THE MnSe-MnS SYSTEM

by

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Abstract:
    Manganous selenide and manganous sulfide form
a continuous solid solution at all temperatures
below the solidus. The system is azeotropic with a
minimum at 1510°C near 10 mole percent MnS.
    Although this series has a NaCl structure, the
central portion has a diffraction pattern with a
false appearance of being simple cubic because the
average anion atomic number is 25, the same as
manganese. The lattice constant has a negative
deviation from ideality.
    The MnSe inclusion found in selenium treated
steels will dissolve sulfur which is present to
give Mn(Se,S).

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INTRODUCTION

Resulfurized steels have intentional additions of sulfur
so that the machinability is improved. The sulfur combines
with manganese in the steel to form MnS inclusions which are
dispersed throughout the steels. The exact mechanism by
which MnS improves the machinability is not fully understood;
however, there is no doubt that the deformation character-
istics are important. The deformation mechanism is well
understood[1] and is closely related to the NaCl-type crystal
of the MnS.

Selenium and tellurium are also added to steels for
machinability enhancement. Like sulfur, selenium combines
with manganese to give MnSe. Much less is known, however,
about the deformation of MnSe except to surmise that it is
comparable to MnS because they have related crystal structures.
This fact has suggested that the two might form solid
solutions with each other, particularly since some sulfur is
always present in steels to which selenium is added. The
purpose of this study was to determine the phase relation-
ships in the MnSe-MnS system. This information will then be
available in analyzing the selenium-sulfur relationships in
free-machining steels.

RELATED SYSTEMS

Both the MnO-MnS and MnSe-MnTe systems have been studied
previously. The MnTe-MnS system is currently being studied by
the present authors.

MnO-MnS systems. Manganous oxide (manganosite) and
manganous sulfide (alabandite) both have an NaCl-type structure.
Early estimates by Wentrup[2] suggested a rather extensive solid
solution of MnS in MnO, and MnO in MnS. This would be by anion
substitution. A eutectic was assigned at 1280°C (2345°F) and

50 w/o MnS (45 m/o MnS).

Later studies by Chao et al[3] revealed that the anion substitution was much more limited than previously expected, being less than two percent. The maximum sulfur substitution for oxygen in MnO was almost equal to the limit of oxygen replacement of sulfur in MnS. The eutectic temperature and composition,--1232°C (2252°F) and 64 w/o MnS (60 m/o MnS),-- also varied somewhat from Wentrup's report. The rather limited mutual solubility of MnO and MnS could lead one to anticipate possible limited solubilities in the MnSe-MnS.

MnSe-MnTe system. These two Mn-VI compounds have been studied by Panson and Johnston[4]. Manganous telluride has a stable NiAs structure below 1040°C where MnTe transforms to the NaCl structure. The above authors show a complete series of solid solutions between MnSe and the high temperature form of MnTe. The solidus and liquidus were not determined. An expanding two-phase field drops from the MnTe transformation temperature until at 500°C a maximum of only 12% of the selenium ions can be replaced by tellurium and only 20% of the tellurium ions can be replaced by selenium. The greater solubility of tellurium in MnSe than sulfur in MnO may be attributed in part (a) to the greater polarizability of the heavier group VI ions, and (b) to the fact that the radius of the Te^{2+} ion is only 10% larger than the radius of the Se^{2+} ion, whereas the S^{2+} ion is 24% larger than the O^{2+} ion (Goldschmidt radii).

EXPERIMENTAL

MnSe-MnS compositions were prepared by mixing and compacting high purity powders of a 1/1 stoichiometric ratio of manganese and (selenium plus sulfur). The powders were reacted in a graphite crucible in an evacuated pyrex tube which was heated to 600°C for one hour. This compact of MnSe,

and MnS was then melted under a vacuum in a graphite crucible
so a non-porous solid resulted. The success of the above
technique depends upon the controlled reaction between
manganese and the Se + S so that the heat of reaction does
not rupture the tube. A graphite crucible within the pyrex
tube proved to be an effective heat sink.

Microscopic observations and Debye-Scherrer x-ray
powder diffraction data were used in the analysis of the
samples. X-ray data for the MnSe and MnS end-members
matched National Bureau of Standards reported by ASTM.[5]

RESULTS AND DISCUSSION

A complete series of solid solutions forms in the MnSe-MnS
system as shown in Fig. 1. There was no evidence of phase
separation at intermediate temperatures. The system is
azeotropic with a minimum near 10 mole percent MnS and at
1510°C, which is 25°C below the melting point of pure MnSe.

The lattice parameter of the solid solution has a
negative variation from ideality as shown in Fig. 2. The
higher polarizability of the large Se^{2+} ion may account for
this. In qualitative terms, the Mn-S interatomic distance is
less variable than the Mn-Se interatomic distance, thus
giving a greater than proportional reduction in the lattice
constant.

The sharpest diffraction lines of samples quenched from
the liquid-solid range were used with the data of Fig. 2 to
establish the solidus compositions of Fig. 1.

Diffraction data for the 50/50 MnSe/MnS composition
appeared to give a simple cubic structure with a lattice
constant of 2.645A because the average atomic number of selenium
and sulfur (34 and 16) is 25,--the atomic number of manganese.
This supports the interpretation of anion substitution. The
NaCl lines which were extinguished because of this coincidence

are still sufficiently weak in 75/25 compositions so they may
be overlooked except by careful observation. This fact should
be considered in all studies of Mn(Se,S) inclusions.

The solubility contrasts between MnO-MnS and MnSe-MnS is
best explained in terms of ion size ratios. The Se^{2+} radius
is only 10 percent greater than the S^{2+} radius (1.91A $\underline{vs}$ 1.74A).
As noted previously, the S^{2+} ion is 24% larger than the O^{2+} ion
(1.74A $\underline{vs}$ 1.32A).

It must be concluded that all selenide inclusions found
in selenium-treated free machining steels also contain the
sulfur which is present. The composition Mn(Se,S) is
appropriate since it indicates anion substitution.

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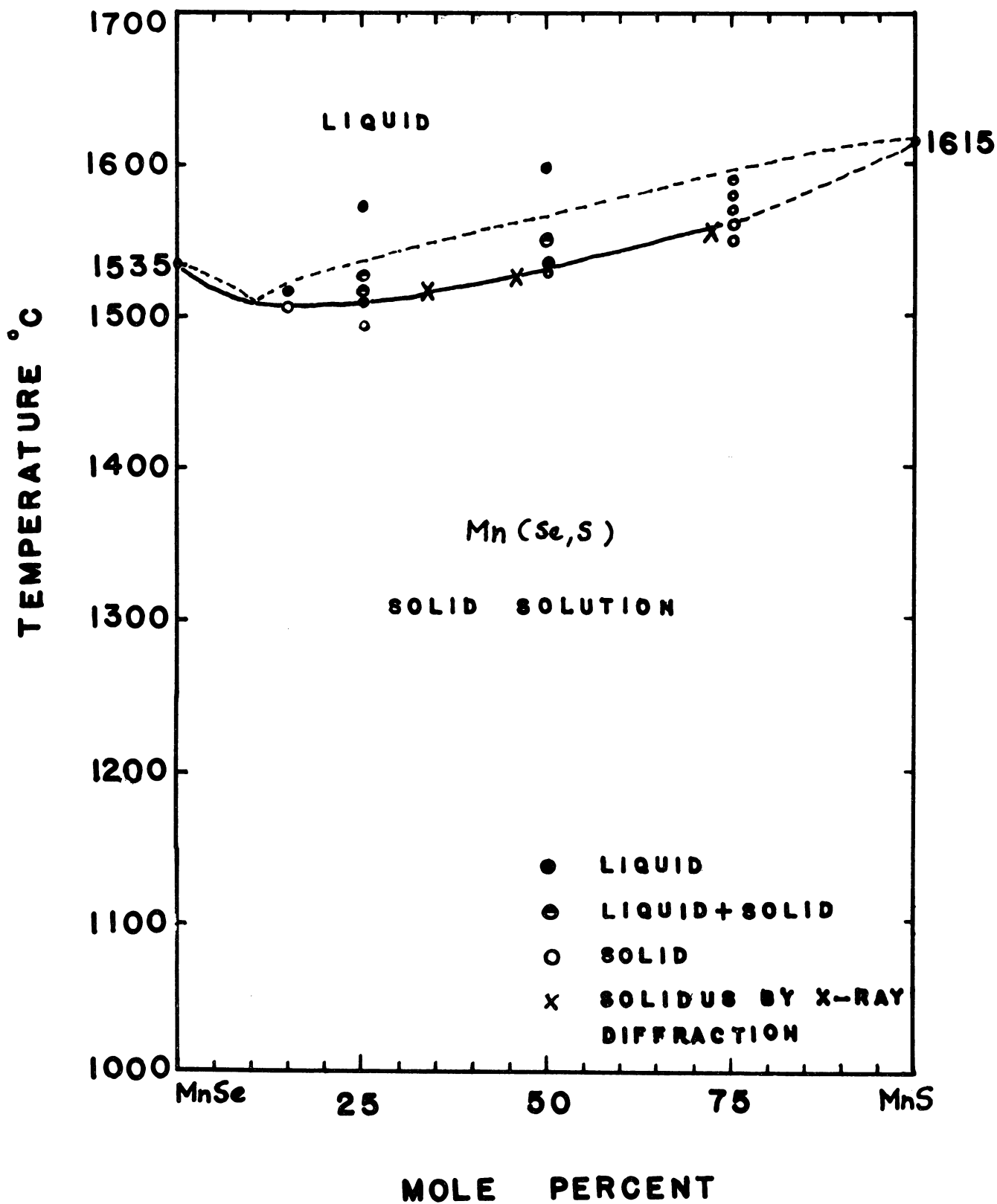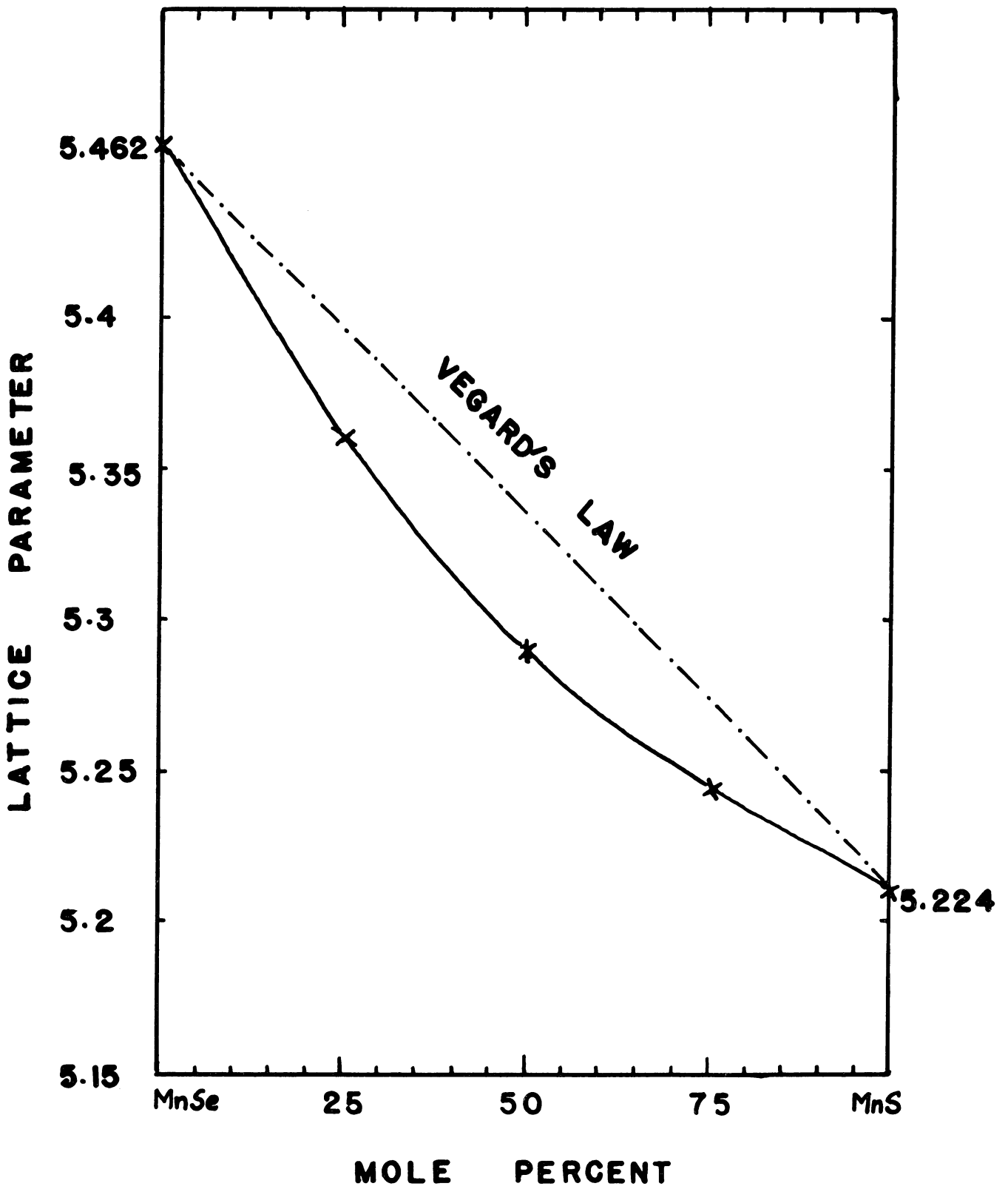   ASTM Diffraction Pattern of MnS, Card No. 6-0518

Fig. 1. MnSe-MnS system.

Fig. 2. Lattice parameters of Mn(Se,S) solid solutions.