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V–Mn–{Sn,Sb} ternary systems

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Abstract

The isothermal section of the phase diagrams of ternary V–Mn–Sn and V–Mn–Sb systems has been investigated at 770 and 870 K, respectively. No ternary compounds were observed. The systems are characterised by the existence of solid solutions based on the binary compounds. The temperature dependence of the electrical resistivity and differential thermopower for $(V,Mn)_3Sb$ solid solution has been measured.

Keywords: Metals; Casting; X-ray diffraction; Phase diagram

1. Introduction

The interaction of Mn and 3d transition metals with Sn and Sb in the ternary systems has been investigated insufficiently. The Ti–Mn–Sn [1] and Ti–Mn–Sb [2] systems were studied in the whole concentration range. Isothermal section at 1270 K were investigated in the {V,Cr,Fe}–Mn–Sn systems at the manganese enriched region [3]. In the {Co,Ni}–Mn–Sn [4] and Ni–Mn–Sb [5,6] systems only some selected alloys were investigated and new compounds were found. The isothermal section of the phase diagram of Cu–Mn–Sn system has been investigated at the 0–25 at.% Sn concentration range [7]. The ternary V–Mn–Sb system was not completely investigated and only two antimonides, VMnSb [8], synthesized at high temperature–high pressure (1170 K, 5 GPa) conditions, and $VMnSb_2$ [9], synthesized at 1070 K, have been obtained.

In this paper we have studied the phase equilibria in the V–Mn–{Sn,Sb} systems at 770 and 870 K, respectively. We also measured the temperature dependence of the electrical resistivity and differential thermopower for $(V,Mn)_3Sb$ solid solution.

The state diagrams of the binary boundary V–Mn, Mn–Sn, Mn–Sb, V–Sn and V–Sb systems were not completely investigated, crystallographic data of the appropriate binary compounds are presented in Refs. [10,11]. The physical properties of binary stannides are summarized in Ref. [12].

2. Experimental details

Samples for investigation were prepared by direct arc melting of the constituent elements (vanadium, purity 99.9 wt.%; manganese, purity 99.99 wt.%; tin, purity 99.999 wt.%; antimony, purity 99.999 wt.%) under high purity argon atmosphere on a water-cooled copper hearth. Weight losses were generally less than 1 wt.%. The ingots were annealed in vacuum quartz tubes at 770 K for 720 h (for the V–Mn–Sn system) and at 870 K for 500 h (for the V–Mn–Sb system) and then quenched in cold water. The phase analysis was carried out using X-ray powder film data obtained by the Debye–Scherrer technique (RKD-57.3 camera, Cr-*K* radiation) and powder patterns obtained using DRON-2.0 diffractometer (Fe-K_α radiation). In view of the large number of phases occurring in the systems, combined X-ray and microscopic metallography examinations were essential. Metallography examinations were carried out using a conventional technique (MIM-8 microscope). Calculations of the unit cell parameters and theoretical patterns were accomplished using the CSD program package [13]. Temperature dependence of the electrical resistivity $\rho(T)$ and the differential thermopower $\alpha(T)$ with respect to the copper electrodes were measured by potentiometric method in the 80–380 K temperature range.

3. Results and discussion

The isothermal section of the phase diagram of the V–Mn–Sn system at 770 K was constructed on the basis of X-ray analysis of the 84 ternary and binary alloys (Fig.

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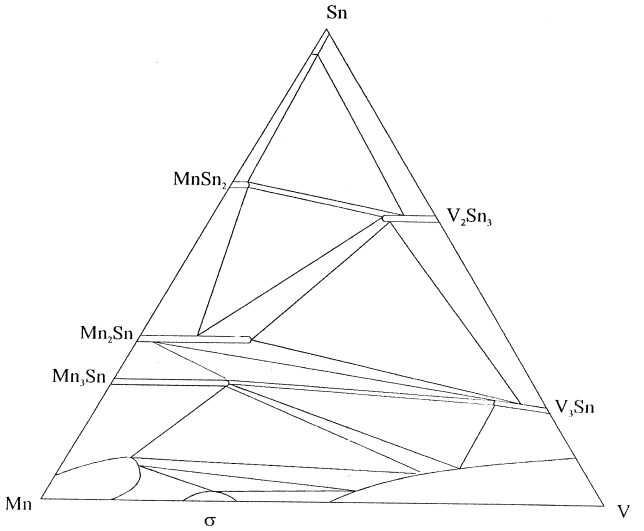

Fig. 1. Isothermal section for the V–Mn–Sn system at 770 K.

1). Phase equilibria are characterized by the existence of the solid solutions based on the appropriate binary compounds, namely Mn_3Sn, Mn_2Sn, V_2Sn_3 and V_3Sn. The extension of these solid solutions reaches 21 at.% of V, 20 at.% of V, 10 at.% of Mn, and 9 at.% of Mn, respectively. The solubility of the third component in $MnSn_2$ was established to be less than 3 at.% of V. At 770 K the bcc phase of vanadium shows a large extension (up to 48 at.% Mn and 10 at.% Sn). No ternary compounds were found in this system.

Ninety ternary and binary alloys for determination of the phase equilibria in the V–Mn–Sb system have been investigated. The isothermal section of the phase diagram at 870 K is shown in Fig. 2. As the result of the phase analysis, no ternary compounds were obtained either. We have also prepared the samples of VMnSb and $VMnSb_2$

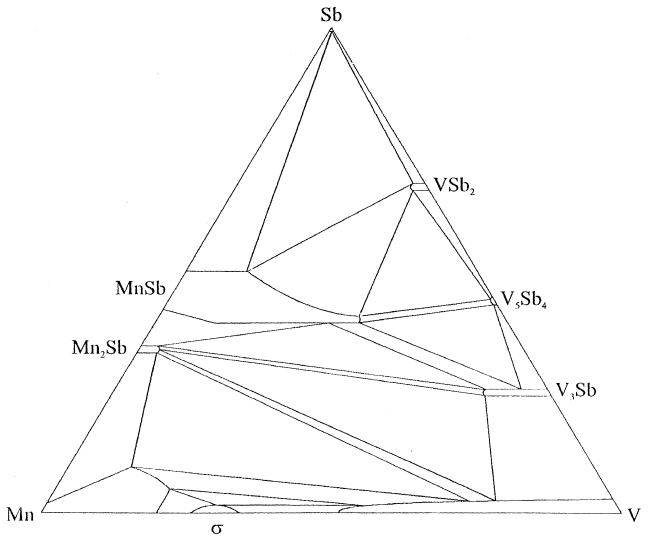

Fig. 2. Isothermal section for the V–Mn–Sb system at 870 K.

nominal compositions reported in Refs. [8,9], but these compounds did not appear at 870 K. X-ray analysis has shown the existence of the solid solution formed on the base of the binary MnSb (NiAs structure type) compound, which can be described as $V_yMn_{x-y}Sb$, where $x=1.0–1.16$ and $y=0.0–0.6$. Only one binary V_5Sb_4 (Ti_5Te_4 structure type) compound does not solve the third component in this system. The solubility of vanadium and antimony in the α-Mn phase extends up to 20 at.% of V and 10 at.% of Sb, respectively. The solubility of the third component in the Mn_2Sb and VSb_2 was established to be less than 3 at.% of V or Mn, respectively.

The solubility of manganese in the V_3Sb compound extends up to 12 at.% of Mn. The cell parameter variations of the $(V,Mn)_3Sb$ solid solutions are presented in Fig. 3. Temperature dependence of the resistivity $\rho(T)$ for $V_{3-x}Mn_xSb$ alloys ($0\leq x\leq 0.4$) are shown in Fig. 4. They have metallic like behaviour with positive temperature coefficients of the resistivity in the whole temperature range (80–380 K). The negative curvature for all $\rho(T)$ plots is probably due to a contribution to the total resistivity of these alloys from charge carriers scattered on the Mn magnetic moments. The observed values of the differential thermopower are small in the whole investigated temperature range (80–380 K) and decrease with Mn content increase.

The solid solution with formula $V_yMn_{x-y}Sb$ is formed due to the insertion of manganese into tetrahedral voids in the MnSb structure and the simultaneous reciprocal substitution of vanadium in place of the manganese sites. It seems possible that the formation of this solid solution is caused by the presence of appropriate octahedral and tetrahedral voids in the MnSb crystal structure. In the Ti–Mn–Sb ternary system, the MnSb compound forms analogous solid solution as well [2]. The solubility of titanium in MnSb extends up to 5 at.% of Ti in contrast with the V–Mn–Sb system. It may be explained by the lesser difference of V and Mn atomic radii than the difference between Ti and Mn atomic radii.

The V–Mn–{Sn,Sb} systems are quite different in comparison with the Ti–Mn–{Sn,Sb}, Ni–Mn–{Sn,Sb}, and {Co,Cu}–Mn–Sn systems. The $TiMnSn_4$ (Mg_2Ni structure type (*ST*)), $Ti_5Mn_{0.45}Sb_{2.55}$ (W_5Si_3 *ST*), Ni_2MnSn ($MnCu_2Al$ *ST*), NiMnSb (MgAgAs *ST*), CoMnSn (Ni_2In *ST*), Co_2MnSn ($MnCu_2Al$ *ST*), Cu_2MnSn ($MnCu_2Al$ *ST*), and Cu_4MnSn ($MgCu_4Sn$ *ST*) compounds are formed in these systems. No ternary intermetallic compounds were found in V–Mn–{Sn,Sb} systems, whereas one or two ternary compounds are formed in every {Ti,Ni,Co,Cu}–Mn–{Sn,Sb} system. The absence of the ternary compounds and the presence of solid solutions in investigated systems may be explained by the certain resemblance of the vanadium and manganese atoms, because the similarity in the atomic radii ($r_V=0.131$ nm, $r_{Mn}=0.130$ nm) and in the electronegativities of vanadium and manganese 1.63 and 1.55, respectively, is well known.

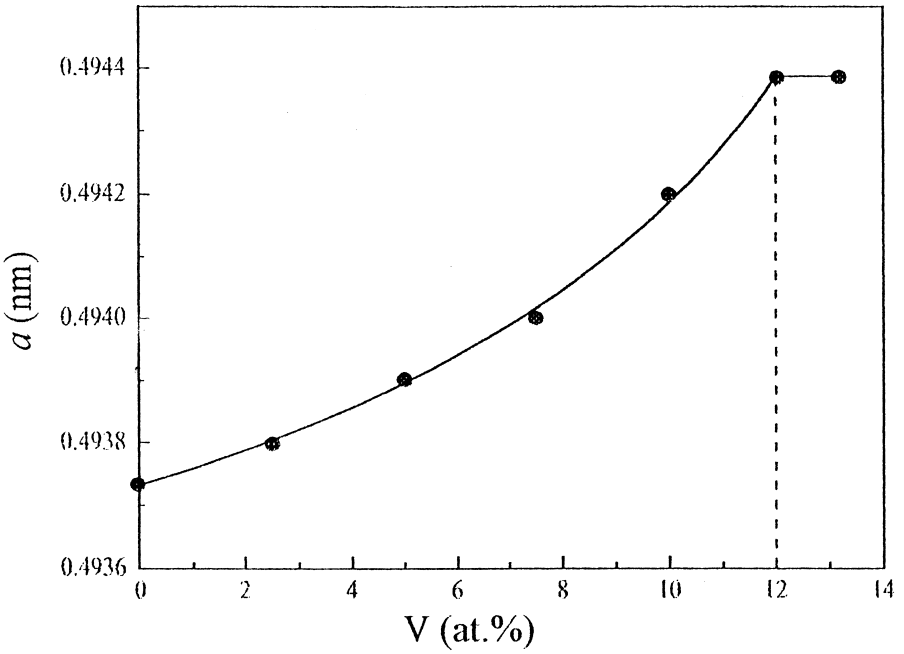

Fig. 3. The cell parameter variations of the $(V,Mn)_3Sb$ solid solution.

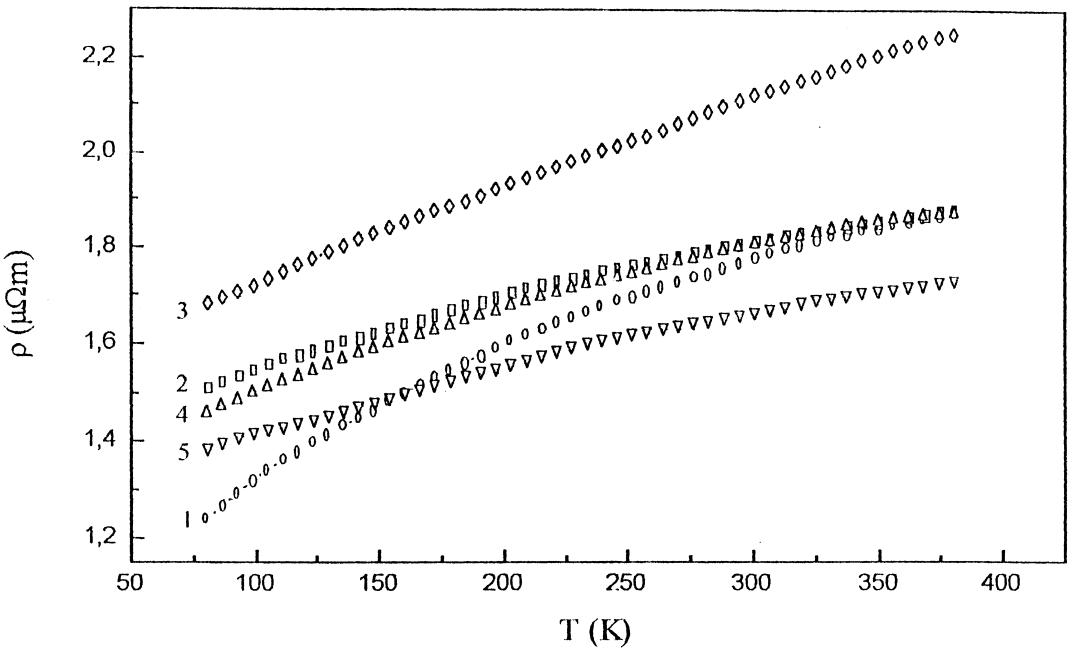

Fig. 4. Temperature dependence of the electrical resistivity of the $V_{3-x}Mn_xSb$ solid solution: (1) $x=0.0$, (2) $x=0.1$, (3) $x=0.2$, (4) $x=0.3$, (5) $x=0.4$.

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