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Progress Report

THE SYSTEM MnTe - MnS

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## ABSTRACT

The phase relationships in the system MnTe - MnS were studied. All phase changes were found to be rapid, therefore differential thermal analysis was used to determine the phase diagram. A eutectic was located at about 90 mole % MnTe at 900°C. Although no solid solution formation could be detected at the MnS side of the system, 8 mole % of MnS entered the solid solution in the high temperature (NaCl) form of MnTe at 800°C; a eutectoid was found at 700°C, where 5 mole % MnS were dissolved in the low temperature (NiAs) modification. The MnTe solid solutions exsolved rapidly during cooling.

## I. INTRODUCTION

The system, MnTe - MnS, was studied to provide background information on the influence of non-metallic inclusions upon the mechanical deformation characteristics of steel.<sup>1</sup> This paper, however, is limited to the phase relationships.

MnS exists in three different crystal forms,<sup>2</sup> the zinc blend and wurtzite structures, in which  $Mn^{2+}$  ions are tetrahedrally coordinated, and the rock salt structure which has octahedral coordination. Since the NaCl phase is the only stable modification,<sup>3</sup> the two tetrahedrally coordinated polymorphs shall not be considered in this investigation.

MnTe has a NiAs structure at room temperature and transforms to the cubic, NaCl structure at 1040°C.<sup>4</sup> The phase transition is rapid for both heating and cooling so that the high temperature crystalline form could not be retained at room temperature.

Because MnO, MnS, and MnSe all crystallize in the NaCl structure and MnTe has a NaCl modification at high temperatures,<sup>5</sup> solid solution formation among these compounds might be expected. It is interesting to note, however, that no extensive solid solution was observed in the system MnO - MnS.<sup>6</sup> There is a complete series of solid solutions in the system, MnS - MnSe.<sup>7</sup> A solid solution series of the NaCl structure was observed at high temperatures of the system MnSe - MnTe. These solid solutions exsolved at low temperatures.<sup>8</sup> The results implied that the bond type plays a more important role in solid solution formation rather than the ionic size. MnO is most ionic among all the compounds.<sup>5</sup> Which did not form solid solutions with compounds is more covalent in nature (MnS).

From the above results, one would probably postulate that the systems MnO - MnSe and MnO - MnTe, will have simple eutectic relationships. However, it is hard to speculate on the nature of the MnTe - MnS system.

## II. EXPERIMENTAL

### 1. SAMPLE PREPARATION

The samples were prepared by mixing and compacting MnTe and MnS powders. The MnTe was previously prepared by mixing and compacting double vacuum distilled metallic manganese and high purity tellurium in stoichiometric ratio modified with 1 wt % excess tellurium. The compacted powders were put in graphite crucible which was sealed in an evacuated Vycor tube. The free space

in the Vycor tube was made minimal to reduce the loss of tellurium. The sealed assembly was then heated slowly to about 500°C where the free manganese and tellurium reacted vigorously, melting the MnTe which formed. Only one phase, MnTe, was detected by x-ray powder patterns and metallographic techniques. The MnS was previously prepared through the sulfur reduction of  $\text{MnSO}_4$ .<sup>1</sup>

Each compact of MnTe - MnS was placed in a graphite crucible and was then sealed in an evacuated Vycor tube. The samples were heated at 1250°C for four hours and furnace cooled.

Although no chemical analysis was performed on the mixture, microscopic examination revealed no third phase. This indicated that the weighed components were all preserved at the final product. A typical microstructure is presented in Figure 1.

## 2. PHASE IDENTIFICATION

X-ray powder patterns were obtained using 114.6 mm Debye-Scherrer camera and  $\text{Fe - K}\alpha$  radiation. Mixtures of cubic MnS and hexagonal MnTe were observed in all of the compositions prepared. No lattice parameter change was noticed among different compositions, indicating no solid solution could be retained at room temperatures between these two end-members. The lattice parameter of MnS was obtained by measuring the back reflection line and extrapolated using Nelson and Riley method.<sup>9</sup> The hexagonal MnTe cell dimension was obtained using the lines (006) and (220) which appeared at about 120.30 and 138.27 degree 2 $\theta$ , respectively.

At room temperature the lattice parameters are:

$$\text{MnS: } 5.244\text{\AA}$$

$$\text{MnTe: } a = 4.145\text{\AA} \quad c = 6.708\text{\AA}$$

These values agree well with the values reported by Taylor and Kagle.<sup>10</sup>

## 3. DIFFERENTIAL THERMAL ANALYSIS

The high temperature equilibrium conditions could not be retained for examinations at room temperature even when the sealed samples (~0.5 gm) were quenched in water. Therefore, we used a differential thermal analysis procedure to determine the phase relationships.

The samples for differential thermal analysis were sealed in an evacuated, 4 mm Vycor tube with a recess in the bottom to accept a thermocouple. An  $\text{Al}_2\text{O}_3$  reference was similarly prepared and the two were placed within a piece of insulating fire brick to dampen spurious temperature changes within the furnace.

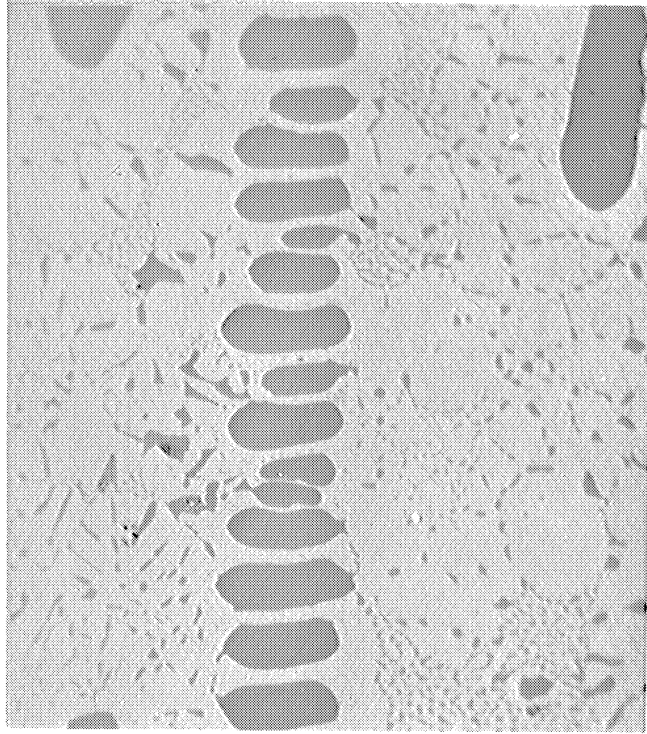


Figure 1. Microstructure of the composition (40 mole % MnS - 60 mole % MnTe) completely melted, furnace cooled to 800°C and then air cooled to room temperature.

Dark, primary MnS dendrite. Light, MnTe plus a fine eutectic structure. X 500.

The furnace was controlled by a mechanically driven rheostat which increased the temperature at a rate of about 15°C per minute.

The differential thermal effect was recorded on a strip chart recorder and calibrated to within  $\pm 5^\circ\text{C}$  against known-phase changes in the system Pb-Sn,<sup>11</sup> and against the  $\alpha$  to  $\beta$ -quartz inversion.<sup>12</sup>

### III. RESULTS

The results of both heating and cooling curves of DTA runs were used to construct the phase diagram as shown in Figure 2. From the points observed, there are no possible alternatives to the diagram as drawn.

### ACKNOWLEDGMENT

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