HARDNESSES OF MnSe-MnS SOLID SOLUTIONS

by

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Abstract:

Manganous selenide (MnSe) is softer than manganous sulfide (MnS) and has a relatively larger decrease in hardness with increased temperatures.

Anion substitution in Mn(Se,S) produces solution-hardening at 20°C but not at higher temperatures.

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INTRODUCTION

Selenium, like sulfur, is added to steels to enhance machinability. Each has a strong preference for manganese to give MnSe and MnS respectively. As shown in a concurrent study[1] the two form a continuous solid solution series by anion substitution and with an NaCl structure. Since sulfur is invariably present in steels to which selenuim is added, these two form Mn(Se,S) inclusions. It has been shown that the deformation of MnS inclusions is related to the relative hardness of MnS and metal matrix.[2,3] It is also assumed that the deformation of the sulfide inclusion contributes to the machinability of the steel. Thus the hardness of Mn(Se,S) has some technical interest. It also presents theoretical interest because it permits us to examine the role of anions on hardness.

HARDNESSES OF SULFIDES

Two studies have examined the hardness of transitional element sulfides. Chao, et al.[2], showed that the hardness of MnS decreases with increases in temperature. This decrease appears to be linear if the DPH hardness number is plotted on the logarithmic scale and closely parallels the elevated temperature hardness of α-ferrite. The same authors found that (Mn,Fe)S compositions show negligible solution-hardening. Below the solubility limit, however, the two-phase mixtures of MnS and FeS produce a harder microstructure because FeS (with an NiAs structure) is appreciably harder than MnS (with its NaCl structure). Minor additions of calcium produced solution-hardening in MnS.

Kiessling and Westman[4] studied the substitution of Ti, V, Cr, Fe and Co in MnS, and concluded that all (Mn,Me)S systems show an increase in hardness within the solubility range. It should be noted, however, that they measured their

hardnesses on quenched samples rather than at elevated temperatures. Since extremely rapid precipitation can occur, however, there may have been a possibility for second-phase hardening.

EXPERIMENTAL

Solid solutions of Mn(Se,S) were prepared from the elements by a technique described elsewhere.[1] No phase separation was detected by either x-ray or optical techniques.

A Tukon microhardness tester provided the 20°C hardness data. A modified Vickers Hardness machine (600 gm) produced the hardness values for higher temperatures. This instrument is described in a previous paper.[2] Its values checked those of the Tukon instrument at 20°C.

RESULTS AND DISCUSSION

Manganese selenide is softer than manganese sulfide (50 DPH vs 125 DPH at 20°C). This is consistent with the lower melting point of MnSe (1535°C) as compared with MnS (1615°C). It is also expected on the basis of larger Se^{2+} ions. Like MnS, MnSe decreases in hardness as the temperature is raised (Fig. 1); however, the decrease is sharper (nearly 50% DPH per 100°C for MnSe compared to 20% DPH per 100°C for MnS).[2]

Solid solutions between MnSe and MnS show a significant positive deviation of the hardness at 20°C (Fig. 2). Thus there is a noticeable hardening of MnSe by sulfide ion substitution for the selenide ion. Selenium substitution into MnS does not increase the hardness of the latter; however, the interpolated values are exceeded, so that there is effective solution-hardening. The positive deviation in hardness disappears at higher temperatures where, within the error of measurement, a linear relationship exists when the logarithm

of the hardness value is plotted against temperature.

Inclusions of Mn(Se,S) are measurably softer than the ferrite matrix of a steel. On the basis of detailed deformation studies of sulfide inclusions,[3] it would be predicted that selenide additions to steel will generally permit inclusions to deform more than the surrounding metal.

REFERENCES

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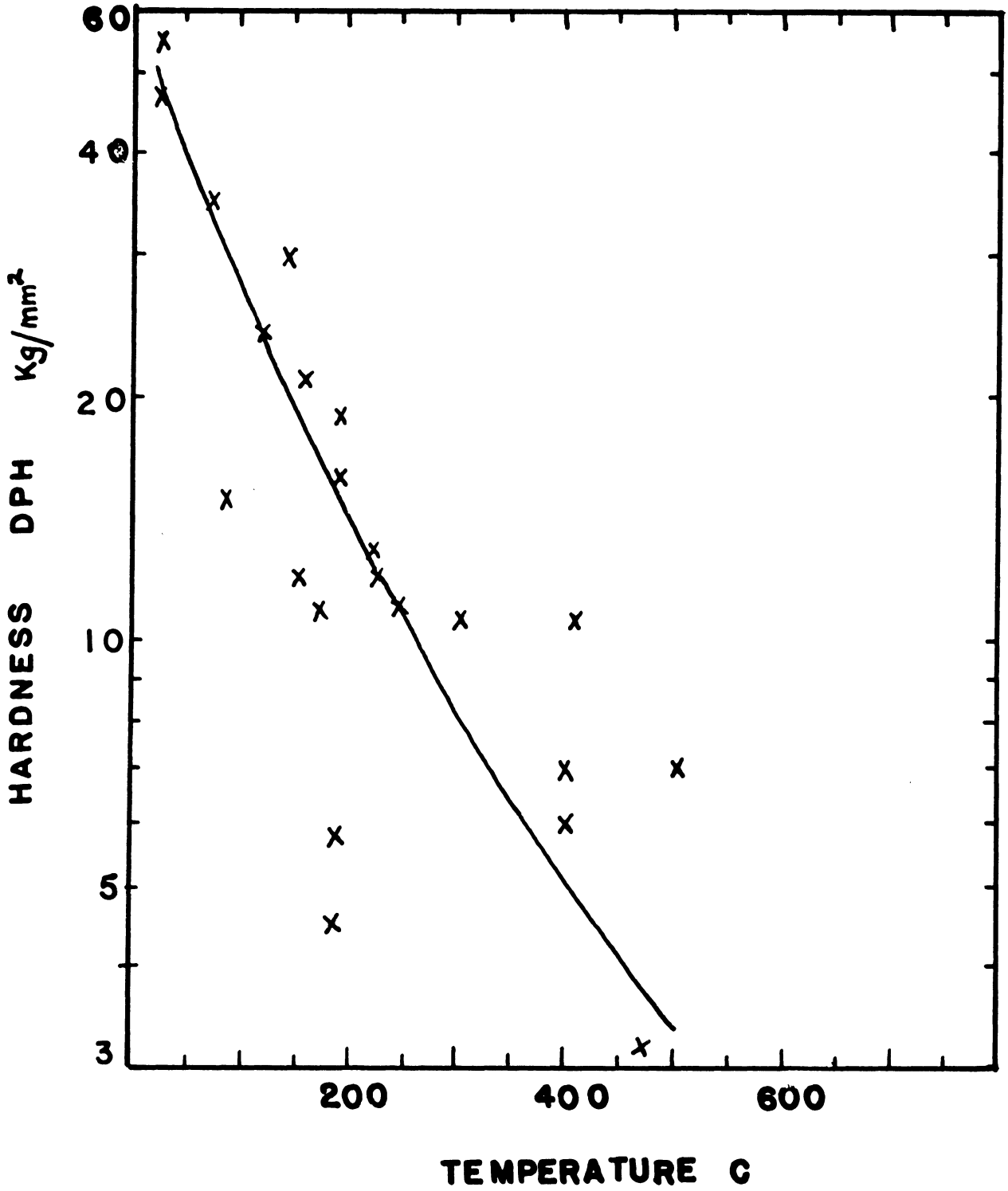

Fig. 1. Hardness of MnSe. Manganese selenide is softer than MnS at comparable temperatures.[2]

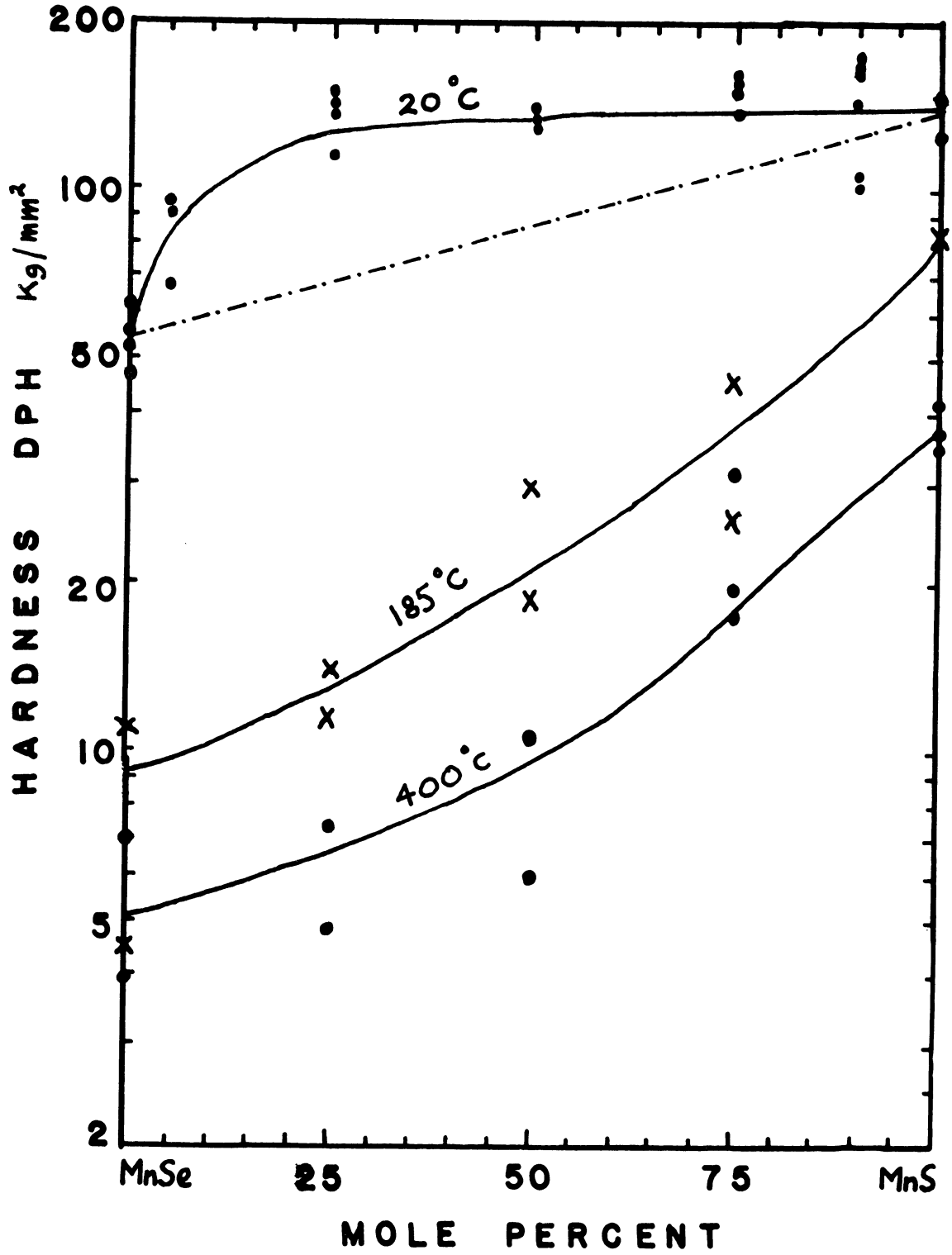

Fig. 2. Hardness of MnSe-MnS solid solutions. The solution-hardening effect at 20°C is not evident at higher temperatures.