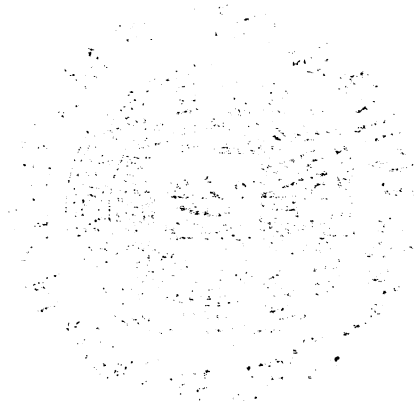


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INCLUSION DEFORMATION:
II. HARDNESS OF MnS-FeS MICROSTRUCTURES

by H. C. Chao, L. H. Van Vlack, F. Oberlin, and L. Thomassen*

ABSTRACT:

The hardness is determined for single crystals and polycrystalline MnS as a function of temperature, crystal orientation, and selected impurities. These data show that the hardness varies markedly with temperature, and that MnS is softer than steels at all temperatures below 1000°C (1832°F). However, it is not quite as soft as the ferrite phase alone.

The hardness of MnS is not increased measurably by solid solution with FeS. However, as the solubility limit is exceeded and FeS is present as a separate phase, there is a significant increase in hardness.

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INTRODUCTION

The variable deformation behavior of sulfide inclusions in steel has suggested that the inclusion hardness is not constant but varies with the several parameters of steelmaking operations. This paper reports a study of manganese sulfide hardnesses as a function of temperature, composition and microstructure. These hardnesses are then compared with those of steels.

PREVIOUS WORK

A companion paper⁽¹⁾ on the mechanism of fracture and deformation in MnS summarizes the previous work concerning the structure and composition of manganese sulfide as it is normally encountered in steel. It also reviews the previous work on the deformation and fracture of NaCl-type phases, and the structure of MnS. That study did reveal that manganese sulfide deforms by the primary glide system of $[[110]]$ $((110))$ plus a secondary glide on the $((111))$ planes. Further, it revealed that although the $((100))$ planes are the prime cleavage planes, fracture occurs during deformation on the $((110))$ planes as a result of the above glide systems.

The phase relationships in the MnS-FeS system were described early by Wentrup,⁽²⁾ in which he indicated a eutectic at 6 percent MnS and 1180°C, and a maximum solubility of 75 percent FeS in MnS at this same temperature. The solubility of MnS in FeS was

reported to be small. Some reproductions of Wentrup's diagram show a eutectic at 10 percent MnS. Various papers⁽³⁾ on nonmetallic inclusions in steel have revealed inclusion microstructures containing the two sulfide phases, FeS and (Mn,Fe)S; however there has been no work done to verify the early phase relationships sketched by Wentrup.

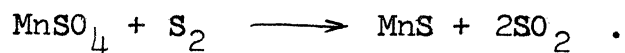
The crystal structures of FeS and MnS are surprisingly similar even though the two phases crystallize in the hexagonal and cubic systems respectively. The FeS has the NiAs-type structure, and the MnS has the NaCl-type structure.⁽⁴⁾ This means that the (0001) plane of FeS and the (111) plane of MnS are identical with a close-packed arrangement of sulfur ions. Further, the iron and manganese cations are present in six-fold interstices between the sulfur atoms in each case. The only difference in the two structures is the sequence of stacking of the close-packed sulfur planes. In the FeS this sequence is ABABABA..., while the sulfur stacking is ABCABCABCAB... in MnS.

The hot hardnesses of steels have been studied by Garofalo et al⁽⁵⁾ in the subeutectoid temperature range. In general, they show a significant reduction of hardness with increased temperatures. However, the ferrite of normal steels presents an exception in the 200 to 400°C range where there is some age-hardening arising from dissolved nitrogen and carbon.

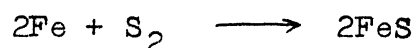
EXPERIMENTAL PROCEDURE

The experimental steps for the study of the hardnesses of MnS-FeS microstructures included the preparation of appropriately pure sulfides in both single crystal and polycrystalline forms, followed by hardness readings through the use of a microindenter at both ambient and elevated temperatures. In addition, it was considered desirable to check the phase relationships of Wentrup. (2)

Sulfide preparation. Manganese sulfide was prepared by two procedures. The first utilized a commercially prepared manganese sulfide which was melted and deoxidized with CS₂. This sulfide proved to contain about 1 percent calcium sulfide in solid solution.⁽¹⁾ Subsequently, purified manganese sulfide was prepared by using reagent grade MnSO₄, which was deoxidized by sulfur according to the reaction



The procedure for this operation is described in the companion paper.⁽¹⁾ Iron sulfide was prepared through the reaction



at 480°C. The iron was in the form of thin pure iron wire.

MnS-FeS samples were prepared by a combination of the purified MnS and FeS.

Hardness measurements. Hardness measurements were made on both single crystal and polycrystalline materials by indentation procedures (Fig. 1). The single crystals were prepared as described in

the paper on the mechanism of MnS deformation⁽¹⁾ while the polycrystalline materials were prepared by more rapid solidification. A Knoop indenter was used in the initial studies on the relationship of hardness with crystal orientation. A diamond or a sapphire pyramid indenter was used for all other measurements. The hot-hardness measurements were made with a modified Vickers machine under a vacuum. Because of the marked softening of the sulfide and metals at elevated temperatures, it became necessary to utilize lighter loads than the standard Vickers hardness loads of 10 kgs. The hardness readings for loads of 600 gm were calibrated against the standard readings utilizing aluminum, copper and iron of hardnesses comparable to the elevated temperature readings for manganese sulfide. Furthermore, wherever possible, the two loadings were checked at high temperatures against each other on MnS and carbon steel and were found to be satisfactory.

Phase relationships. The eutectic region of the FeS-MnS phase diagram was checked by normal sample quenching and micrographic procedures. To obtain the solid solubility limit the above procedure was utilized plus hot hardness measurements.

RESULTS AND DISCUSSION

Results will be presented as follows: (1) the hardness of MnS as a function of crystal orientation, temperature, and impurities; (2) the hardnesses of (Mn,Fe)S solid solutions;

(3) the hardnesses of (Mn,Fe)S-FeS microstructures; and (4) the phase relationships in the MnS-FeS system.

Hardness of MnS. The hardness on the (100) surface of pure MnS was 142 DPH. The hardnesses on the three most common planes of MnS are shown in Table I for selected Knoop indenter orientations. It is significant that there is more variation between the hardnesses of two different orientations on one plane than there is between planes. This difference is associated with the strong preference for deformation according to the slip system $[[110]]((110))$ which would be favored by appropriate indentation orientations.⁽¹⁾

When a pyramid indenter was used, there was very little difference in hardness observed between the single crystal and the polycrystalline MnS (Fig. 2). It cannot be concluded that the grain boundaries are ineffectual in resisting deformation in manganese sulfide. Rather, the indentation procedure for measuring hardness gives a stress pattern which is comparable to the complexity of the stress pattern that would arise in polycrystalline material.

The hardness of MnS decreases as the temperature is raised, as shown in Fig. 2. This is of specific interest when it is compared directly with the hardness of iron and steel (Fig. 3). Although the MnS is harder than the ferrite which is found in normal steels, it is softer than the microstructures which are present in most steels. Manganese sulfide is also softer than ferrite which has undergone precipitation hardening reactions in the 200 to 300°C

range. Finally, manganese sulfide has a hardness comparable to a carbon-free δ -iron, and less than a carbon-containing austenite at the lower end of the hot-working range. (Both the diamond and the ruby indentors fail to provide a satisfactory means of hardness measurements above 1000°C. The diamond indenter dissolves in the iron and the ruby indenter starts to undergo extensive plastic deformation.)

The presence of calcium within the manganese sulfide structure produces a measurable increase in hardness at all temperature levels up to 800°C (Fig. 4). Likewise, the presence of oxygen as an oxide precipitate in the grain boundaries increases the hardness.

Hardness of (Mn,Fe)S. Replacement of the manganese ions by iron ions made no significant difference in the hardness of the sulfide phase, as shown in Fig. 5. The contrast in the effects of calcium and iron ions on the hardness of MnS warrants some discussion. It is possible that the contrast arises from the difference in ion size ratio. The calcium ion has an approximately 17 percent larger radius than the manganese, whereas the iron ion has only a 9 percent smaller radius. However, it is equally probable that the contrast arises from the strongly ionic nature of the calcium ion as compared with the less ionic behavior of the more equivalent manganese and iron atoms. As such, dislocation movements around the calcium impurities would be restricted much more than through a crystal containing manganese and iron ions.

Hardnesses of polyphase sulfides. The polyphase sulfide of interest is the combination of $(\text{Mn,Fe})\text{S}$ and FeS . In Fig. 6 the curves of Fig. 5 are extended into the two phase region at lower temperatures. The increase in hardness corresponds closely, but not exactly, to the solubility limit as described by Wentrup.⁽²⁾ The explanation for this increase in hardness is shown in Fig. 7, which reveals a fine Widmanstätten precipitate of FeS within the MnS crystal. The Widmanstätten precipitate occurred only as 45° traces (and not as 90° traces) on the (100) surface of MnS . Therefore it is concluded that the precipitation planes within MnS are the $((111))$ planes. It is assumed that the coherency occurs on the (0001) plane in the FeS because the sulfur atoms can be common to the two phases. The reason for the increase in hardness with this precipitation is most probably the inability of the dislocation movements to change glide systems at the phase boundary.

The hardnesses of microstructures consisting wholly of FeS are difficult to measure because the FeS is extremely brittle as contrasted to the MnS . Thus fracturing was common under the indenter and a true reading is not obtainable. However, it is apparent that whenever FeS is present within a microstructure containing the NaCl -type phase of MnS , or $(\text{Mn,Fe})\text{S}$, that the hardness is increased. This is shown in Table II for several compositions at room temperature. It is to be concluded, therefore, that solid FeS is generally harder than solid MnS . (Hot shortness of steel production does not arise from the above brittleness; rather, hot shortness is associated with the low melting temperature of FeS .)

The FeS-MnS phase diagram. The phase relationships in the FeS-MnS system were checked within this study. The original diagram of Wentrup⁽²⁾ was corroborated with the eutectic temperature at $1181 \pm 6^\circ\text{C}$ and the eutectic composition at 6 percent MnS. The maximum solubility of FeS in MnS was found to be 72 percent as contrasted to 75 percent originally. This slight change is further supported by the hardness values of Fig. 6 which show second-phase hardening $50\text{-}100^\circ\text{C}$ above those temperatures anticipated from Wentrup's curves.

CONCLUSIONS

A summary of the main conclusions of this study are as follows:

(1) Single crystals of MnS have less variation of hardness between crystal planes than for different orientations on one crystal plane. Furthermore, the average hardness which is measured on any one plane is comparable to the hardness of polycrystalline MnS.

(2) The decrease in hardness of MnS with temperature is comparable to the decrease in hardness of steels with temperature. Although the hardness of MnS is greater than that of the ferrite phase in steels and comparable to the hardness of carbon-free γ -iron at higher temperatures, the hardness of MnS is less than the hardness of the total microstructure of carbon-containing steels at all temperatures which were studied.

(3) Although calcium in solid solution will increase the hardness of MnS, essentially no change is observed in the hardness of MnS when the manganese is replaced by iron.

(4) The hardnesses of sulfides increase measurably if the solubility limit of FeS in MnS is exceeded so that a two-phase microstructure results.

(5) The phase relationships of the FeS-MnS system were corroborated except for a slight change in the solubility limit of FeS in MnS.

ACKNOWLEDGEMENTS

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TABLE I

Hardnesses on Three Most Common MnS Planes
 Sample C of Fig. 4
 (Rockwell B units)

P l a n e	D i r e c t i o n *				
	[010]	[011]	[101]	[111]	[112]
(100)	81	86			
(101)	80		89	88	
(111)			79		79

* Direction of the long axis of the Knoop indenter.

TABLE II

DPH Hardness of FeS-MnS System at 20° C

% FeS	DPH
0	142
25	142
50	147
75	178

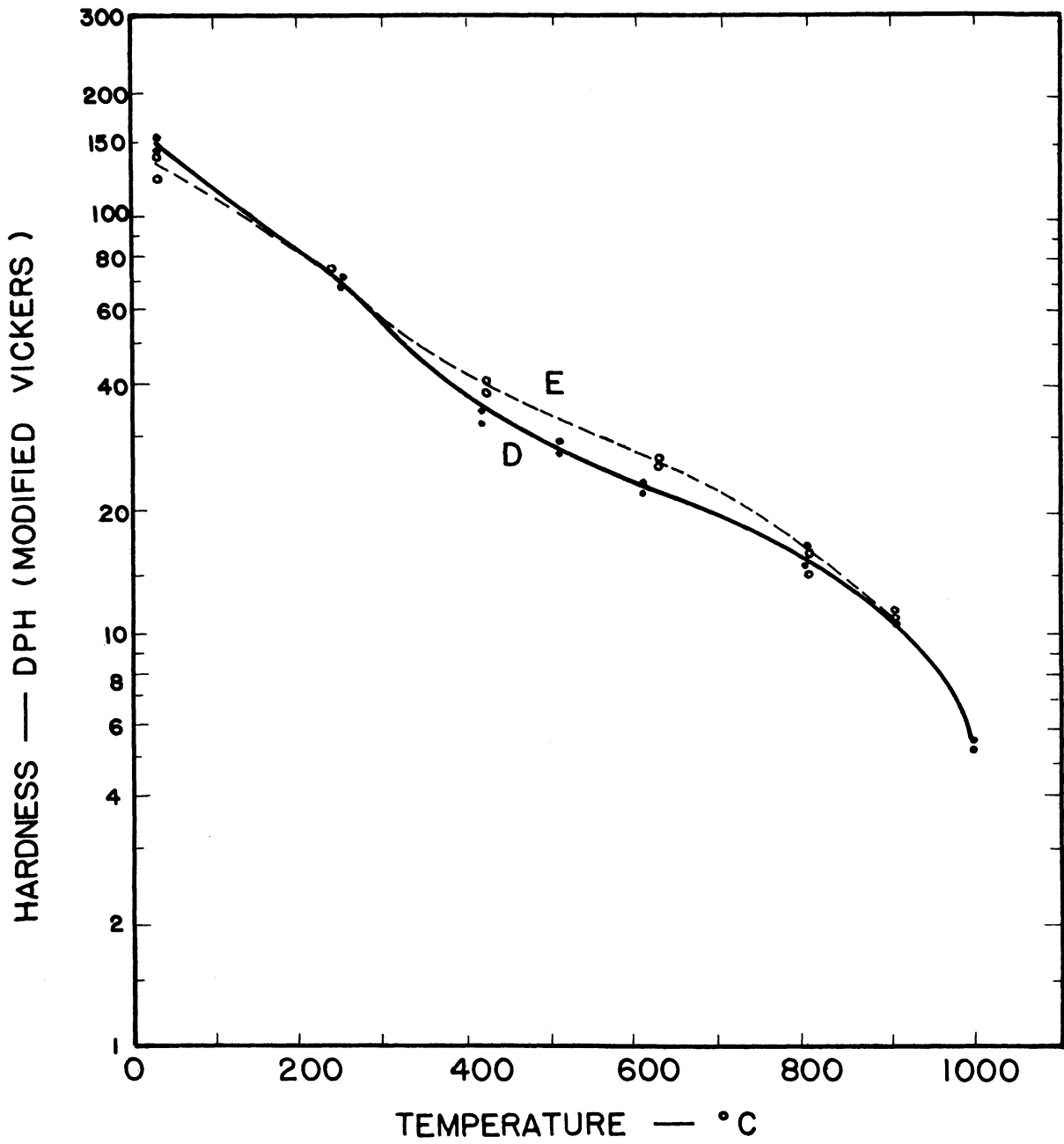


Fig. 2. Hardness vs. temperature.
 (E) Polycrystalline MnS
 (D) Single crystal MnS

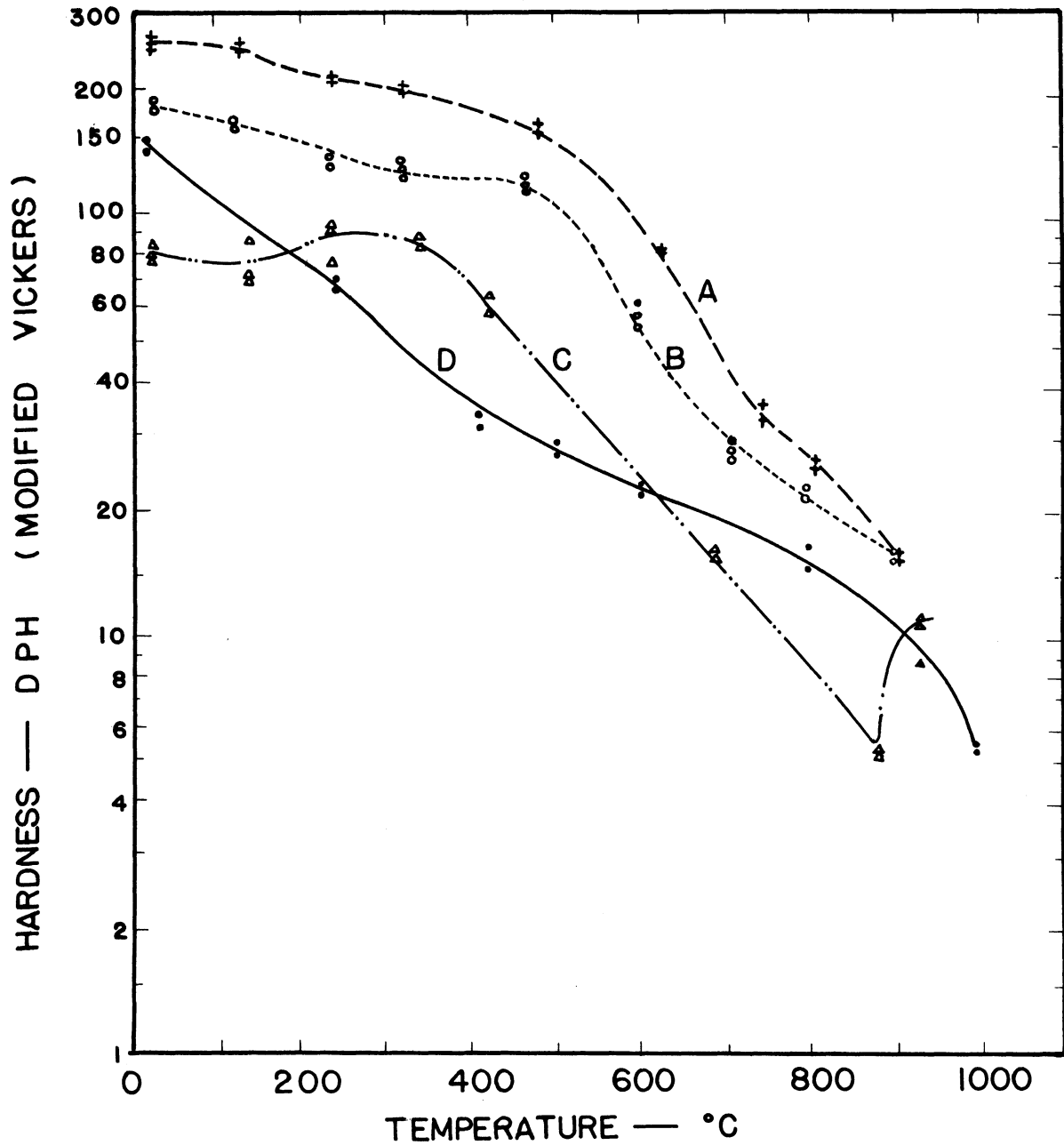


Fig. 3. Hardness vs. temperature.

- (A) 1080 steel
- (B) 1040 steel
- (C) Low metalloid steel
- (D) Single crystal MnS

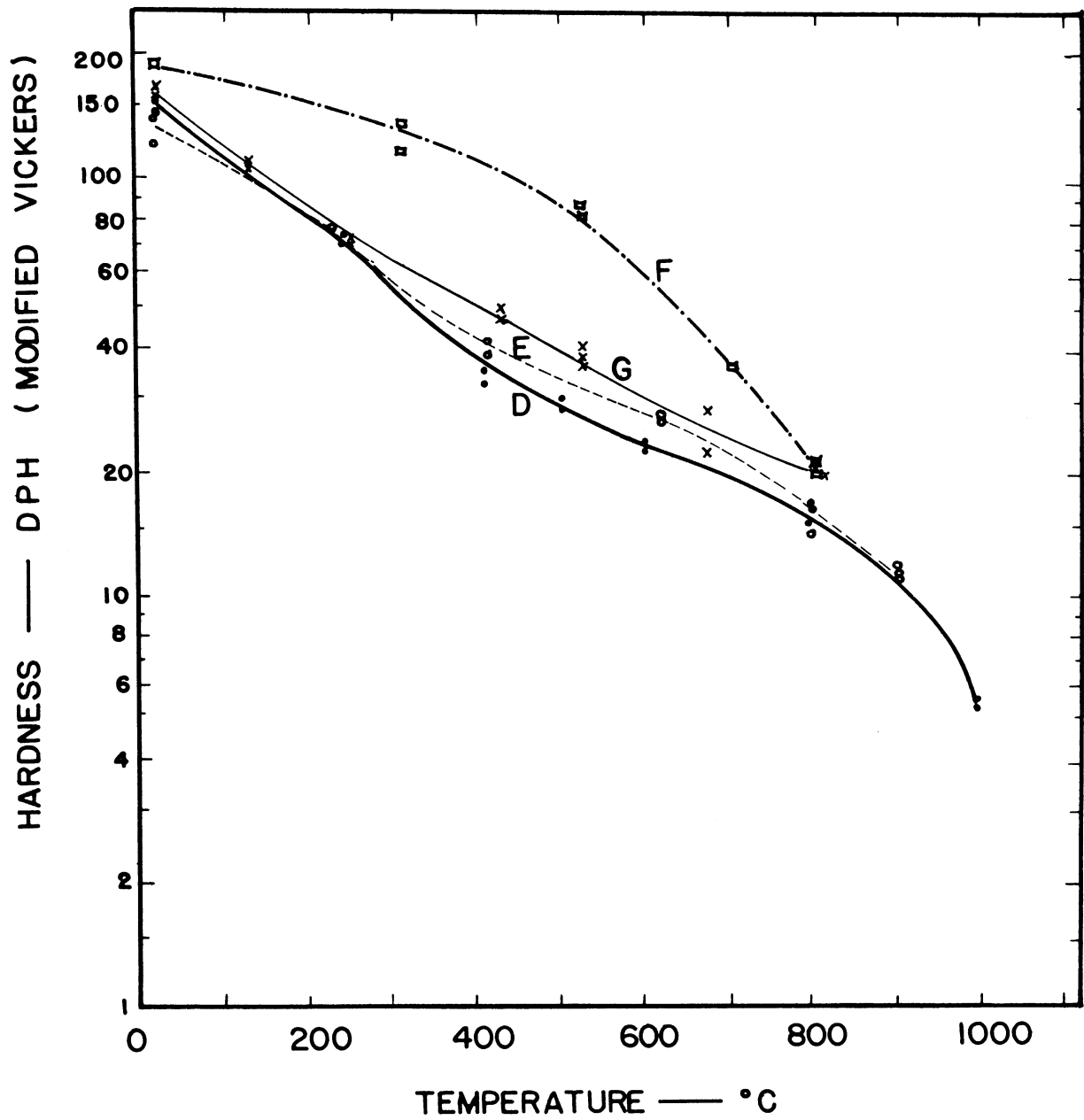


Fig. 4. Hardness vs. temperature.

- (D) Single crystal MnS (purest)
- (E) Polycrystalline MnS (purest)
- (F) Single crystal MnS (with Ca)
- (G) Polycrystalline MnS (with MnO)

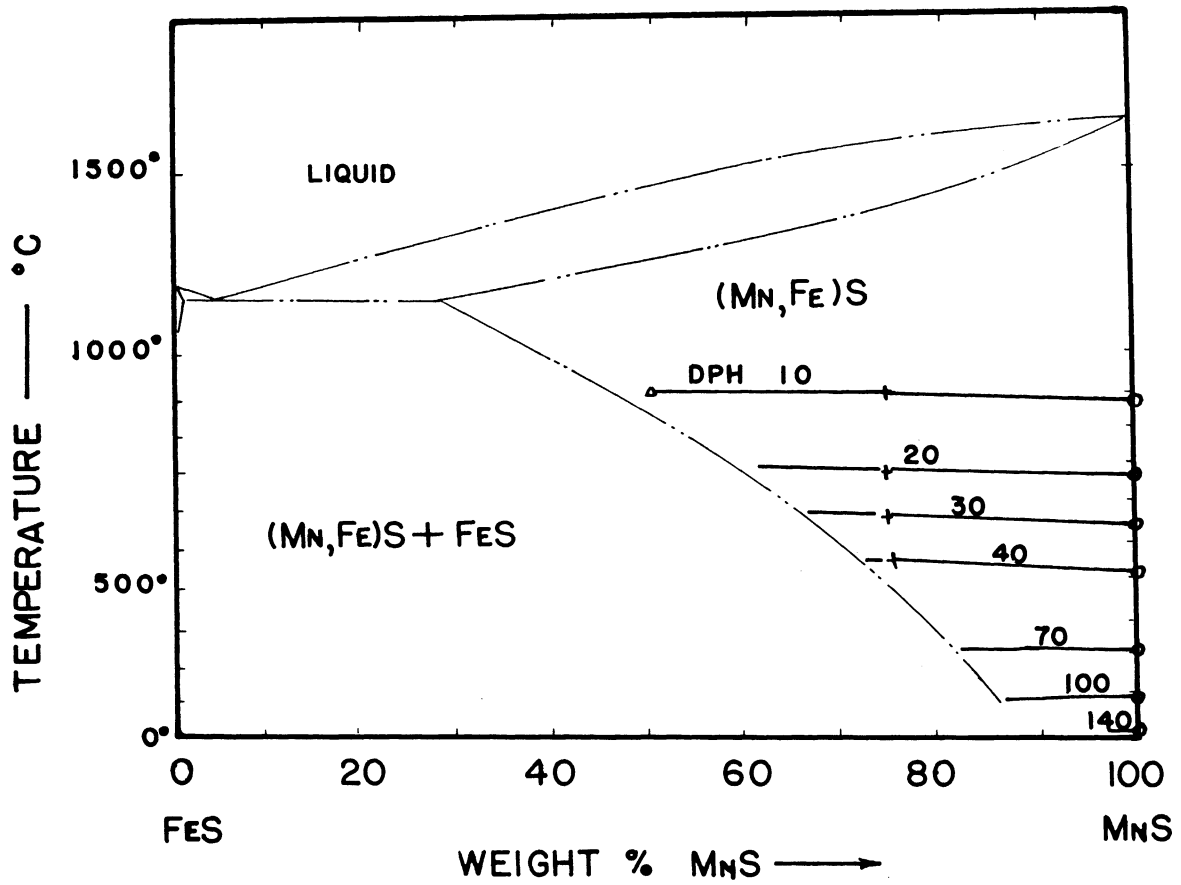


Fig. 5. Hardnesses of (Mn,Fe)S. There are negligible changes in hardness in the solid solution range.

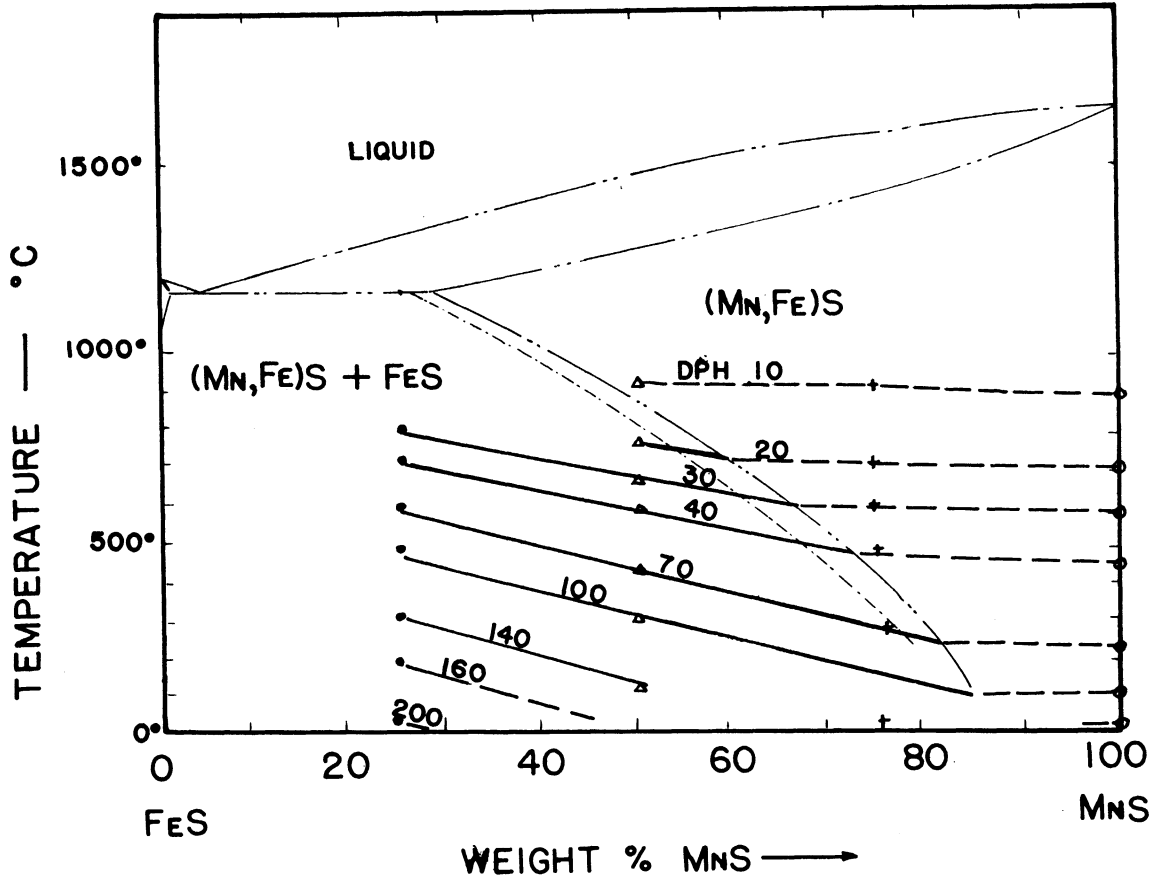


Fig. 6. Hardnesses of FeS + (Mn,Fe)S. The solubility limit of the FeS-MnS diagram of Wentrup⁽²⁾ has been modified slightly to compare to the changes in hardness. The hardness increases as the FeS phase content increases.

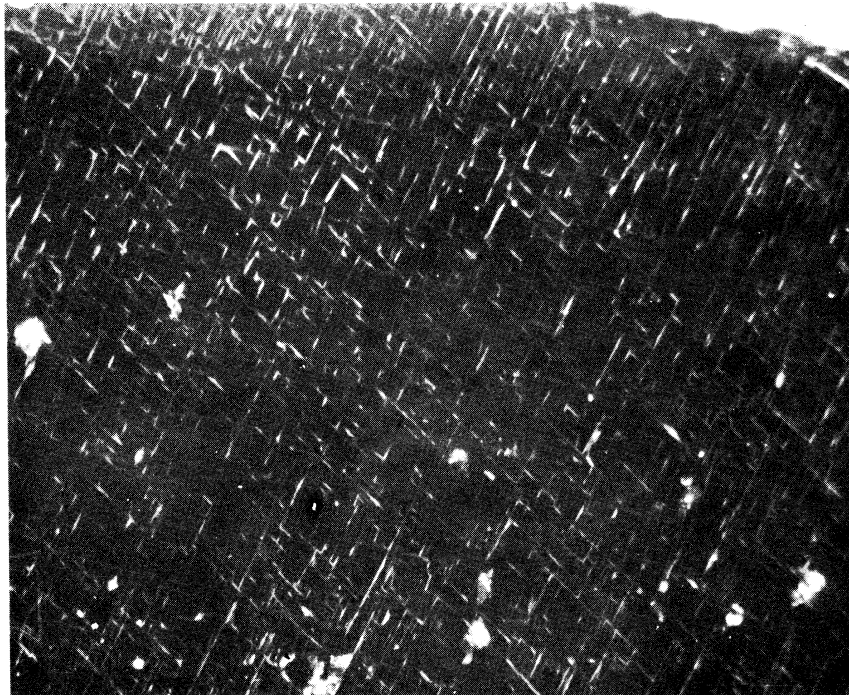


Fig. 7. Precipitation of FeS from (Mn,Fe)S. Example:
MnS/FeS = 50/50. Polarized light. X 250.

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