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Identification of Inclusions in Steel by Microradiography

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INTRODUCTION

It is necessary to investigate the solution chemistry of the non-metallic elements in iron to understand the chemistry of steelmaking. Most of these elements have an appreciable solubility in liquid iron, but may be separated from the iron by precipitation of an insoluble compound with another metal. They may also separate from the iron when the metal is cooled and solidified; in these circumstances an iron salt, or the salt of another metal may be formed. The distribution of a non-metallic element between such phases and what is still in solid solution may be described by an equilibrium constant that can be calculated from the free energy of formation of the compounds in the system. This procedure is the same as that used to describe solubility and precipitation phenomena in aqueous solution; however, since steelmaking involves temperatures in excess of 1500° C., the free energies of formation at these temperatures must be considered. Such calculations have not eliminated the need to examine and analyze precipitates in steel.

The separation of precipitates from aqueous solutions for examination is generally a routine matter, and presents no great difficulty. In many cases the analogous separation for the study of precipitates in steels presents a very formidable problem. Some very stable precipitates such as aluminum oxide are easily separated by dissolution of the iron in acids; less stable precipitates such as iron oxides or borides require more elaborate procedures.

The precipitates in steel, or inclusions as they are more commonly called, not only reflect the chemistry of the molten state, but also may affect the physical properties of the cooled metal (1). For instance, a metallic salt may precipitate before or after the steel solidifies. In the latter case the inclusions are found to surround the grains or crystallites of iron. Such a precipitate will become liquid before the iron matrix and therefore will act as the weakest link in the matrix at elevated temperatures. A high melting precipitate will usually appear as an angular inclusion surrounded by iron. Such inclusions are not usually found to affect the strength of the matrix.

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Obviously, a knowledge of the morphology and location of inclusions in steel is an aid in both studying the chemistry and predicting the physical properties of steel. This information is generally obtained by polishing and chemically etching the surface of a steel sample, and subsequently observing the surface through a light microscope. Much has been published describing the physical and chemical procedures for preparing samples for microphotography. The technique has several serious disadvantages; only the surface can be viewed, and a thorough knowledge of the chemical reactivity of the inclusions is necessary to understand the action of the chemical etchants on the surface. In order to partially overcome these disadvantages, the technique of microradiography has been used. This technique permits examination of inclusions that are surrounded by metal, and segregations of specific elements can be detected and identified. It has been used in this application by G. L. Clark, W. Betteridge and others (2, 3). For these same reasons the technique is of potential use in petrography, biology, ceramics, and many other fields in which heterogeneous solids are investigated. An extensive bibliography of applications of the technique has been prepared by Eastman Kodak Co. (4, 5).

EXPERIMENTAL

Radiography depends on the fact that x-rays will readily penetrate matter, and that the transmitted x-rays can be photographically recorded. Highly absorbing volumes will appear as "shadows" on the photographic plate. If the photographic plate is enlarged so as to detect microscopic "shadows," the technique is called microradiography.

The decrease in the initial intensity, I_0, of an x-ray beam to a value, "I," as it passes through a sample may be written

$$I = I_0 \, e^{-\mu d}$$

where μ is the linear absorption coefficient, and d is the distance traversed in the sample. For a given element, absorption increases sharply with wavelength until a sharp discontinuity is reached at the "absorption edge" (Figure 1). The absorption edge corresponds to radiation which will excite the K, L, or M spectra of the absorbing element. At this wavelength the absorption coefficient abruptly falls and then slowly begins to rise again. The wavelengths of the absorption edges are unique for each element, and elements can therefore be identified by them. The linear absorption coefficient μ may be written

$$\mu = k \, N^4 \lambda^3$$

where N is the atomic number and λ is the wavelength. "k" is a constant between absorption edges. It is apparent that absorption also increases rapidly with atomic number.
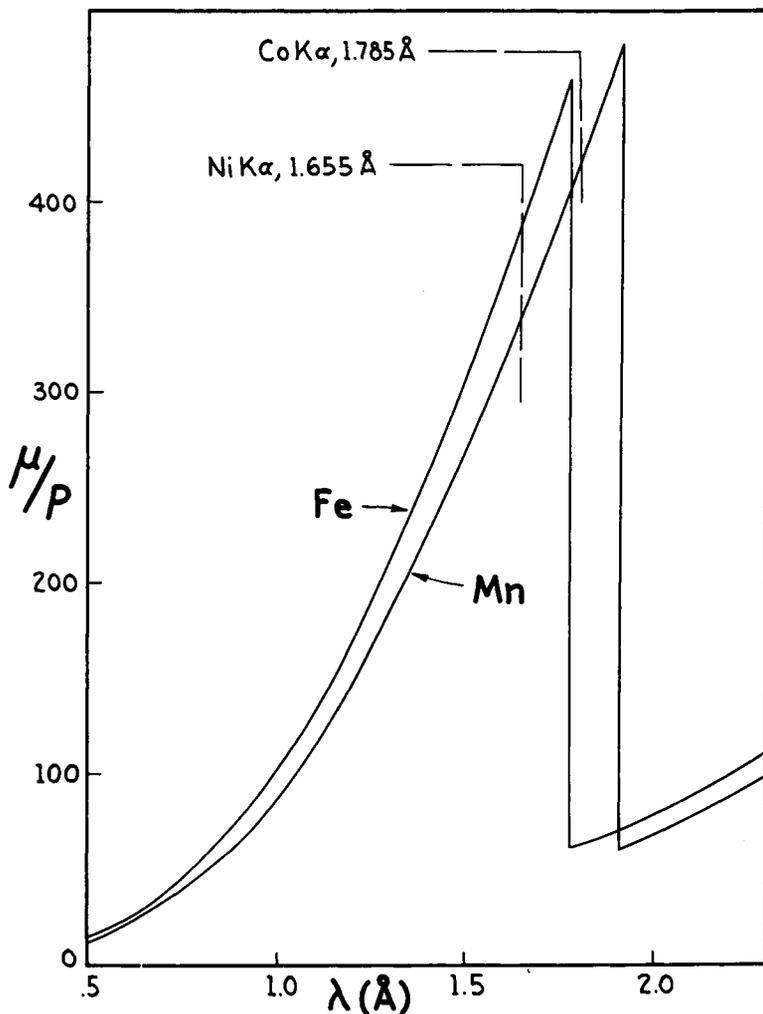
Figure 1.   Mass absorption coefficient, μ/ρ, plotted as a function of wavelength for iron and manganese. (Values taken from Internationale Tabellen.)

Versatility depends on the range and specific x-ray wavelengths that are available. For a single tube, the emitted x-rays can be modified by the use of filters and voltage setting. The wavelength of the continuous white radiation abruptly cuts off at a minimum wavelength dependent on the operating voltage. The relation is,

$$\lambda_{min.} = 12,350/V$$

where $\lambda_{min.}$ is the minimum wavelength in angstroms, and V is the peak operating voltage. Superimposed on this background are the line spectra of the target element. This radiation of specific wavelength is the most useful. One spectral emission, usually the $K\alpha$

doublet, can be used exclusively of other spectral emissions such as the Kβ by use of a filter element that has an absorption peak corresponding to the wavelength of the undesirable spectral line.

For examination of a particular material, careful consideration must be given to the number of available combinations of target materials, filters, and operating voltages, to produce the best possible microradiograph.

The number of commercially available tubes with different targets is limited. However, with a single high intensity source, such as is available with a tungsten tube, secondary sources may be produced by bombardment with x-rays by the primary source. The approach has not been generally used for microradiography because of inherent problems of low intensity and long exposures.

To avoid confusion from overlapping, the samples must be of a thickness that is only several times greater than the size of the inclusions of interest. For steel, foils two to five thousandths of an inch thick permit most inclusions to be easily distinguished from their surroundings. Such foils are easily prepared by mounting flat samples on a magnetic chuck and grinding them to the proper thickness with a soft wheel. Highly polished surface finishes such as those necessary for photomicrographs are not usually necessary.
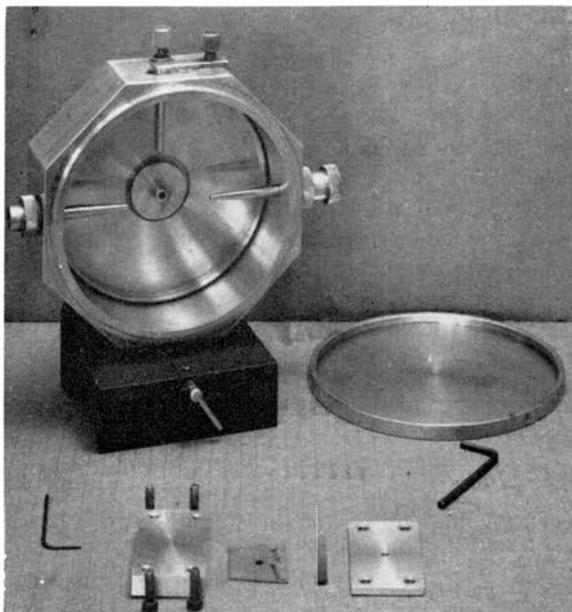

Figure 2.   Flat Plate Camera for Microradiography. The flat plate camera is shown disassembled with a developed plate and metal foil in the foreground. Four Allen screws hold the foil and photographic plate in close contact. An Allen set screw (not visible) holds the flat plate camera on the sample mount of the Debye-Scherrer camera in the background. The aperture is 1/8 inch in diameter.
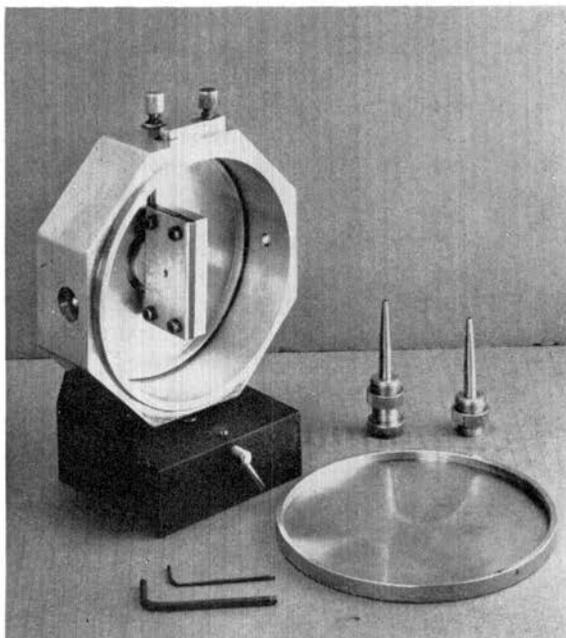
Figure 3.   Flat Plate Camera Mounted for Exposure. The flat plate camera is mounted for X-ray exposure. The black masking tape prevents light leakage between the plates and subsequent blackening of the plate. The entrance slit can be used to collimate the beam for greater resolution. For magnification of X100, use of the entrance slit does not visually improve the negative.

     The magnification that can be attained depends on the degree to which the photographic plate can be enlarged. A resolving power of more than 1000 lines per mm. is claimed for Kodak 649-0 spectroscopic plates. These plates were developed with D-19 developer as recommended. Magnifications of 200X were easily obtained from the negatives, which were enlarged in a metallograph, and contact prints were prepared from the metallographic plates. All microradiographs in this article are magnified 100X. Since these prints are from a third photographic process, they correspond in appearance to the original negative.

     Collimation of the x-ray beam, and good sample to film contact are necessary for maximum resolution. This has been done by the use of a simple flat plate camera which was conveniently mounted in a Debye-Scherrer powder camera (Figs. 2 and 3). If a crystallite in the sample is in proper orientation, diffraction of the x-ray beam may take place, and the diffracted beam may appear on the negative as a dark spot. On first sight, this would be indistinguishable from a void or volume of low absorption in the sample. However, since the flat plate camera can be rotated on its mount, the dark spot can be eliminated by a few degrees rotation of the sample, if diffraction took place. The slight rotation will have only a negligible effect on the
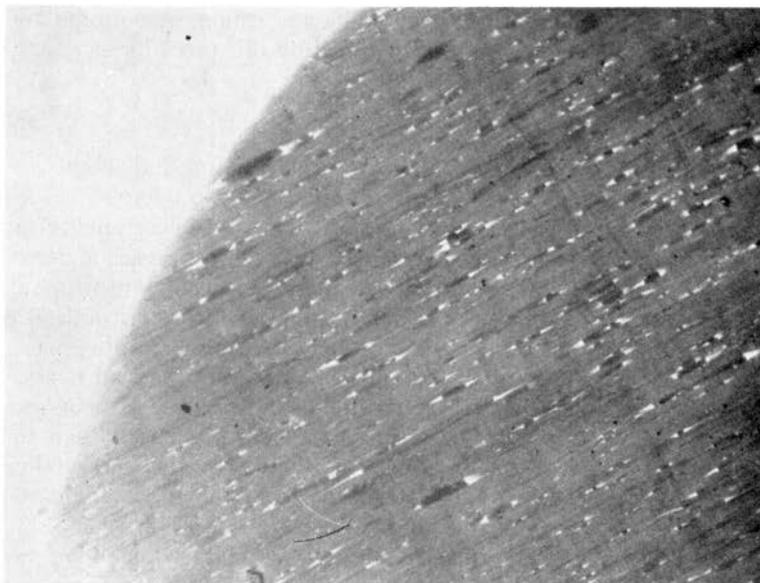
Figure 4. Microradiograph of a Leaded High Sulfur Steel. This steel contains approximately .30% sulfur and .75% manganese. The inclusions are elongated in the direction of rolling. CrKα radiation was used to prepare the microradiograph. The highly absorbing lead bearing areas appear as white 'tails'. The sulfide center of the inclusions is the least dense material in the steel, and therefore appears darkest on the photograph. Magnification is 100X.

Figure 5. Microradiograph of a Leaded Steel. This steel is similar in composition to the steel in Figure 4 except that the sulfur content is below .05%. The lead is again noted to be associated with the non-metallic matter in the steel. The microradiograph was prepared by the same procedure as in Figure 4. The streaks running perpendicular to the rolling direction are caused by grinding roughness on the surface of the foil.

appearance of the negative as caused by absorption. Absorption and diffraction effects are easily distinguished by this procedure.

RESULTS

Lead is added to steel to improve machinability, and in this capacity has become an important additive in the production of the free-machining steels (6). Because lead has an atomic number far greater than any other element alloyed to most plain carbon steels, metallic lead or a lead salt should absorb x-rays much more than any other constituent. Figures 4 and 5 are microradiographs of leaded steels. The latter steel contains less than .5% sulfur and the former contains approximately .30% sulfur. In both cases the lead is associated with non-metallic matter in the form of two-phase inclusions. The non-metallic part of the inclusion absorbs less x-rays than the iron matrix, and therefore appears darker than the surrounding matrix. It is not possible to determine from the microradiograph whether the lead is in the metallic form or exists as an inorganic salt. Chemical and thermodynamic considerations would lead one to expect the lead to be metallic. However, the most important information that is derived from these data is the fact that the lead and non-metallic matter are physically associated. These two-phase inclusions were probably one-phase liquid droplets in the steel at elevated temperatures.

The steels in figures 4 and 5 both contain approximately .75% manganese and .10% carbon. Electrolytic separation of the metal from the non-metallic matter, and x-ray diffraction analysis of the residue, indicated the presence of large amounts of manganese sulfide in the high sulfur steel. The non-metallic phase of the inclusions in this steel could reasonably be assumed to be manganese sulfide. Microradiographs were used to confirm this conclusion. Figure 6 is a microradiograph of the same inclusions seen in Figure 4 except that $CoK\alpha$ radiation was used rather than Cr radiation. $CoK\alpha$ radiation falls on the short wave side of the "K" absorption edge of manganese (Figure 1), and manganese rich areas are therefore very absorptive. It is apparent that the non-metallic centers which previously appeared darker than the iron matrix are now lighter. However, the manganese sulfide is still not as absorptive as the lead. It may therefore be concluded that manganese is concentrated in those volumes which previously had only been identified as being non-metallic.

The preceding microradiographs were prepared from steels that had been reduced in size. The inclusions were therefore elongated in the direction of rolling. Figure 7 illustrates the appearance of sulfide inclusions in a non-leaded steel before the ingot is reduced in size. The arrangement of the inclusions on a line, which corresponds to a sheet in the metal, is a result of concentration of the inclusions at the

Figure 6.   Microradiograph of a Leaded High Sulfur Steel. This microradiograph, prepared with CoKα radiation which falls on the short wavelength side of the absorption edge of manganese, includes the same inclusions examined in Figure 4. It is apparent that the centers of the inclusions are now lighter than the iron matrix. This results from using a radiation which falls on the top of the K-absorption edge of manganese, but not of iron. The centers therefore must contain manganese.

grain boundaries. Many of the same inclusions, when examined with CoKα radiation, are found to consist of at least two phases (Figure 8), one of which contains little or no manganese. This concentration gradient of manganese is also noted when a foil is prepared from a section perpendicular to the rolling direction of a reduced piece of steel. A microradiograph of such foil is shown in Figure 9. The inclusions are elongated in the direction perpendicular to the plane of the film. In most inclusions it is evident that the centers are either devoid of manganese or contain only a small amount of this element. The same inclusions are shown in Figure 10. This microradiograph was prepared with Ni radiation, which falls on the short wave side of both the iron and manganese absorption edges (Figure 1). The manganese phase and iron matrix are now almost indistinguishable, but the centers remain very non-absorptive. It may be concluded that the center phase does not contain iron either. The only other material in the steel in sufficient quantity to account for the inclusion centers is silica. It can be shown with other radiations that this center phase is indeed less dense than manganese sulfide, as would be the relationship of silica to manganese sulfide. This effect can be noted in Figure 7, which was prepared with a molybdenum target tube.
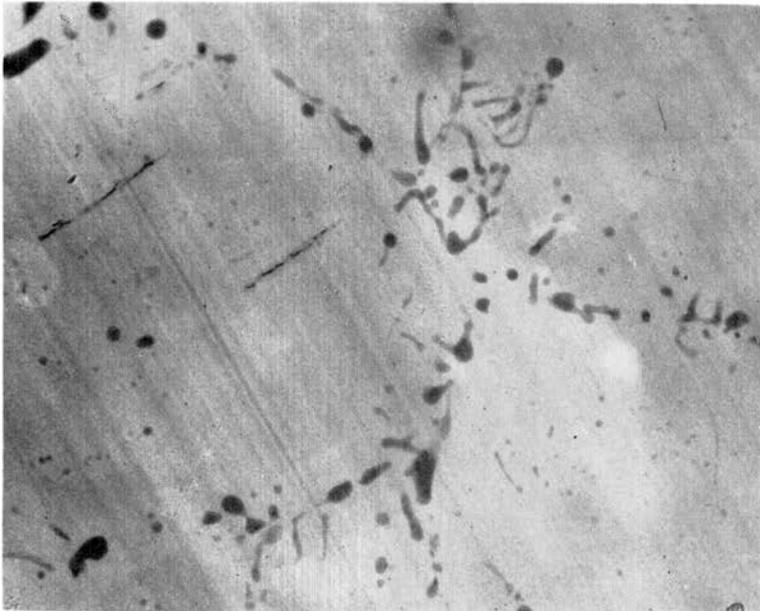
Figure 7.　Microradiograph of Inclusions in an Ingot. The microradiograph was prepared with MoKα radiation. The steel contained approximately .30% sulfur and .80% manganese. Magnification is X100.
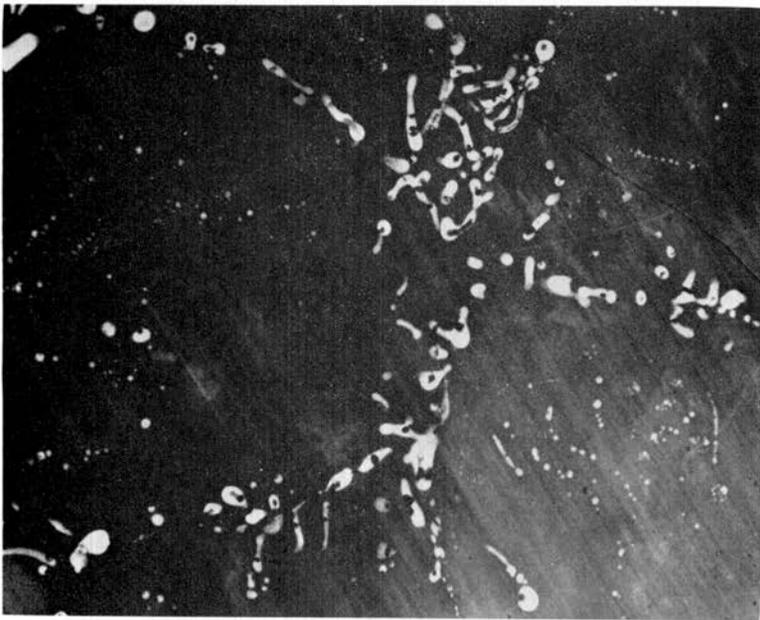

Figure 8.　Microradiograph of Inclusions in an Ingot. The same inclusions are examined as those in Figure 7 except that CoKα radiation was used to prepare the microradiograph. The concentration of manganese in the major phase of two phase inclusions is evident.
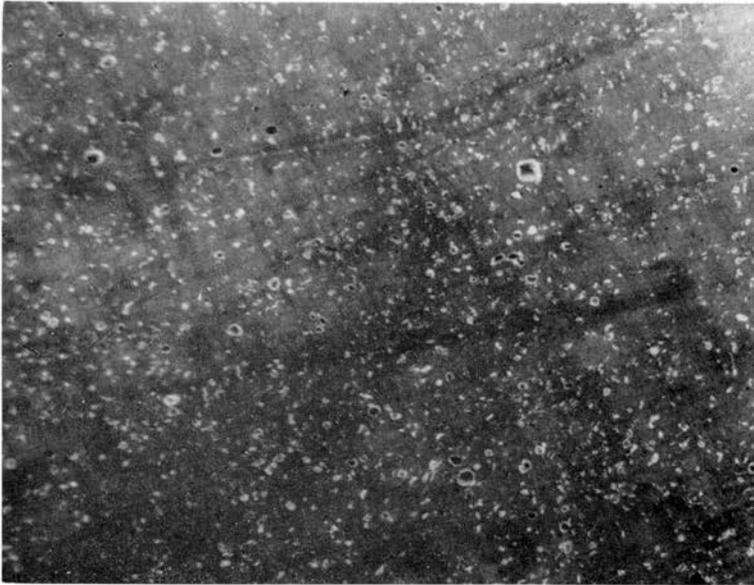
Figure 9.   Microradiograph of Inclusions in a High Sulfur Steel. The microradiograph was prepared with CoKα radiation. The inclusions are elongated perpendicular to the plane of the picture and approximate the thickness of the foil in length. The centers of the inclusions contain little or no manganese.
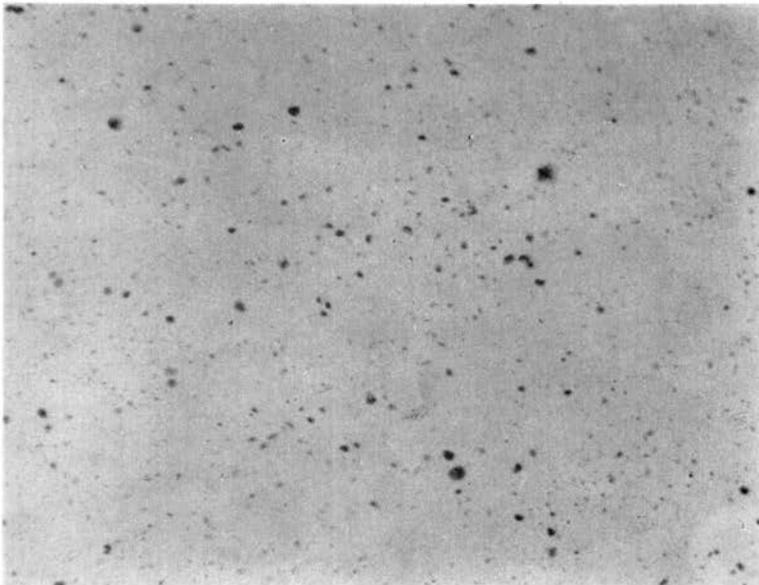

Figure 10.   Microradiograph of Inclusions in a High Sulfur Steel. These are the same inclusions shown in Figure 9. Unfiltered Ni radiation was used to prepare the the microradiograph. Note that those volumes which do not contain manganese have very low absorption coefficients. NiKα radiation falls on the K-absorption edge of both Fe and Mn. The steel matrix therefore appears very light.
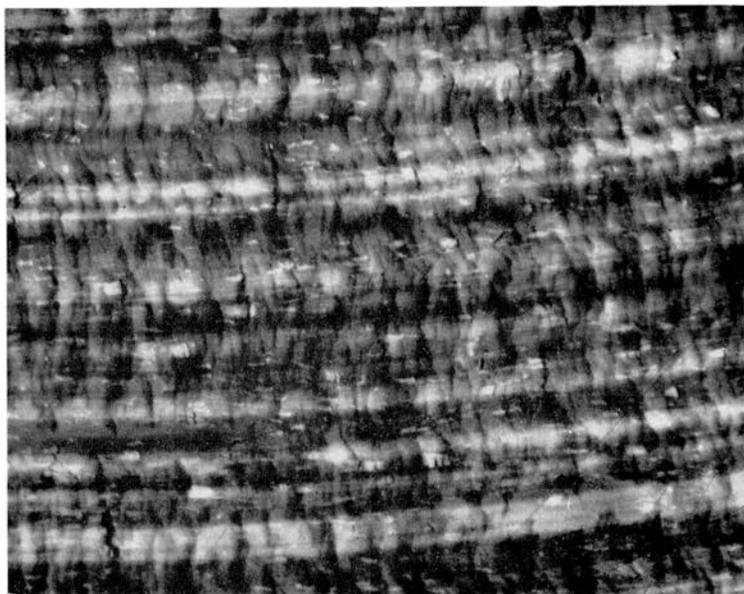
Figure 11. Microradiograph of a Steel Chip. The microradiograph was prepared with CoKα radiation. Magnification is 100X. Fissures and grooves appear dark. Machining took place in direction of streaks. Smearing of sulfide inclusions in the direction of machining is evident.
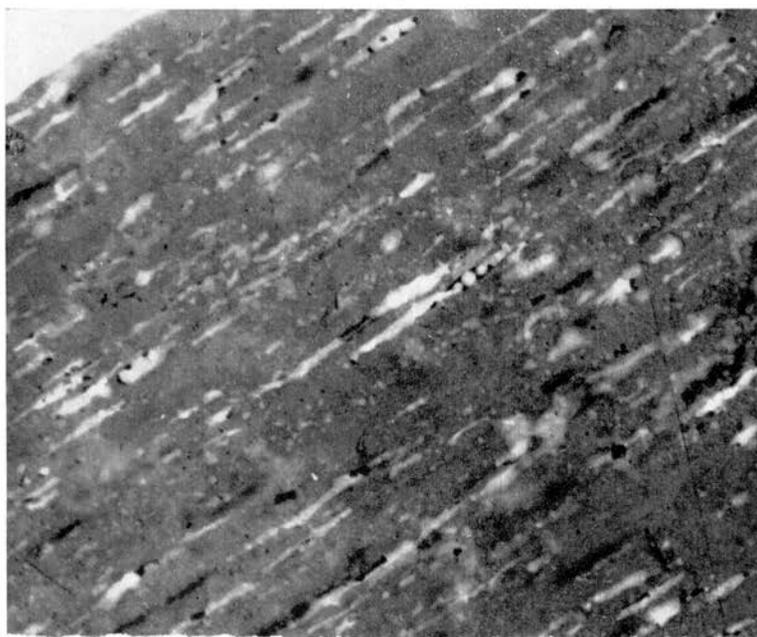

Figure 12. Microradiograph of Heated Inclusions (1000° C.). Manganese bearing volumes appear white because CoKα radiation, which falls on the short wave side of the manganese absorption edge, was used. Voids appear black. Note how some molten inclusions have coalesced to liquid droplets inside an inclusion near the center of the field.

Microradiographs can also be prepared of irregular sections, and the effect of mechanical or thermal treatments of the matrix on single inclusions can be noted. A microradiograph of a chip of steel produced in machining is shown in Figure 11.

Figure 12 is a microradiograph of a cold rolled steel which contains sulfide inclusions and has been heated to 1000° C. That melting occurred at this temperature is apparent from the appearance of the inclusions. This non-metallic matter in steel was found to be composed largely of manganese sulfide by x-ray diffraction. Pure manganese sulfide (MnS) does not decompose or melt at temperatures several hundred degrees in excess of the temperature of the heated foil. The lower observed melting temperature is probably a result of the solid solution of other elements in the manganese sulfide lattice.

Future comparative investigations of pure compounds and inclusions in steel may yield more information about the composition of precipitates in steel, and the chemical reactions which yield such precipitates.

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