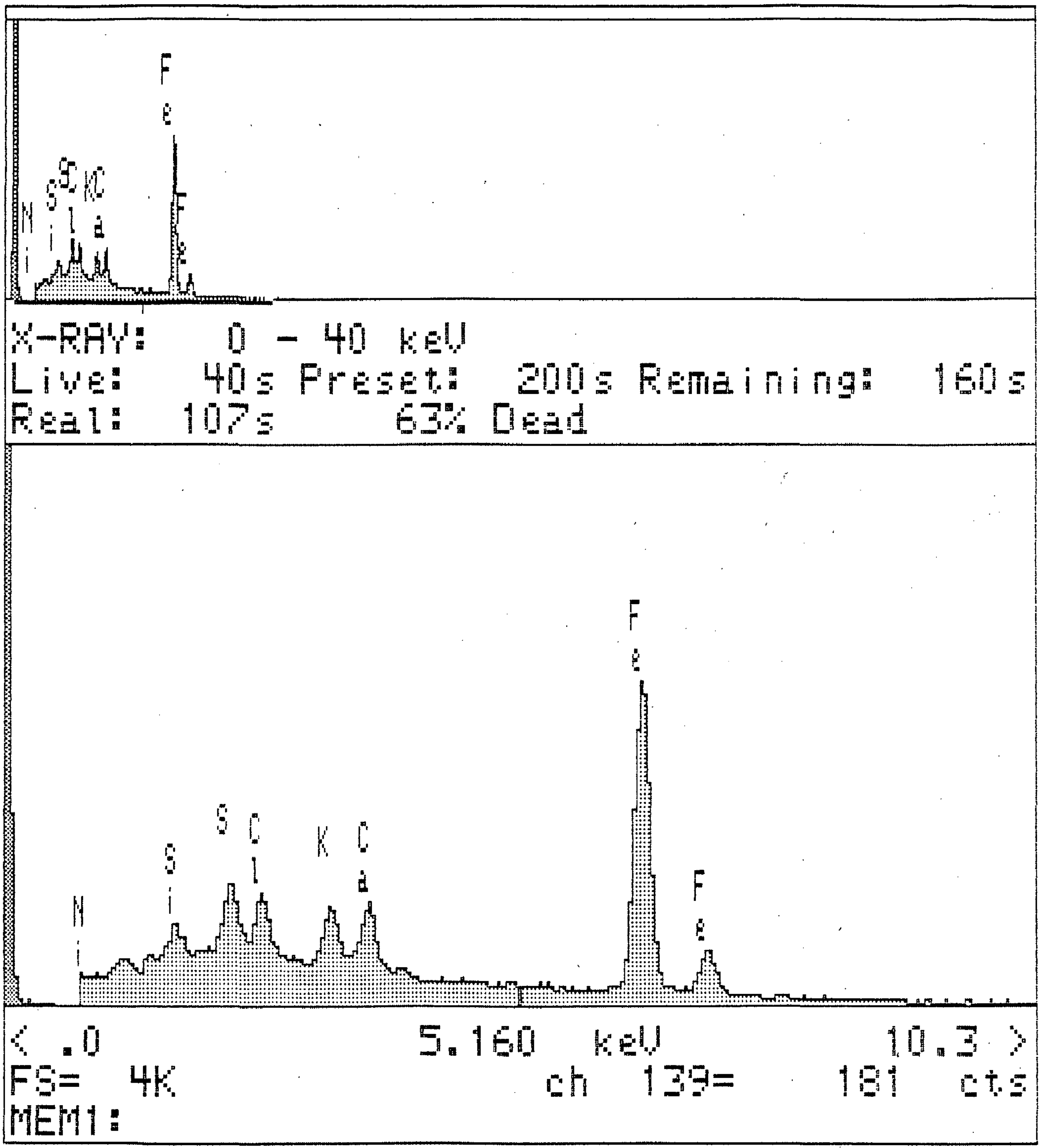
Fig.48. SEM pictures of inclusions analysed by JEOL superprobe EPMA, in case of heat No.5 (IS:1030, foundry grades) at stage A (after melt out).

It is surprising how so much of Al_2O_3 as seen in Fig.44 and Fig.47 has come into the inclusion at this stage of the processing of this heat. The only possibility is that this Al_2O_3 might have been picked-up from the gangue part of the Iron ore charged into the furnace along with the scrap and other additives such as petroleum coke and lime stone. But as the carbon boil proceeds soon after it is possible that many of these inclusions would float out to the surface and join the slag.

SEM pictures of some of the inclusions observed and examined are shown in Fig.48. SEM /octires shown in Fig.48/1 belongs to the inclusion whose microanalysis is shown in Fig.41. Similarly the SEM pictures shown in Fig.48/2 pertains to the histogram shown in Fig.42. SEM picture shown in Fig.48/3 pertains to histogram shown in Fig.44. The last SEM picture shown in this plate (Fig.48/4) pertains to histogram shown in Fig.46.

5.4.5 **Heat No.7, Stage B (After Refining):**

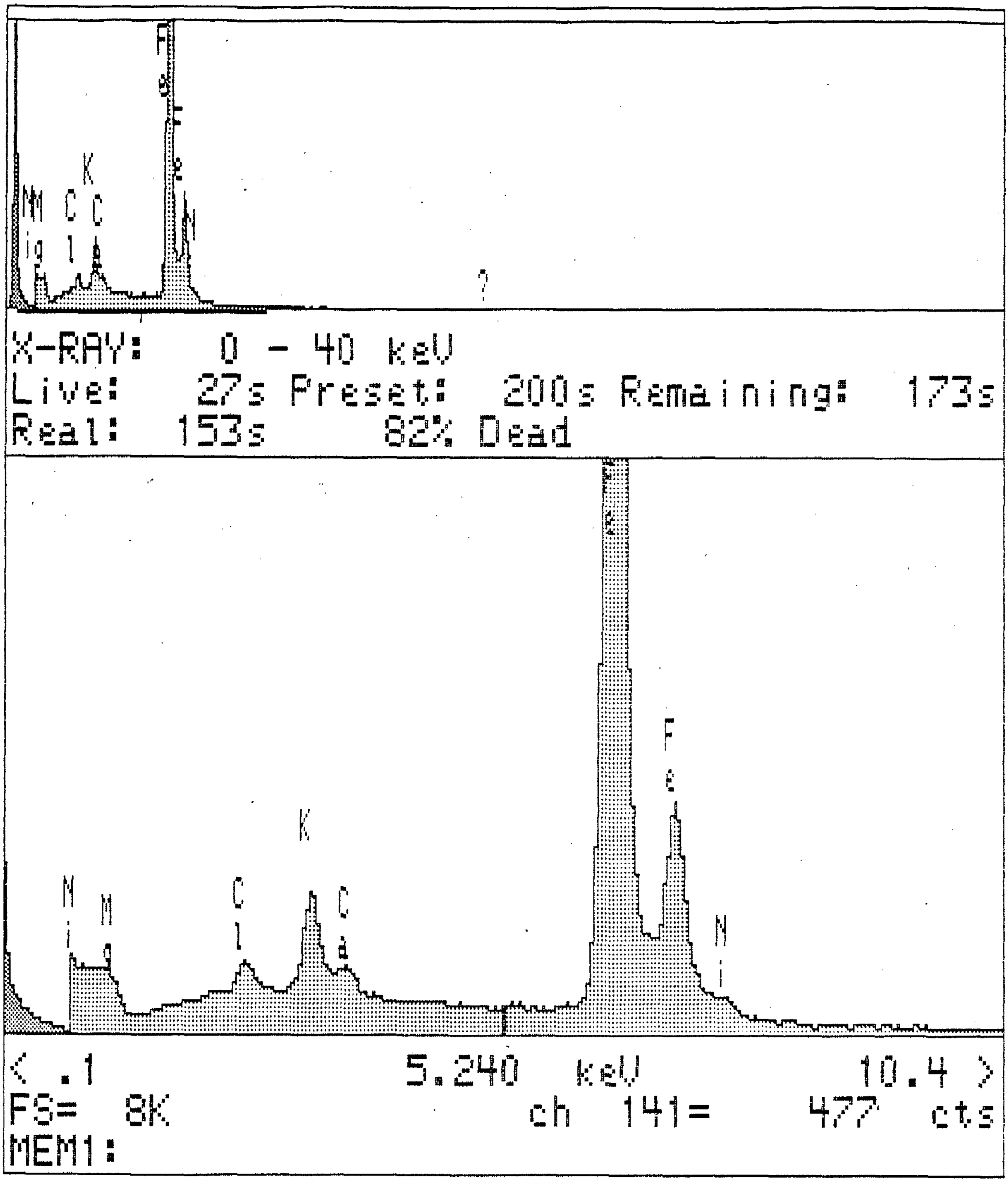
The inclusion observed in this case was relatively a big piece of approx. 60x50 µm in size. This inclusion appeared to be very complex in the sense that different locations of this inclusion showed different analysis. It appeared that at few locations Ca was localised. Generally this inclusion consisted of FeO with some traces of Si and S. It is surprising as to how such a big inclusion



```
X-RAY:    0 - 40 keV
Live:    40s Preset:   200s Remaining:   160s
Real:   107s      63% Dead
```

```
< .0              5.160  keV            10.3 >
FS=  4K              ch  139=       181  cts
MEM1:
```

Fig.49. Spot/Point analysis of inclusion observed in the steel specimen drawn from heat No.7 at stage B. (After refining). Using JEOL superprobe Micro-analyser Model JXA-8600M.



```
X-RAY:    0 - 40 keV
Live:    27s Preset:   200s Remaining:   173s
Real:  153s      82% Dead
```

```
< .1                5.240  keV            10.4 >
FS=  8K                  ch  141=      477  cts
MEM1:
```

Fig.50. Spot/Point analysis of another inclusion observed in the steel specimen drawn from heat No.7 at stage B. (After refining).

was retained in the melt even after carbon boil. It appears probable that carbon boil was not carried out very effectively in this case. It is apparent from the chemistry of the spot also (Table 3.7). It can be seen from the data recorded in this table that opening carbon of this heat was 0.50. The carbon boil was carried out but even after the third sample drawn from the heat C was 0.41 signifying that a carbon boil of only 9 points was allowed. This level of carbon boil is infact on the lower side and not really adequate. In such a case of inadequate carbon boil, many large pieces entrained with the liquid metal will not be able to float out effectively. It appears from the practice of U.P. Steels that the level of carbon boil carried out in different heats is rather in consistent. In some cases, the carbon boil is carried out to a level of 52 prints (Table 3.1) while on the other hand this carbon boil is reduced down to only 14 points (Table 3.2). In the present case (Table 3.7) the carbon boil has been carried out through 9 points only which is apparently inadequate. Similar features can be observed from the microanalysis results shown in Fig.50. The inclusions basically contains FeO with little amounts of Ca and Mg which is indicative of the fact that this inclusion also contains some lime piece in it. This lime piece must be in the process of digestion along with FeO and apparently the digestion is yet not complete. It is probable that the carbon boil was started prematurally i.e. before the slag could be shaped up properly. This represents in fact a slightly improper or defective practice.

CHAPTER - 6.0

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDIES

6.1 Conclusions:

The following conclusions are arrived at from the present study ;

(1) On an optical examination of specimens drawn from four different heats and four different stages of processing of different heats, it was found that large many morphologies of inclusions exist in the specimens. The common morphologies observed were; Globular, stringer type, massive, plate like, semi angular and pearl necklace type.

(2) Morphologies corresponding to stage A (after melt out) were mostly massive and large sized. The pearl necklace morphology of inclusions was commonly observed corresponding to stage B (after oxidation). The inclusions corresponding to stage C & D (after refining and in the ladle respectively) were found to be generally small sized (in the range of 5 to 8 μm) and rounded in shape.

(3) The detailed optical examination of these inclusions revealed that many times they were complex in nature, meaning thereby that over two or three minerals were present in the same inclusion. It also became apparent that some inclusions were in the process of dissolution. It was a common observation that many tiny inclusions were bunched together and were in the process of coagulation in an attempt to form a larger single mass. In pearl necklace type of formation, it was apparent that many tiny FeO particles had joined together at their ends and that at few locations they had almost fused into each other. From optical observations it was also clear that many inclusions were under going alteration through chemical reactions. This was happening predominantly in those cases where the inclusions were of larger size.

(4) The industrial practice of classifying inclusions as per IS: 4168;1982 in different categories like sulphides, alumina, silicates and oxides and grades 1 to 5 is rather inaccurate as individual inclusions are usually found to be of lot many shapes mentioned at serial no.1 above and that they are usually complex in nature. This implies that the simple shapes mentioned in IS 4168 ; 1982 are usually not found in practical steel making situations. This practice however may be considered good enough for routine inspection in the industry.

(5) Quantitative metallographic examination of longitudinal as well as transverse specimen belonging to eight different heats revealed that larger number of inclusions are usually present in the longitudinal section compared to the transverse one. Usually maximum no. of inclusions were found corresponding to stage B (after refining) which progressively decreased after stage C (reducing period) and in the ladle (stage D). The overall examination of the melting practice and the quantitative metallographic data reveal as that a standard and consistent steel making practice is not followed carefully at M/S U.P. Steels.

(6) Even examination of the inclusions in specimen 1(D) revealed that the inclusions are mostly globular in shape but very complex in composition. These inclusions were either sulphides of iron and manganese with some chromium in them or a mixture of iron and manganese silicates containing some Al_2O_3 and CaO. The sulphides were mostly globular and small in dimensions (4 to 5 µm). This specimen was also found to contain some eroded refractory particles of about 13 µm average size. This eroded refractory piece had undergone some alterations in its composition due to reaction with steel.

(7) Inclusions observed in specimen 4(C) contain primarly sulphides of iron and manganese while some inclusions contained a mixture of $FeO+SiO_2+CaO$. The complex nature of inclusions is presumably because of desulphurization and deoxidation going on during stage C and because of some alloy additions to achieve the above purpose.

(8) The inclusions observed in specimen 5(A) are basically silicates of iron and manganese and the inclusions found are of larger size in dimensions. In some instances independent FeO & SiO_2 inclusions are found in the steel. Some inclusions were found to contain a mixture of $FeO+MnO+CaO+Al_2O_3$. Some other inclusions contained silicates of iron and manganese with some Al_2O_3 in it.

(9) Specimen 7(B) was found to contain predominantly a mixture of $CaO-FeO-SiO_2$. This implies that these were basically silicate inclusions.

6.2 Suggestions for Further Studies:

The following suggestions can be made for future studies in view of the results of present investigation.

(1) A particular quality of steel where cleanliness ratings are very stringent should be selected for a detailed study of the occurrence of non-metallic inclusions.

(2) The above heat should be followed from the begining i.e. right from the stage of selection of charge materials. This heat should be boiled properly and at least two to three specimens should be drawn from each stage (stage A to D). The additions during reducing period and in the ladle. Should be worked out carefully and noted. The deoxidation practice can be varied slightly in each case and at least such three to four heats should be observed carefully. The objective of this study will be to examine as to how the shape, size and composition of inclusions vary in the finished steel with a slight change in the deoxidation practice. Thus in all four/five heats of the same grade should be examined rather than examining several grades at a time.

(3) In addition to the spot analysis, the line analysis of entire inclusion should be carried out to ascertain the presence of different minerals in the same inclusion. For this purpose, the old practice of identifying the presence of different minerals in an inclusion using polarized light in a optical microscope should be revived.

(4) It is suggested that for quantitative metallographic studies, automatic counting techniques should be employed rather than making manual observations. This is likely to improve the accuracy and reliability of these observations.

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