Mechanical Properties of Manganese Sulphides in the
Temperature Range between Room Temperature and 1000 °C

By Fumio MATSUNO,** Shun-ichi NISHIKIDA**
and Hisashi IKESAKI**

Synopsis
Manganese sulphide powders, prepared by a sulphur deoxidation of MnSO₄, were melted at 1700 °C in a graphite crucible, and then solidified into buttons, about 20 mm diameter and 15 mm long. Several kinds of bulk manganese sulphide with additives were prepared from powder mixtures of MnS and one of Al₂O₃, SiO₂, MnO, CaO, CaS, and FeS. In the temperature range from room temperature to about 1000 °C, their microhardness and nominal yield strength were measured and the following results were obtained,

(1) Purified MnS samples had almost the same hardness as those reported so far. Their nominal yield strength varied with temperature from about 9 kgf/mm² at room temperature to about 2 kgf/mm² around 1000 °C.

(2) Additions of impurities into MnS brought about increases in both hardness and nominal yield strength. The hardening is presumably caused by solid solution of oxygen and calcium. The nominal yield strength varied with temperature from about 11 to 12 kgf/mm² at room temperature, to about 2 to 5 kgf/mm² around 1000 °C depending on kinds of additives.

I. Introduction
Manganese sulphide inclusions in steels are plastically deformable during hot working. This brings about the elongation of MnS inclusions, leading to the situation that they sometimes cause harmful effects on various kinds of properties of steels, unless they are at a very low volume fraction or are of modified composition and properties. The extent to which a MnS inclusion deforms depends primarily on the ratio of the flow stress of the inclusion, which is proportional to hardness, to that of the matrix. Accordingly, numerous studies have concentrated on the relations between the relative degree of deformation of MnS inclusions and the hardness ratio of MnS inclusions to those of steels.

MnS inclusions in steels have invariably the NaCl type crystal structure (α-MnS), although it has been known that they can be precipitated from molten steel in three different morphologies, Types I, II, and III. Their deformability has been shown to increase progressively from Types I to III and this has been understood to arise from the difference in the oxygen content, increase of which has been reported to bring about hardening of MnS.

In addition to studies on MnS inclusions in situ, many kinds of bulk synthetic manganese sulphide have been studied to obtain their physical and chemical aspects of properties. Solid solubilities of various kinds of elements and compounds and their effects on hardness of MnS have been studied extensively. Mechanisms of deformation and fracture of single crystals of MnS have been well established.

Although numerous works have been done so far, on MnS inclusions as outlined above, there is still not enough data on mechanical properties of MnS, because the recent development of shape control techniques has brought about changes in composition of sulphide inclusions in steels. Thus, this study aimed to investigate the mechanical properties of MnS with and without various kinds of additives. For this purpose, polycrystalline MnS with and without additives were synthesized and their hardness was measured in the temperature range from room temperature to about 1000 °C. In addition, bend strength was assessed by using a three point bending test for some samples.

II. Experimental
1. Preparation of Manganese Sulphide
MnS powder was prepared by a sulphur deoxidation of MnSO₄ reagent of JIS special grade as shown in Fig. 1. This method was, in principle, the same as Chao et al.’s. MnSO₄, 20 to 30 g, was heated

![Fig. 1. Schematic illustration of MnS powder preparation apparatus.](image-url)
at 800 °C for about 3 hr in sulphur vapour, of which pressure was 1 atm. After cooling, it was mixed and reheated in the same way as before. This procedure was repeated at least twice to obtain highly purified MnS powder. As-prepared powders of MnS were dark green in colour and were composed of single α-phase. The lattice constant for the purified MnS was 5.225 Å which agreed well with the reported values.

As the sulphide would be oxidized with time to MnSO₄ if left in the powdered form with a large surface area, the prepared powder was melted at 1700 °C for 15 min and solidified in a graphite crucible, about 20 mm in inner diameter and 50 mm in depth. In order to prepare MnS samples with various kinds of oxides and sulphides, every additive was mixed into the prepared MnS powder immediately before melting so that the powder mixtures had the compositions shown in Table 1. Among additives, Al₂O₃ and SiO₂ were reagents of JIS special grade, respectively. MnO was prepared by heating MnO₂ reagent of JIS special grade at 1350 °C for 4 hr in Ar gas. CaO was prepared by heating CaCO₃ reagent at 1000 °C for 1 hr in air. CaS was prepared by heating CaCO₃ reagent at 1200 °C for 5 hr in 1%H₂S–10%H₂–Ar gas. FeS was obtained by precipitating ferrous chloride aqueous solution with ammonium sulphide aqueous solution.

MnS buttons obtained as described above were cut into pieces by a fret saw. Then, every piece was finished by grinding and polishing to a specimen with desirable dimensions for various kinds of measurements.

2. Examination of Samples

Some of samples for every system were examined microscopically and EMPA analyses were carried out on the matrix of manganese sulphide and precipitates as well. Hardness for every sample and bend strength for some samples were measured in the temperature range from room temperature to about 1000 °C.

In addition to manganese sulphide, samples of pure iron of which chemical compositions were shown in Table 2 were measured in terms of hardness and deformation stress in order to examine the accuracy of the measurement and make comparisons between MnS and iron. They were finished into specimens with the same size as those of MnS and annealed at 650 °C for 1 hr in 10%H₂–Ar gas atmosphere before the measurement to remove any strain induced by cold working.

1. High Temperature Hardness Measurement

A commercial high-temperature microhardness tester was used for the microhardness measurement. Specimens of manganese sulphides, 10×5×5 mm, finished by polishing, were heated to the desired temperatures up to 1000 °C in vacuum, about 2×10⁻⁵ Torr, and microhardness indentations were performed. Temperature control was made by a thermocouple spot-welded to the surface of specimen holder on which a specimen was installed by means of a screw. A diamond indenter of Vickers pyramidal form was used, and heated to the same temperature as the specimen. The load used was, usually, 100 g. A known rate of indenter lowering was used. The indenter was kept touching the specimen for 8 sec.

2. High Temperature Bend Strength Measurement

A three point bending test was used for the assessment of bend strength of manganese sulphide specimens. Two kinds of testing methods were employed. The first one was a constant strain rate bending test by means of a commercial tension tester with a load cell of maximum 50 kg. In the test, a specimen was installed in a device, as shown in Fig. 2. After evacuation, either Ar gas or 2%H₂–He gas was admitted into a quartz glass tube to protect the specimen from oxidation and its flow rate was maintained at about 1 l/min during the whole run. Argon gas was used for the bending test in the temperature range below 500 °C. Then, temperature was raised and stabilized to the desired one. Bending tests were carried out at a constant cross-head speed of 1 mm/min. Load–time curves changed from a straight line to a curve as shown in Fig. 4(a). The nominal yield strength for each specimen was calculated from the load, P, at the point where the straight

\[
\begin{array}{|c|c|c|c|}
\hline
\text{System} & \text{Sample} & \text{Added material} & \text{Amount of addition (wt%)} \\
\hline
A & A & - & - \\
B & B-1 & Al₂O₃ & 1.0 \\
& B-2 & Al₂O₃ & 2.0 \\
& B-5 & Al₂O₃ & 5.0 \\
C & C-1 & SiO₂ & 1.0 \\
& C-2 & SiO₂ & 2.0 \\
& C-5 & SiO₂ & 5.0 \\
D & D-1 & MnO & 1.0 \\
& D-2 & MnO & 2.0 \\
& D-5 & MnO & 5.0 \\
E & E-0.5 & GaO & 0.5 \\
& E-2 & GaO & 2.0 \\
& E-5 & GaO & 5.0 \\
F & F-1 & FeS & 1.0 \\
& F-2 & FeS & 2.0 \\
& F-5 & FeS & 5.0 \\
G & G-0.5 & CaS & 0.5 \\
& G-2 & CaS & 2.0 \\
& G-5 & CaS & 5.0 \\
\hline
\end{array}
\]

\[
\text{Table 2. Chemical compositions of pure iron.}
\]

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0027</td>
<td>0.01</td>
<td>0.014</td>
<td>0.003</td>
<td>0.0008</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Research Article
line changed into a curve, according to the following formula:

\[ \sigma(n, y) = \frac{3PL}{2wt^2} \] ......................(1)

where, \( \sigma(n, y) \): nominal yield strength (kgf/mm²) 
\( P \): load at the point where a load–time curve changes from a straight line to a curve 
\( L \): distance between the lower fulcrums, 6 mm 
\( w \): width of a specimen (mm) 
\( t \): thickness of a specimen (mm).

Measurements were carried out at least three times, usually five times, at a particular temperature. Every value quoted in the present report is a mean value of them. Specimens used were about 10 mm long, 5 mm wide, and 0.3 to 0.8 mm thick. Each specimen was finished by polishing finally on silicon carbide paper of grade 1200. The width and thickness of each specimen were measured at several points with a micrometer and mean values of them were used for the calculation of the nominal yield strength. Specimens were finished so that the differences in both width and thickness were within \( \pm 3 \% \) at every spot.

The second method of three point bending test was a constant load bending test by means of a commercial tester. As shown in Fig. 3, a specimen was installed in a device in which a load, 100 g, was put on the center of the specimen after balancing the weight of a loading rod with counter weights. Then, the specimen was heated at 15 °C/min in Ar gas stream. The displacement of the loading rod due to the bending of the specimen was detected by a differential transformer installed on the other side of the lever arm of a balance. Displacement–time curves revealed, as shown in Fig. 4-(b) for an example, that specimens started to bend at a certain temperature depending on the dimensions of specimens and their compositions as well. The temperature at which the bending began was defined, as shown in Fig. 4(b), by the intersection of two tangent lines which touched the displacement–time curve near the turning point, and the nominal yield stress at that temperature was calculated according to the formula (1). A specimen holder was made of quartz glass and the distance between the lower fulcrums was 10 mm. Dimensions of specimens were finished in the same way as those for the constant strain rate bending test.

**III. Results**

1. *Purified Manganese Sulphide*

Photograph 1 gives an example of microstructures of the sample A which was etched by an aqueous solution containing 1 vol\% of concentrated H₂SO₄, 1 vol\% of concentrated H₃PO₄, and 1 vol\% of a saturated solution of oxalic acid. Crystals were generally so large in size that some of them reached more than 10 mm as seen in Photo. 1(a). No phases other than manganese sulphide were observed microscopically. Chemical analyses revealed that sulphur contents of specimens were 37 ± 0.3 wt\%, in agreement with the stoichiometric composition, 36.9 wt\%.
Figure 5 gives microhardness values of the sample A, as a function of temperature. The present data agree well with Chao et al.'s and also with the hardness of actual MnS inclusions of Type I in a steel with a low oxygen content. This means that the sample A was equivalent to actual MnS inclusions, at least, in terms of hardness. As shown in Fig. 5, the sample A was larger in hardness than iron in the temperature range below about 200 °C.

Figure 6 shows the nominal yield strength of sample A and pure iron as a function of temperature. For MnS samples, the nominal yield strength was determined independently by the two different three point bending tests. Results obtained by the two methods showed a fairly good agreement, as seen in Fig. 6. The same result was also obtained in other MnS samples as described later. The nominal yield strength of sample A was about 9 kgf/mm² at room temperature and decreased gradually with the increase of temperature to about 2 kgf/mm² around 900 °C. Figure 6 shows clearly that the plastic deformation of purified MnS occurs at smaller stress than the pure iron in the temperature ranges below about 650 °C and over about 900 °C as well.

In the constant strain rate bending tests, load-time curves for manganese sulphide specimens changed clearly from a straight line to a curve in the temperature range over 325 °C. Below 300 °C, the duration for a curve was extremely short and specimens were usually doubled immediately after the elastic deformation. Fracture surfaces of specimens tested in this temperature range showed the typical mode of brittle fracture as shown in Photo. 2(a). In the temperature range over 325 °C, specimens were ruptured after considerable plastic deformations. When tests were terminated before specimens came to rupture, plastically deformed specimens were obtained, as shown in Photo. 3(a). Microscopically, numerous slip lines were observed, as seen in Photo. 3(c), at the outer part of curvature. Fracture surfaces of specimens tested at 325 °C were mostly the mode of brittle fracture. However, slip traces were observed in considerable parts of them, as shown in Photo. 2(b). This meant clearly that specimens were
doubled after some plastic deformation.

2. Manganese Sulphides with Additives

1. Microstructure

As graphite crucibles were used for melting samples at 1700 °C for 15 min, complex reactions occurred among manganese sulphide, additives, and carbon which crucibles were composed of. The melting temperature, 1700 °C, seemed to be high enough for such reactions as the oxidation of MnS by added oxides, e.g., MnS + CaO = MnO + CaS, and the reduction and carbonization of added oxides by carbon to proceed simultaneously. As a consequence, compounds other than MnS and additives were precipitated without exception in the samples with additives. They were analysed qualitatively by EPMA, resulting in Table 3.

Among compounds other than MnS and additives, manganese carbides, denoted as Mn-C, Mn-Al-C, and Mn-Ca-C in Table 3, were formed in all samples with additives except the sample F. As shown in Photo. 4, they were precipitated within grains and on grain boundaries as well. They were easily identified microscopically from their features that they looked like metallic particles at first and then coloured gradually if they were left in an atmosphere with humidity. As the ones in the system B contained small amounts of aluminium, and in the systems E and G with calcium, they are denoted as Mn-Al-C and Mn-Ca-C, respectively, in Table 3. In the case of system F, precipitated carbide was iron carbide, probably Fe3C, which precipitated mostly on grain boundaries and looked like metallic particles and never coloured like manganese carbides.

It was Al2O3 and MnO that were precipitated in the same phase as additives. As shown in Photo. 4(a), Al2O3 was precipitated as needle-like crystals, while it consisted originally of granular ones. This shows that they were not unreacted residues of additives, but precipitates from melt. The same way of precipitation was suggested in the case of MnO from the difference in crystal morphology between the raw material and precipitates, although no microstructures are given in the present report. In the case that SiO2 was an additive, most of precipitates were manganese carbide as shown in Photo. 4(b). In addition, manganese silicate was precipitated in C-2 and C-5, although its quantity was quite small. Oxide precipitates in the system E were manganese oxides with CaO as solid-solution, (Mn, Ca)O. They were smaller in amount than carbides, and were

<table>
<thead>
<tr>
<th>System</th>
<th>Added material</th>
<th>Kinds of precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Al2O3</td>
<td>Mn-Al-C, Mn-Al-C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al2O3, Al2O3</td>
</tr>
<tr>
<td>C</td>
<td>SiO2</td>
<td>Mn-C, Mn-Si-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn-C</td>
</tr>
<tr>
<td>D</td>
<td>MnO</td>
<td>Mn-C, Mn-C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MnO, MnO</td>
</tr>
<tr>
<td>E</td>
<td>CaO</td>
<td>Mn-Ca-C, Mn-Ca-C</td>
</tr>
<tr>
<td></td>
<td>(Mn, Ca)O</td>
<td>(Mn, Ca)O</td>
</tr>
<tr>
<td>F</td>
<td>FeC</td>
<td>Fe-C, Fe-C</td>
</tr>
<tr>
<td>G</td>
<td>CaS</td>
<td>Mn-Ca-C, Mn-Ca-C</td>
</tr>
</tbody>
</table>

* X : B, C, D, E, F, G.
Mn-C : manganese carbide
Mn-Al-C, Mn-Ca-C: manganese carbide containing small amount of aluminium and calcium, respectively
(Mn, Ca)O: manganese oxide with CaO as solid solution
Mn-Si-O : manganese silicon oxide
FeC : iron carbide, probably Fe3C

Table 3. Various kinds of precipitates observed in systems, B to G.

(a): B-1 (b): C-1 (c): E-0.5 (d): G-2
o: oxide, Al2O3
c: Carbide

Photo. 3. Microstructure of manganese sulphide A, bent at 400 °C at the constant strain rate bending test, etched by the same aqua as shown in Photo. 1.

Photo. 4. Microstructures of various kinds of manganese sulphides.

Research Article
usually observed on grain boundaries.

Microscopically, all of samples with additives were smaller in grain size than the sample A. Among them, the sample B was the smallest in grain size, as seen in Photo. 4. As a whole, grains decreased in size with the amount of additives.

Matrices of the sample A and those with the smallest amount of additives for the systems B to G were analysed quantitatively by EPMA, resulting in Table 4. All of samples with additives were less in manganese content than the sample A. In the sample C-1, silicon was found to be very small in content. In the case of sample F-1, iron was very small in content in the matrix because iron was mostly changed into iron carbide.

2. Mechanical Properties

Microhardness indentations were carried out at positions where no precipitates were observed microscopically. Results of the systems B and C were shown in Fig. 7, comparing with the sample A. In the temperature range below about 100 °C, these systems were almost the same in hardness as the sample A, while they were larger in the higher temperature range. It is noticed that differences in hardness becomes larger in the intermediate temperature range studied. Differences in hardness between B-1 and B-5 as well as between C-1 and C-5 were small.

Figure 8 gives hardness of the systems D and E as a function of temperature. In the case of the system D, of which additives was MnO, differences in hardness from the sample A were comparatively small in D-1 in the whole temperature range studied, while they are large in D-5, especially in the temperature range from about 400 °C to 800 °C. In the case of the system E, differences in hardness were large, even though the amount of the additives was 0.5 wt%, and they increase in the higher temperature range in the order of the amount of CaO added.

Figure 9 shows hardness of the systems F and G. The system F was almost equal in hardness to the system A, even though FeS was added by 5 wt%. The system G showed, as a whole, large increases in hardness. In this system, G-5 was the hardest. G-2 and G-0.5 were nearly the same in hardness in the whole temperature range studied.

The three point bending tests showed that samples abundant in precipitate lacked in reproducibility of the measurement. Some of them were too fragile to prepare test pieces. Accordingly, measurements were concentrated on samples of systems B, C, and G, of which amounts of additives were 1.0, 1.0, 0.5, and 0.5 wt%, respectively, resulting in Figs. 10 and 11 in which the nominal yield strength of them and the system A as well were given. As seen in figures, good agreements were observed between the two methods of three point bending test. As compared with the nominal yield strength of sample A, every sample revealed higher nominal yield strength in the lower temperature range. Samples of the systems B and C decreased their nominal yield strength with increased temperature and they were almost the same in nominal yield strength as that of purified MnS at over about 600 °C for B-1 and over 800 °C for C-1. Samples of the systems E and G were higher in nominal yield strength than the others in the whole temperature range studied.

When the constant strain rate bending tests were

---

Table 4. Compositions of manganese sulphide matrices determined by EPMA. (wt%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>65.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B-1</td>
<td>64.6</td>
<td>0.20</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C-1</td>
<td>64.8</td>
<td>&lt;0.01</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>D-1</td>
<td>65.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>E-0.5</td>
<td>64.7</td>
<td>—</td>
<td>0.39</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>F-1</td>
<td>65.2</td>
<td>—</td>
<td>—</td>
<td>&lt;0.01</td>
<td>—</td>
</tr>
<tr>
<td>G-0.5</td>
<td>64.2</td>
<td>—</td>
<td>0.25</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

---

Fig. 7. Microhardness, Hv, of manganese sulphides of B and C systems as a function of temperature.

Fig. 8. Microhardness, Hv, of manganese sulphides of D and E systems as a function of temperature.

Fig. 9. Microhardness, Hv, of manganese sulphides of F and G systems as a function of temperature.
terminated before specimens came to rupture, it was possible to obtain plastically deformed specimens when testing temperature was over 500 °C for the systems B and C, and over 700 °C for the systems E and G. In these temperature ranges, the time from the beginning of plastic deformation to the rupture was prolonged with increased temperature. As a whole, the temperatures at which specimens with additives began to deform plastically were higher than that of the purified MnS by about 200 to 400 °C.

IV. Discussion

1. Preparation of Samples

In the present study, samples were melted in graphite crucibles at 1700 °C for 15 min. As a consequence, many kinds of compounds were formed in samples with additives, as summarized in Table 3. In order to understand these results, chemical reactions involved in the present study will be discussed in the following on the basis of the free energy diagrams for oxides, sulphides, and carbides.19

(A) Sulphide-C systems: Reactions and their approximate standard free energy changes, ΔG°, at 1700 °C are:

2Mn + S₂ = 2MnS
ΔG° = -70 kcal

2Fe + S₂ = 2FeS
ΔG° = -30 kcal

2Ca + S₂ = 2CaS
ΔG° = -160 kcal

7/3Mn + C = 1/3Mn₇C₃
ΔG° = -15 kcal

3Fe + C = Fe₃C
ΔG° = -1 kcal

1/2Ca + C = 1/2CaC₂
ΔG° = -10 kcal

Combinations of (2) and (5), (3) and (6), and (4) and (7), give:

7MnS + 3C = Mn₇C₃ + 7/2S₂
Δ(ΔG°) = +200 kcal

6FeS + 2C = 2Fe₃C + 3S₂
Δ(ΔG°) = +88 kcal

2CaS + 4C = 2CaC₂ + S₂
Δ(ΔG°) = +140 kcal

The reactions (8) to (10) mean that sulphides are more stable than carbides at 1700 °C.

(B) MnS-oxide systems: According to the free energy diagram19 shown in Fig. 12 for the reaction:

2MeO + S₂ = 2MeS + O₂
Δ(ΔG°) = +2.3RT ln(P₅⁰/P₈₁)....(11)

oxides, which produce sulphides with smaller Δ(ΔG°) than 2 MnS, are able to change into sulphides by the reaction (11). Among Al₂O₃, SiO₂, MnO, and CaO, it is CaO that can change into sulphide at 1700 °C.

(C) Oxide-C systems: Figure 13 gives the free energy changes, Δ(ΔG°), for the reaction:

2MeO + S₂ = 2MeS + O₂
Δ(ΔG°) = 2.3RT ln(P₅⁰/P₈₁)....(11)

In the system Me₃C-O with the existence of excess carbon, the partial oxygen pressure is determined by the reaction:

2CO = 2C + O₂ ....(13)

The dotted line in Fig. 13 shows the Δ(ΔG°) for this reaction. Reactions (12) and (13) give:
2MexO + 2(y + 1)C = 2MexC + 2CO  
...........................(14)

The free energy changes of the reaction (14) are easily calculated from Fig. 13. The oxides are stable in the area above the dotted line, while carbides are stable under the dotted line. According to Fig. 13, MnO and SiO₂ can change into carbides at 1,700 °C, while Al₂O₃ and CaO can not change.

In the present study, some of results were in good agreement with the thermodynamic discussions described above, while some of them are not. This is partly because the thermodynamic discussions are limited to reactions between two compounds. Each system in the present study will be understood as follows:

System A: The thermodynamic data predict that no reactions occur between MnS and carbon at 1,700 °C. This explains well the microstructure of sample A in which there were observed little compounds other than MnS microscopically. This implies that the preparation of MnS powder was good enough to prohibit the formation of compounds other than MnS.

System B: According to the thermodynamic data shown in Fig. 12 and Fig. 13, Al₂O₃ can change to neither sulphide nor carbide, while carbides including Mn and Al were observed in this system in addition to Al₂O₃. According to the phase diagram of Al₂O₃–Al₄C₃ system, however, there are two intermediate compounds, Al₄O₄C and Al₂OC, between Al₂O₃ and Al₄C₃. It seems that these oxi-carbides may be formed as intermediate compounds and they may help Mn–Al–carbides to be formed.

System C: SiO₂ can not change into sulphide while it can change into SiC as shown in Figs. 12 and 13. However, SiC was not found in this system. Moreover, silicon was found to be very small in content in the matrix of this system as shown in Table 4. As well known, SiO₂ turns into volatile compounds such as SiO in the reducing atmosphere at high temperature. It seems that some of such volatile compounds may contribute to the oxidation of MnS which, in turn, leads to the formation of Mn–carbide.

System D: MnO can easily change into carbide at high temperature as seen in Figs. 12 and 13. This is the reason why manganese carbide were observed in most of systems with additives.

System E: CaO can oxidize MnS and change itself into sulphide as seen in Fig. 12, resulting in the formation of MnO. (Mn, Ca)O observed in this system may be formed as a result of this reaction as well as a solid solution reaction of MnO with CaO, which still remains unreacted. The carbide, Mn–Ca–C, may be resulted in by the reaction between (Mn, Ca)O and carbon.

System F: FeS can not change to carbide thermodynamically, while Fe₃C was observed in this system. It seems that this was probably by the low purity of FeS which was prepared by a precipitation method from an aqueous solution. The fact that Fe₃C was formed in MnS implies that FeS used was probably full of iron oxides.

System G: CaS can not change to carbide. A solid solution with CaS is expected to be formed, as MnS has been shown to have a wide composition range of solid-solution with CaS. In this system, the compound other than MnS was manganese calcium carbide, Mn–Ca–C, as shown in Table 3. This carbide must be formed from oxide impurities, probably Ca(OH)₂ which is formed inevitably in the CaS powder by the attack of humidity, in the similar way as the system E. The content of manganese–calcium carbide of this system was less than the other systems with additives as shown in Photo. 4, meaning that CaS used was comparatively of high purity.

2. Mechanical Properties

1. Microhardness

The hardness of α-Fe and γ-Fe shown in Fig. 5 is in agreement with the reported data. This shows that the measurements were done with accuracy.

In the case of the sample A, its microhardness was in good agreement with Chao et al.'s over the whole temperature range studied, as shown in Fig. 5. As the preparation method of MnS of the present study was basically the same as theirs, this shows that MnS used in this study was the same, at least, in hardness as Chao et al.'s.

Any samples except the system F were larger in hardness than the sample A as shown in Figs. 7 to 9. As described earlier, many precipitates were formed in MnS matrices. Therefore, their effects on hardening must be discussed first. As well known, hardening or strengthening of materials is, in general, prompted by hindering dislocations to move or multiply in materials. Such situations are accomplished by: (i) decreasing in grain size, (ii) solid-solutioning of other elements, (iii) precipitation and dispersion of other phases, (iv) strain induced by working, (v) ordering of the crystal lattice, and so on.

In the case of samples with additives, samples are smaller in grain size than the sample A and are full in precipitates. Moreover, they contain some elements other than Mn and S as shown in Table 4.
Accordingly, mechanisms, which may contribute to the hardening observed in the present study, seem to be either one of (i) to (iii) or any combinations of them. Among these, however, the effect of grain size seems to be less important. This is because traces of indentations were usually much smaller in size than individual grain of samples. In addition, indentations were carried out avoiding positions where precipitates were observed microscopically. So, it is also expected that the effect of precipitates is less important, although there still remain uncertainties that small sized precipitates which can hardly be observed by an optical microscope or precipitates existing internally may have effect on hardening. From above discussions, it can be expected that increases in hardness in the systems B to E and G are probably derived from the solid-solution hardening.

With regard to the solid-solution hardening of MnS, extensive studies have been done so far. The solid solubilities of 1st and 2nd long period transition elements in α-MnS at 1 100 °C, and their effects on microhardness at room temperature have been examined. These elements have been shown to bring about increases in hardness of (Mn, Me)S phase compared with MnS. When calcium is in solid solution, it has been reported that MnS increases in hardness. This has been confirmed with synthesized samples with 1 wt% Ca in the temperature range up to 800 °C and with various amounts of MnO at room temperature. Chao et al. have shown that pure manganese sulphide can dissolve up to 1.7 wt% MnO at the eutectic temperature of 1 232 °C. Furthermore, they have measured the hardness of MnS containing detectable amount of MnO at temperature up to 800 °C and observed some increase in hardness.

Although oxygen dissolved in MnS is hardly detected quantitatively, the fact that considerable amounts of manganese carbide were formed in the systems B and C suggests that Al₂O₃ and SiO₂ react with MnS respectively at 1 700 °C probably through carbon’s help. As a result of this, Al and O, or Si and O, may dissolve into MnS in the systems B and C respectively, and this may increase the hardness of MnS. In the case of system B, the difference in hardness is small between B-1 and B-5, as shown in Fig. 7(a). This is probably because reactions among Al₂O₃, MnS, and C proceed slowly and the difference in amount of dissolved Al and O is small between them. In the case of system C, the difference in hardness is also small between C-1 and C-5. This is probably because the reaction between SiO₂ and C proceeds rapidly and, as a consequence, Si escapes from the sample as volatile compounds, resulting in the small difference in amount of dissolved Si and O. This presumption agrees with the fact that Si was very small in content in this system.

In the case of system D, the difference in hardness between D-1 and D-5 seems to show the effect of oxygen. The reason why D-5 was larger in hardness than D-1 is probably that the former is larger in oxygen content than the latter.

In the system E, an additive was CaO which can change into CaS through the reaction between CaO and MnS thermodynamically. So, increases in hardness shown in Fig. 8(b) may be caused by both CaO and CaS. As compared with the system G of which additive was CaS, the system E was a little larger in hardness than the system G. It seems that the samples of the system E are solid solutions with both CaO and CaS, while those of the system F are solid solutions only with CaS. Differences in hardness between them are presumably caused by this difference in composition.

When an additive was FeS, the extent of hardening was comparatively small even when it was added by 5 wt%, as shown in Fig. 9(a). This is mostly because iron dissolved in MnS was small in content. As discussed before, FeS used was presumed to be of low purity. It seems that this caused the low content of iron in MnS, resulting in a slight change in hardness compared with the sample A.

2. Deformability

The plastic deformability of α-MnS single crystals, which have the NaCl type structure, has been studied by means of a diamond hardness indentor. It has been well established that α-MnS has the primary glide system of {110}⟨110⟩, which is commonly observed in all reported rock salt-type crystals such as NaCl, LiF, MgO, and so on, and that a secondary glide system involving {111} plane is developed subsequent to {110} fracturing in α-MnS, unlike many other NaCl-type materials. It has also been shown that slips occur even at room temperature in the case of α-MnS single crystals.

In the constant strain rate three point bending test, plastically deformed samples were obtained in the temperature range over 325 °C for the sample A, while this was accomplished in the temperature range over 500 °C for the systems E and G. In the sample A, specimens were not single crystals, but polycrystals although they were of good purity. This seems to be the reason why they did not show any plasticity in the temperature range below 300 °C. The other samples were also polycrystals which were smaller in grain size than the sample A, and they contained, furthermore, many precipitates. These seem to increase the temperature ranges in which plastically deformed samples were obtained.

3. Nominal Yield Strength

As shown in Figs. 10 and 11, the nominal yield strength increased in the case of samples with additives. As compared them with their hardness values, it is noticed that the nominal yield strength corresponds approximately to the hardness. This implies that samples are strengthened mostly by solid-solution of other elements such as O and Ca, as described earlier, although there still remain uncertainties that very small precipitates, which are unable to observe through an optical microscope, may contribute to the strengthening. Among additives, CaO and CaS were the most prominent in hardening and strengthening. These effects seem to be utilized partly in the recent developed calcium treatment of...
Numerous studies have been concentrated so far on the relations between the relative degree of deformation of MnS inclusions and the hardness ratio of MnS to steel.\(^1\)\(^-\)\(^7\) The extent to which a MnS inclusion deforms has been reported to be superior to the steel matrix in the temperature range where MnS is smaller in hardness than steel matrix. It appears that this can also be explained in terms of the nominal yield strength of both phases.

**V. Conclusion**

Several kinds of bulk polycrystalline manganese sulphide were synthesized and studied on their microhardness and nominal yield strength comparing with pure iron in the temperature range from room temperature to about 1 000 °C. Results are summarized as follows.

1. Purified manganese sulphide samples were almost the same in hardness as those reported for bulk synthesized α-MnS and actual MnS inclusions in steels as well, in the temperature range studied. Their nominal yield strength varied with temperature from 9 kgf/mm\(^2\) at room temperature to about 2 kgf/mm\(^2\) around 1 000 °C.

2. Bulk manganese sulphide samples prepared from powder mixtures consisting of manganese sulphide and any one of additives of \(\text{Al}_2\text{O}_3\), \(\text{SiO}_2\), \(\text{MnO}\), \(\text{CaS}\), and \(\text{FeS}\), contained compounds other than MnS, and were larger in hardness and nominal yield strength than the purified one. Among additives studied, \(\text{CaO}\) and \(\text{CaS}\) had the largest effect on hardening and strengthening of manganese sulphide.

**Acknowledgements**

The authors would like to express their sincere gratitude to Dr. K. Nishioka, Managing Director, General Manager of Central Research Laboratories of Sumitomo Metal Industries, Ltd., for the permission of publishing the present paper. They also would like to acknowledge the continuous encouragement and helpful guidance from Dr. F. Terasaki, Assistant General Manager of Central Research Laboratories, and Dr. Y. Ohmori, Assistant to General Manager.

**REFERENCES**