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Phase boundaries in the PdGe–PtGe and Pd_2Ge–Pt_2Ge subsystems

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Abstract

Four Pt–Ge binary alloys and 25 Pt–Pd–Ge ternary alloys (16 for the Pt_2Ge–Pd_2Ge section and 9 for the PtGe–PdGe section) were investigated by differential thermal analysis with the help of a Setaram high-temperature calorimeter and a multicell apparatus built in the laboratory.

The data obtained in this way confirmed the incongruent melting process of Pt_2Ge in agreement with the assessment of Oya and Suzuki. They allow us to show that the PtGe–PdGe section corresponds to a spindle-shaped diagram, i.e. complete miscibility in the solid state. For Pt_2Ge–Pd_2Ge the extent of the spindle-shaped diagram is limited to the $0.1 < x_{Pd_2Ge} < 1$ range due to the peritectic decomposition of Pt_2Ge.

Keywords: Platinum; Palladium; Germanium; Phase boundaries; Differential thermal analysis

1. Introduction

In a previous work [1] we deduced some phase boundaries at high temperature in the Pd–Pt–Ge system from the breaks in the curves of the integral enthalpy of formation of the ternary alloy with respect to concentration. The results suggested that the PdGe–PtGe and Pd_2Ge–Pt_2Ge subsystems lead in the solid state to solid solutions in the whole range of concentration. In order to check such a hypothesis and to assess the phase diagrams of both subsystems we performed some differential thermal analysis (DTA) measurements at high temperature. During this investigation the question arose of whether or not the Pt_2Ge compound melts congruently. We also made some DTA measurements on the Pt–Ge system around the composition corresponding to the Pt_2Ge compound to settle the question of the nature of its melting process.

2. Previous work

In two recent papers [2,3], Okamoto published the assessed phase diagrams of the Pt–Ge and Pd–Ge binaries. The Pd–Ge phase diagram deduced from thermal, metallographic and X-ray investigations of Khalaff and Schubert [4] shows two congruently melting compounds namely PdGe ($T^{fus} = 1103$ K) and Pd_2Ge ($T^{fus} = 1568$ K). According to the differential thermal analysis, metallographic and X-ray determinations of Oya and Suzuki [5] the Pt–Ge phase diagram shows only one congruently melting compound, PtGe ($T^{fus} = 1343$ K), whereas Pt_2Ge undergoes a peritectic reaction to give Pt_3Ge and a liquid phase at 1068 K. However, according to Jain and Bhan [6], Pt_2Ge melts congruently at 1077 K. PtGe and PdGe are both orthorhombic (MnP type). Pt_2Ge and Pd_2Ge are hexagonal (Fe_2P type).

In a previous paper [1], we determined at 1269 K the enthalpy of formation of the Pt–Pd–Ge ternary alloys by direct reaction calorimetry. From the breaks of the integral enthalpy curves plotted with respect to concentration, we deduced some phase boundaries of the system. The results suggest clearly the existence of an extended solid solution between Pt_2Ge and Pd_2Ge (Fig. 1) from pure Pd_2Ge to the middle range of concentration. Moreover, the enthalpy of formation shows very small departures from ideality when referred to the pure solid binary compounds. However, we did not establish whether or not the solid solution extends

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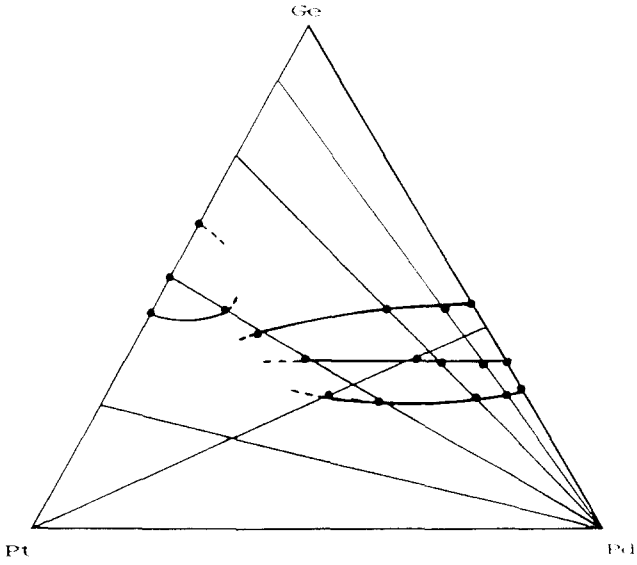

Fig. 1. Phase boundaries at 1269 K deduced from the breaks of the integral enthalpy curves with respect to composition corresponding to the section mentioned by straight lines.

to the pure Pt_2Ge compound due to its low melting point. No definite conclusion was reached about the possibility of a solid solution between PtGe and PdGe for the same reason.

3. Results

3.1. The Pt–Ge binary system

In order to settle the question of the melting of the Pt_2Ge compound we prepared four samples with mole fractions of Pt $x_{Pt}=0.62$, 0.64, 0.666 and 0.68, and we investigated these by differential thermal analysis. The DTA investigations were realized with the help of a multicell DTA apparatus (300–1800 K) for which one of us (J.R.) has requested a European patent. We observed on heating the differential thermograms shown in Fig. 2.

For $x_{Pt}=0.666$, the thermogram shows a single thermal arrest at about 1069 K, which corresponds to the temperature of decomposition of Pt_2Ge according to Oya and Suzuki. The heat flow goes to zero at 1093 K. This is 24 K higher and corresponds to the end of the dissolution of Pt_2Ge in the melt when in equilibrium, as shown by a small thermal effect. Such a behaviour corresponds to a peritectic decomposition of the Pt_2Ge compound.

For $x_{Pt}=0.62$ and 0.64, the thermograms show two thermal arrests ($T\simeq 1056$ K and 1079 K) corresponding to the reactions $Pt_3Ge_2+Pt_2Ge \rightarrow Pt_3Ge_2+$ liquid and Pt_3Ge_2+ liquid $\rightarrow$ PtGe + liquid respectively. As shown

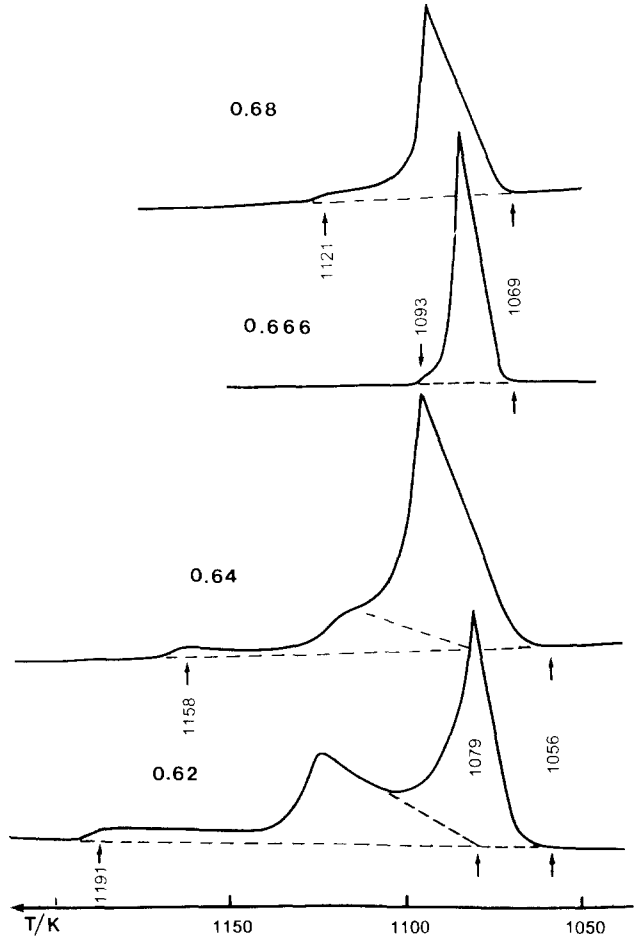

Fig. 2. Differential thermograms (heat flows vs. temperature) obtained on heating for some Pt–Ge binary alloys with the help of the multicell DTA apparatus for $x_{Pt}=0.62$, 0.64, 0.666 and 0.68, i.e. around the Pt_2Ge compound. The ends of the thermal effects at high temperature correspond to the liquidus temperatures.

by the figure, the high-temperature thermal arrest is more important for $x_{Pt}=0.62$ than for 0.64. The onset of the second thermal arrest, obtained by extrapolation, is easier to determine for $x_{Pt}=0.62$. The results agree well with the phase diagram of Oya and Suzuki, but the $Pt_3Ge_2+Pt_2Ge$ eutectic appears to be shifted towards pure Pt_2Ge since the reaction between Pt_3Ge_2 and the liquid is still present for $x_{Pt}=0.64$. After the high-temperature endothermic peak for $x_{Pt}=0.62$, the dissolution of the solid Pt_3Ge compound in the liquid phase extends to 1191 K. This is at a higher temperature (50 K) than suggested by the diagram of Oya and Suzuki, in agreement with the shift of the eutectic.

For $x_{Pt}=0.68$, we observed only one thermal arrest, corresponding to the reaction $Pt_2Ge+Pt_3Ge \rightarrow Pt_3Ge+$ liquid. The temperature observed for the liquidus is about 1121 K, i.e. 50 K lower than that mentioned by Oya and Suzuki.

The whole set of DTA results in this investigation agrees well with the conclusion of Oya and Suzuki regarding the peritectic decomposition of Pt_2Ge.

3.2. The Pt_2Ge–Pd_2Ge pseudo-binary system

Nine Pt–Pd–Ge samples were synthesized by melting together the pure components (metallic impurities less than 10^{-3} at.%) in suitable proportions. After four or five cycles of crystallization and fusion and annealing at about 1000 K, they were cooled to room temperature. The DTA experiments were performed mainly with the help of a Setaram high-temperature calorimeter, but also with the help of the multicell apparatus used for the previous investigation of the Pt–Ge binary. In the case of the Setaram calorimeter, the sample was placed in an alumina crucible and heated at a heating rate of 200 K h^{-1}. The thermograms obtained are similar to those observed for the PdGe–PtGe section in the whole range of concentration (see Fig. 4 later). The melting process begins without thermal arrest and clearly corresponds to a spindle-shaped diagram. It is the case only for $0.1 < x_{Pd_2Ge} < 1$. Moreover, cooling down the alloys for xPd_2Ge around 0.7, we observed systematically some undercooling phenomena for $1230 < T/K < 1250$.

Fig. 3 shows the results obtained with respect to composition. They correspond to complete miscibility of Pd_2Ge and Pt_2Ge in the solid state from pure Pd_2Ge to about $x_{Pd_2Ge} \simeq 0.1$. Due to the peritectic decomposition of Pt_2Ge, the phase relations are more complex in the Pt_2Ge-rich domain ($0 < x_{Pd_2Ge} < 0.1$), as shown by the solid points of Fig. 3, which suggest a plateau. However, it is not the purpose of this work to clarify this point.

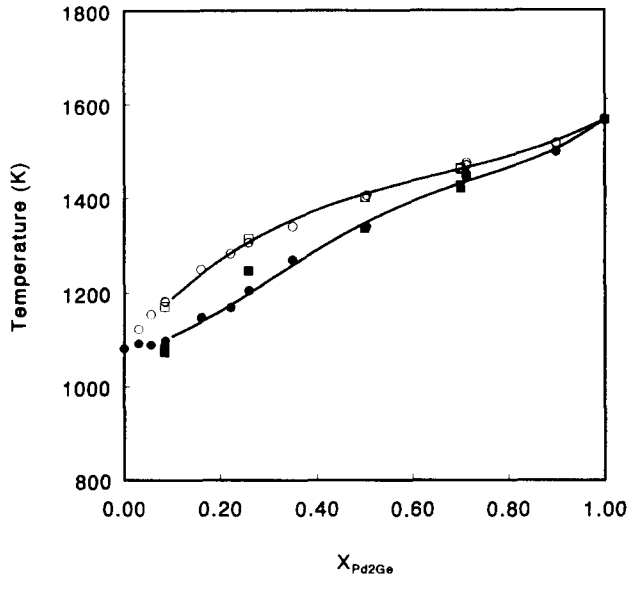

Fig. 3. Phase diagram of the Pd_2Ge–Pt_2Ge subsystem. Solid symbols: solidus temperatures; open symbols: liquidus temperatures. Circles and squares are obtained with the help of the Setaram high-temperature calorimeter and with the help of the multicell apparatus respectively.

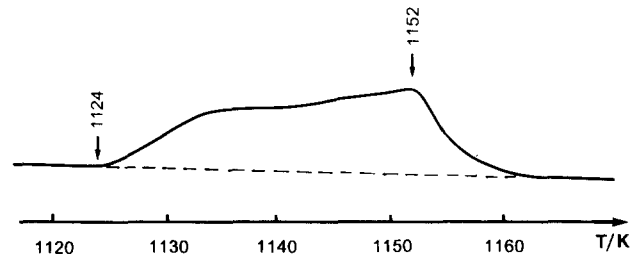

Fig. 4. Differential thermograms (heat flow vs. temperature) obtained on heating with the help of a Setaram high-temperature calorimeter for a PtGe–PdGe alloy ($x_{PdGe} = 0.904$). The onset of the thermal effect corresponds to the solidus temperature and the end (beginning of the exponential decrease at 1152 K) to the liquidus temperature.

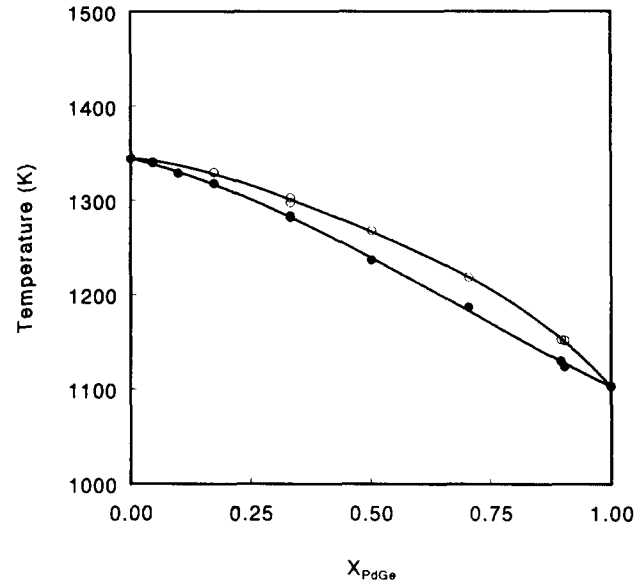

Fig. 5. Phase diagram of the PdGe–PtGe subsystem. Solid circles (solidus temperatures) and open circles (liquidus temperatures) are obtained with the help of the Setaram high-temperature calorimeter.

3.3. The PtGe–PdGe pseudo-binary system

The thermograms observed in the whole range of concentration are very similar to those obtained for the Pt_2Ge–Pd_2Ge pseudo-binary system for $x_{Pd_2Ge} > 0.1$. As an example, Fig. 4 shows the thermogram obtained for $x_{PdGe} = 0.904$. The heat effect begins at 1124 K without thermal arrest and the dissolution of the solid phase ends at 1152 K corresponding to the liquidus temperature. The corresponding phase diagram is shown in Fig. 5. The two compounds are completely miscible in the solid state from pure PdGe to pure PtGe.

4. Conclusion

The DTA experiments performed in this work lead to the conclusion that the congruently melting intermediate compounds PtGe and PdGe form a solid solution in the whole range of concentration. The corresponding phase diagram is a spindle-shaped one. Due to the peritectic decomposition of Pt_2Ge, the phase diagram of the Pt_2Ge–Pd_2Ge subsystem is spindle-shaped only for $0.1 < x_{Pd_2Ge} < 1$. From the point of view of their phase diagrams, both subsystems show positive deviations from additivity except for Pd_2Ge–Pt_2Ge near pure Pd_2Ge and Pt_2Ge. Such a behaviour corresponds to negative deviations from ideality stronger in the solid state than in the melt, which can lead to some ordering phenomena in the solid.

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