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Partial phase diagram of Pd-Ag-Ru-Gd quaternary system

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Abstract: On the basis of the Ag-Pd-Gd, Ag-Ru-Gd and Pd-Ru-Gd ternary systems, the partial phase diagram of Pd-Ag-Ru-Gd(Gd<25% atom fraction) quaternary system has been studied by means of X-ray diffraction analysis, differential thermal analysis, electron probe microanalysis and optical microscopy. The 700℃ isothermal sections of the Ag-Pd-5Ru-Gd, Ag-Pd-20Ru-Gd and Ag-Pd-50Ru-Gd (Gd≤25% atom fraction) phase diagrams were determined respectively. And the 700℃ isothermal section of the Pd-Ag-Ru-Gd (Gd≤25% atom fraction) quaternary system phase diagram was finally inferred. The section consists of four single-phase regions: solid solution Pd(Ag), (Ru), Pd_3Gd and $Ag_{51}Gd_{14}$; five two-phase regions: Pd(Ag)+(Ru), Pd(Ag)+ $Ag_{51}Gd_{14}$, (Ru)+ $Ag_{51}Gd_{14}$, Pd(Ag)+ Pd_3Gd and (Ru)+ Pd_3Gd; three three-phase regions: Pd(Ag)+ Pd_3Gd+(Ru), Pd(Ag)+ $Ag_{51}Gd_{14}$+(Ru) and (Ru)+ $Ag_{51}Gd_{14}$+ Pd_3Gd; one four-phase region Pd(Ag)+ (Ru)+ $Ag_{51}Gd_{14}$+ Pd_3Gd. No new quaternary intermetallic phase is found.

Key words: Pd-Ag-Ru-Gd quaternary system; phase diagram; alloys

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1 Introduction

The Pd-Ag-Ru-Gd quaternary system is directly related to the six binary systems, Ag-Pd, Ag-Gd, Ag-Ru, Pd-Gd, Pd-Ru, and Gd-Ru. The phase diagrams of these binary systems have already been studied.

Many paper on the Ag-Pd binary system were published formerly. There is an Ag-Pd binary isomorphous phase diagram in the reference[1]. The equilibrium phases of the Ag-Pd system include the liquid, L, and the fcc continuous solid solution (Ag, Pd).

The Ag-Gd binary system has already been studied by some authors[2-5]. Recently Gschneidner and Calderwood[6] summed up the previous works and obtained a more complete Ag-Gd binary system phase diagram with three intermetallic compounds: $Ag_{51}Gd_{14}$, Ag_2Gd and AgGd.

Loebich and Raub[7] studied the Pd-Gd binary system comprehensively. They reported a complete Pd-Gd binary phase diagram with seven intermetallic compounds: $GdPd_3$, $GdPd_2$, Gd_2Pd_3, Gd_4Pd_5, GdPd, Gd_3Pd_2 and Gd_5Pd_2. They also studied and reported the Gd-Ru binary system phase diagram with four intermetallics: $GdRu_2$, Gd_2Ru, $Gd_{73}Ru_{27}$ and Gd_3Ru[8].

Karakaya and Thompson[9] published the assessed Ag-rich part (Ru<10%, atom fraction) of the Ag-Ru binary system phase diagram. The Ag-rich part of Ag-Ru system is characterized by liquid-phase immiscibility and a eu-

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tectic reaction at 3.1% Ru (atom fraction) and 920℃ in which the last Ag-rich liquid solidifies.

The Pd-Ru system phase diagram has been studied by Darling and Yorke[10], Obrowski and Zwingmann[11], and Kleykamp[12]. They all agreed that the phase diagram is of a simple peritectic form. The phase diagram of the peritectic form was also found by Rudnitskii and Polyakova[13], but they suggested that there is an intermediate phase (β) in the system. However, no other investigation has confirmed the existence of the intermediate phase (β). Gurler[14] has reported a computer assessment of the Pd-Ru system. The assessed Pd-Ru phase diagram agrees with the phase diagram obtained in references[10−12].

The Pd-Ag-Ru-Gd quaternary system has relation to the four ternary systems: Ag-Pd-Gd, Pd-Ru-Gd, Ag-Pd-Ru and Ag-Ru-Gd. Zhang and Chen[15], and Zhang *et al.*[19] reported the room temperature, 750℃ and 700℃ isothermal sections of the Ag-Pd-Gd (Gd≤25% atom fraction) phase diagram. They all consist of three single-phase regions: Pd(Ag), Pd_3Gd and $Ag_{51}Gd_{14}$; three two-phase regions: Pd(Ag)+ Pd_3Gd, Pd(Ag)+ $Ag_{51}Gd_{14}$ and $Ag_{51}Gd_{14}$+ Pd_3Gd; one three-phase region: Pd(Ag)+ $Ag_{51}Gd_{14}$+ Pd_3Gd, respectively.

Zhang and Chen[16] also published the partial 700℃ isothermal section of the Pd-Ru-Gd system phase diagram. The section consists of seven single-phase regions: (Ru), (Pd), $GdPd_3$, $GdPd_2$, Gd_4Pd_5, GdPd and the new ternary intermetallic compound Pd_2RuGd_2; eleven two-phase regions: (Pd)+(Ru), (Pd)+ $GdPd_3$, $GdPd_3$+$GdPd_2$, $GdPd_2$+Gd_4Pd_5, Gd_4Pd_5+GdPd, GdPd+Pd_2RuGd_2 Gd_4Pd_5+Pd_2RuGd_2, $GdPd_2$ +Pd_2RuGd_2, $GdPd_3$+Pd_2RuGd_2, $GdPd_3$+(Ru) and (Ru)+Pd_2RuGd_2; five three-phase regions: GdPd+ Gd_4Pd_5+Pd_2RuGd_2, Gd_4Pd_5+$GdPd_2$+Pd_2RuGd_2, $GdPd_3$+$GdPd_2$+Pd_2RuGd_2, $GdPd_3$+(Pd)+(Ru) and (Ru)+$GdPd_3$+Pd_2RuGd_2.

Zhang *et al.*[17] studied the Ag-Pd-Ru ternary system and reported the 700℃ isothermal section of the phase diagram. It was found that on this section there are a single-phase region (Ag or Pd) along the Ag-Pd side, a small single-phase region (Ru) and a wide two-phase region Ag+Ru between these single-phase regions. The alloys in the Ag-Ru-rich range of the Ag-Pd-Ru ternary system are difficult to be homogenized after solidifying because the liquid alloys exhibit immiscibility.

Xu *et al.*[18], published the 700℃ isothermal section of the Ag-Ru-Gd (Gd<33.3%, atom fraction) ternary phase diagram. The section consists of five single-phase regions: (Ag), (Ru), $Ag_{51}Gd_{14}$, Ag_2Gd and $GdRu_2$; seven two-phase regions: (Ag) + (Ru), (Ag) + $Ag_{51}Gd_{14}$, $Ag_{51}Gd_{14}$ + Ag_2Gd, Ag_2Gd+$GdRu_2$, $GdRu_2$+(Ru), $Ag_{51}Gd_{14}$+(Ru) and $Ag_{51}Gd_{14}$+$GdRu_2$; three three-phase regions: $Ag_{51}Gd_{14}$+Ag_2Gd+$GdRu_2$, $Ag_{51}Gd_{14}$+(Ru)+$GdRu_2$ and (Ag)+(Ru)+$Ag_{51}Gd_{14}$.

On the basis of the published partial phase diagrams of the Ag-Pd-Gd, Pd-Ru-Gd, Ag-Pd-Ru and Ag-Ru-Gd ternary system, Zhang *et al.*[19] studied the 700℃ isothermal section of the Pd-Ag-5Ru-Gd (Gd≤25%, atom fraction) quaternary system phase diagram. In this paper, we further report our results on the 700℃ isothermal section of the Pd-Ag-20Ru-Gd and Pd-Ag-50Ru-Gd phase diagram, and then infer the 700℃ isothermal section of the Pd-Ag-Ru-Gd (Gd≤5%, atom fraction) quaternary phase diagram.

2 Experimental details

All the alloys were prepared from palladium (99.99% purity), silver (99.99% purity), ruthenium (99.99% purity) and gadolinium (99.9% purity) using an induction furnace. For degassing, stoichiometric mixtures of palladium, silver and ruthenium were refined in vacuum. Corresponding amounts of gadolinium were then added. The alloys were melted in boron nitride crucibles under a pure argon atmosphere. After remelting, the melts were cooled quickly, and homogeneous lumps of the alloys were obtained. All the specimens were sealed in silica tubes filled with argon. To determine the isothermal section at 700℃, the specimens were homogenized at 700℃ for 20 days, and then brine quenched. It was determined by chemical analysis that the weight losses of the alloy elements are less than 0.5% for both palladium and ruthenium, and 1.5% for both silver and gadolinium during melting and heat treatment. The experiments were corrected accordingly.

The structure of the specimens was determined by X-ray diffraction analysis and was examined also by metallograph. The X-ray diffraction experiments were performed in a Rigaku (RV—200 model) diffractometer, using Cu Kα radiation (λ=0.15405 nm). Diffraction data were adjusted with silicon powder as an internal standard. The element distribution in a part of the alloy specimens was determined in an electroprobe microanalyser (EPMA—8705Q model).

3 Results and discussion

3.1 Four ternary system phase diagrams relating to the Pd-Ag-Ru-Gd quaternary system

For the convenience of observation, the 700℃ isothermal sections of the Ag-Pd-Gd (Gd≤25%, atom fraction)[19], Pd-Ru-Gd (Gd≤25%, atom fraction)[16], Ag-Pd-Ru[17] and Ag-Ru-Gd[18] (Gd≤33.3%, atom fraction) have been shown together in Fig. 1. It was also found, that the solid solubility of silver in Pd_3Gd at 700℃ is about 24% atom fraction[19]; of ruthenium 7.5% (atom fraction)[16], and the solid solubility of

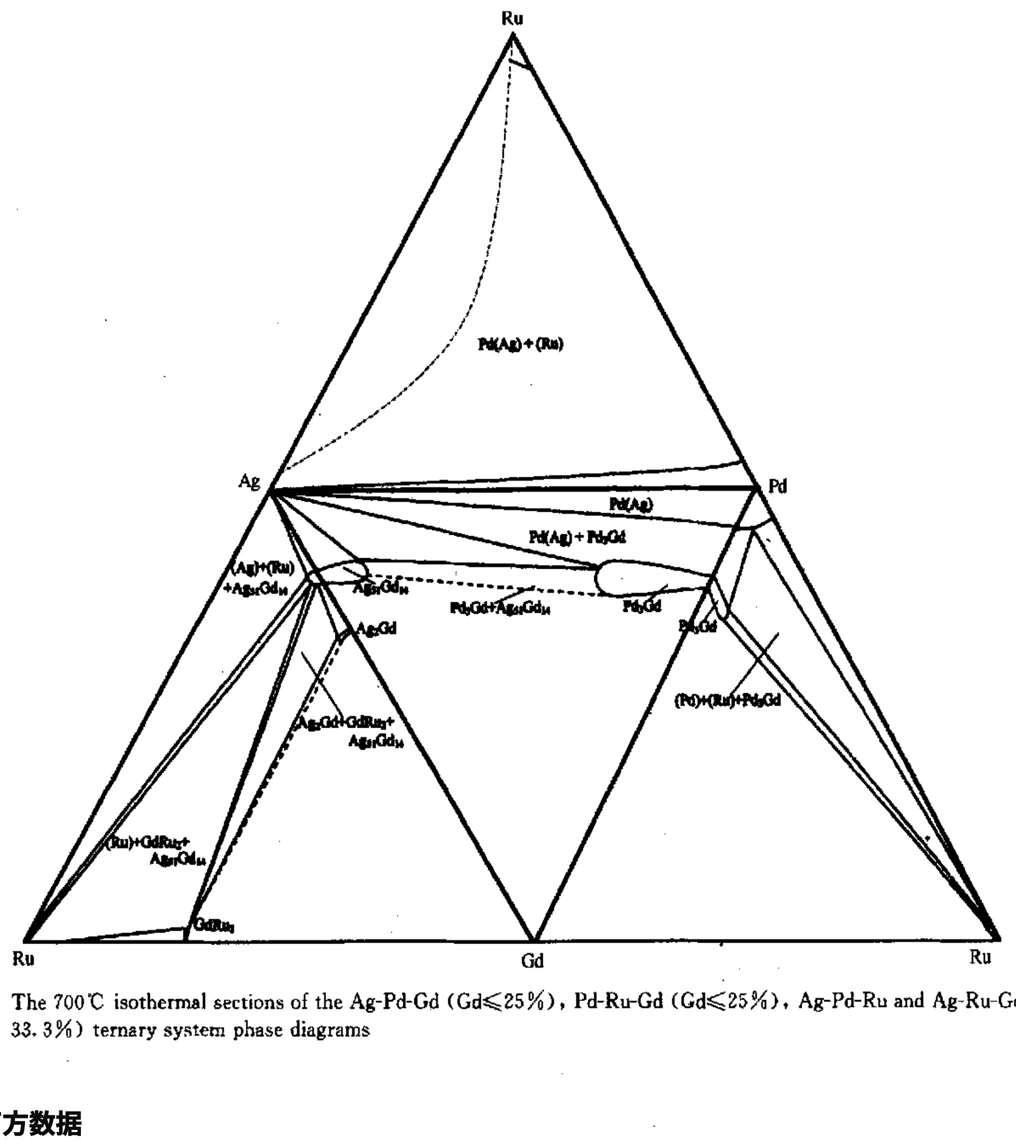

Fig. 1 The 700℃ isothermal sections of the Ag-Pd-Gd (Gd≤25%), Pd-Ru-Gd (Gd≤25%), Ag-Pd-Ru and Ag-Ru-Gd (Gd≤33.3%) ternary system phase diagrams

palladium in $Ag_{51}Gd_{14}$ at 700℃ is about 9% atom fraction[19]; of ruthenium 1% atom fraction[18].

3.2 The 700℃ isothermal sections of the Pd-Ag-5Ru-Gd, Pd-Ag-20Ru-Gd and Pd-Ag-50Ru-Gd (Gd≤25%, atom fration) quaternary phase diagram

The 700℃ isothermal section of the Pd-Ag-5Ru-Gd (Gd≤25%, atom fraction) phase diagram was reported in reference[19]. As shown in Fig. 4(c), the section consists of the following two single-phase regions: solid solution Pd(Ag) and Pd_3Gd; four two-phase regions: Pd(Ag)+(Ru), Pd_3Gd+(Ru), Pd_3Gd+Pd(Ag) and $Ag_{51}Gd_{14}$+(Ru); three three-phase regions: Pd_3Gd+$Ag_{51}Gd_{14}$+(Ru), $Ag_{51}Gd_{14}$+Pd(Ag)+(Ru) and Pd_3Gd+Pd(Ag)+(Ru); one four-phase region: Pd_3Gd+$Ag_{51}Gd_{14}$+Pd(Ag)+(Ru).

In this work, the 700℃ isothermal sections of the Pd-Ag-50Ru-Gd and Pd-Ag-20Ru-Gd (Gd≤25% atom fraction) quaternary phase diagram have been studied by the X-ray diffraction disappearing-phase method, and checked by metallography. The compositions of the specimens are represented by the symbols, such as ○, △ and ◆, in Fig. 2 and Fig. 3. The experiments confirm that there is a wide two-phase region,

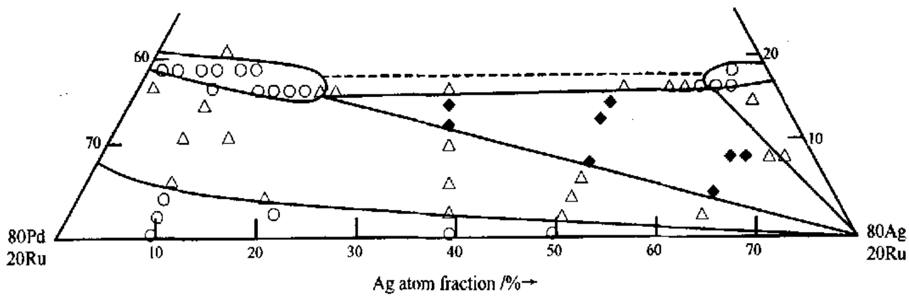

Fig. 2 Phase fields in 700℃ isothermal section of Pd-Ag-20Ru-Gd (Gd≤25%) quaternary system phase diagram examined by X-ray diffraction disappearing-phase method

○—binary phase; △—ternary phase; ◆—quaternary phase

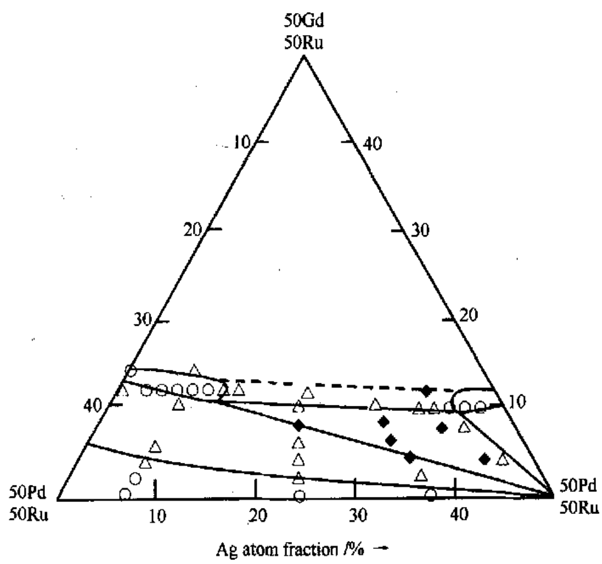

Fig. 3 Phase fields in 700℃ isothermal section of Pd-Ag-50Ru-Gd (Gd≤25%) quaternary system phase diagram examined by X-ray diffraction disappearing-phase method

○—binary phase; △—ternary phase; ◆—quaternary phase

Pd (Ag)+(Ru), along the palladium-silver-ruthenium-rich side of the 700℃ isothermal section of the Pd-Ag-Ru-Gd quaternary phase diagram, and there is not any single-phase region in either of the partial sections. According to the experiment results from the X-ray diffraction analysis and microscopic metallography, both sections are obtained as is shown in Fig. 4(a) and (b) respectively. To sum up, the 700 ℃ is

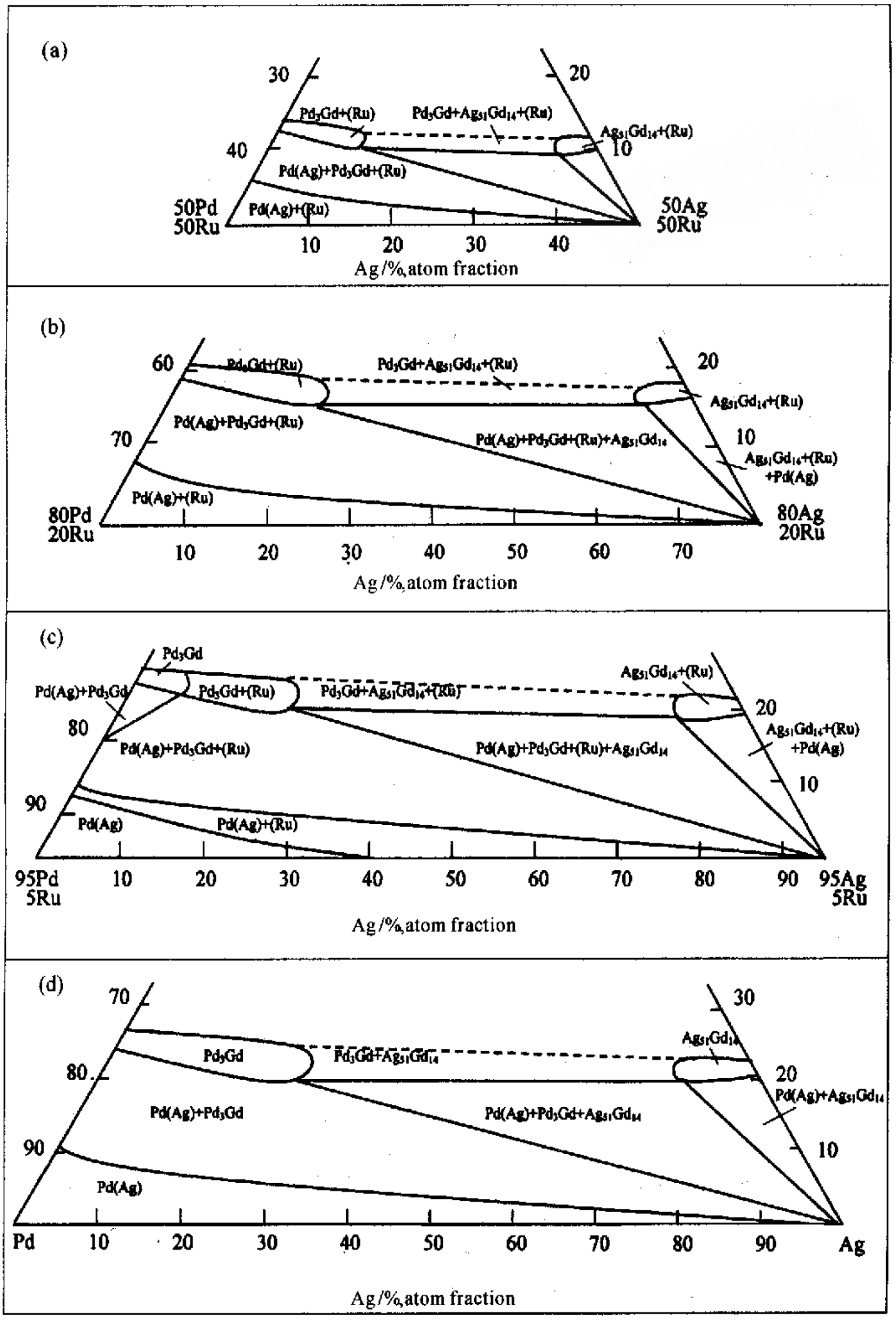

Fig. 4 The several 700℃ isothermal sections of the Pd-Ag-xRu-Gd (Gd<25%) quaternary system phase diagrams: (a) x=50, (b) x=20, (c) x=5, (d) x=0

othermal section of either the Pd-Ag-50Ru-Gd or Pd-Ag-20Ru-Gd (Gd≤25% atom fraction) quaternary phase diagram all consists of three two-phase regions: Pd(Ag)+(Ru), Pd_3Gd+(Ru) and $Ag_{51}Gd_{14}$+(Ru); three three-phase regions: Pd(Ag)+Pd_3Gd+(Ru), Pd_3Gd+$Ag_{51}Gd_{14}$+(Ru) and $Ag_{51}Gd_{14}$+(Ru)+Pd(Ag); one four-phase region Pd(Ag)+Pd_3Gd+(Ru)+$Ag_{51}Gd_{14}$. Both the sections resemble each other in form, and no new quaternary intermetallic phase was found. The limits of the two-phase regions, (Pd_3Gd+(Ru)), (Pd(Ag)+(Ru)) and ($Ag_{51}Gd_{14}$+(Ru)), are almost inversely proportional to the ruthenium content on the 700℃ isothermal sections of Pd-Ag-5Ru-Gd, Pd-Ag-20Ru-Gd and Pd-Ag-50Ru-Gd (Gd ≤25% atom fraction) quaternary phase diagram.

3.3 The 700℃ isothermal section of the Pd-Ag-Ru-Gd(Gd≤25%) quaternary system phase diagram

According to Fig. 4, the 700℃ isothermal section of the Pd-Ag-Ru-Gd (Gd≤25% atom fraction) quaternary phase diagram can be inferred. As shown in Fig. 5, the isothermal section is a partial tetrahedron. It consists of four single-phase regions: solid solution Pd (Ag) (polyhedron MLSTUM in Fig. 5), Pd_3Gd (EFKHGNE), $Ag_{51}Gd_{14}$ (IJORQPI) and (Ru) (ABCDVA); five two-phase regions: Pd(Ag)+(Ru) (LSUL-(Ru)), Pd_3Gd+(Ru) (EFKNE-(Ru)), $Ag_{51}Gd_{14}$+(Ru) (IJORI-(Ru)), Pd(Ag)+Pd_3Gd (ENULMGE) and Pd(Ag)+$Ag_{51}Gd_{14}$ (UQROU); three three-phase regions: Pd(Ag)+Pd_3Gd+(Ru)

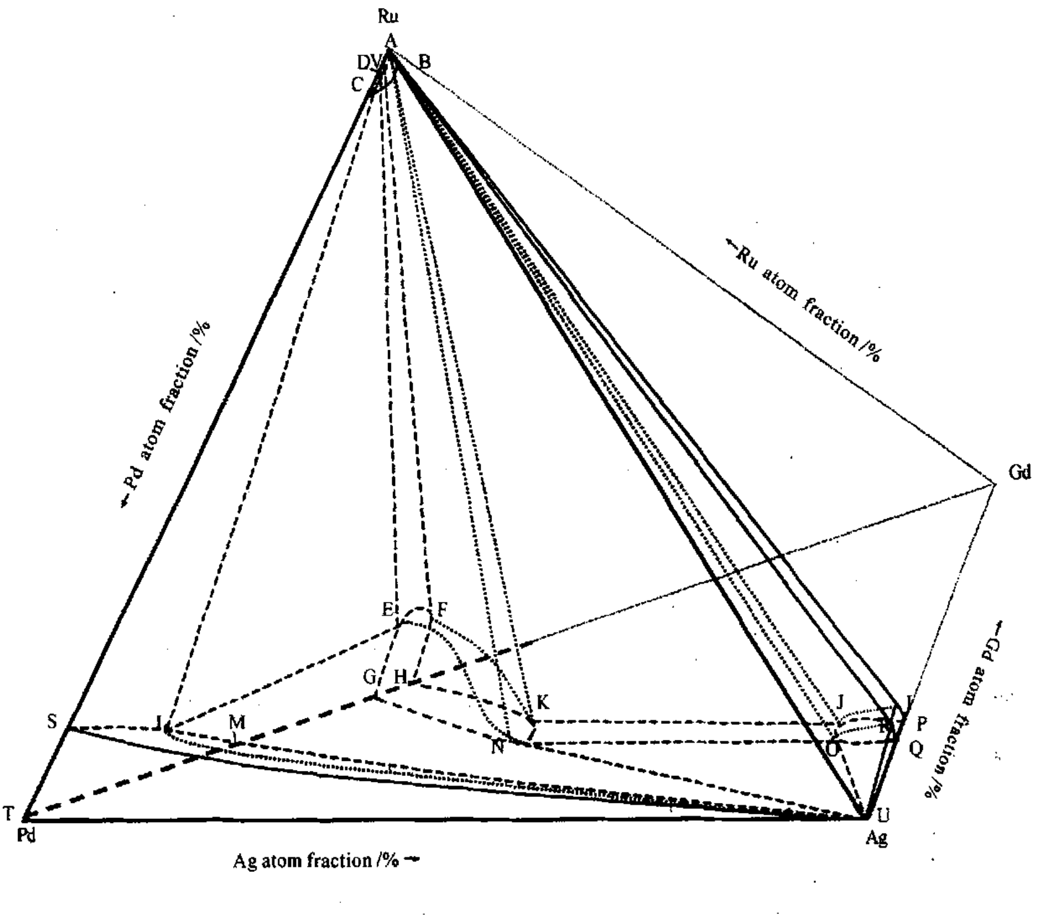

Fig. 5 The 700℃ isothermal section of the Pd-Ag-Ru-Gd quaternary system phase diagram

(ELUNE-(Ru)), Pd(Ag)+$Ag_{51}Gd_{14}$+(Ru) (ROUR-(Ru)) and Pd_3Gd+$Ag_{51}Gd_{14}$+(Ru) (JKNOJ-(Ru)); one four-phase region, Pd(Ag)+Pd_3Gd+$Ag_{51}Gd_{14}$+(Ru) (ONUO-(Ru)). The solid solubility of palladium in $Ag_{51}Gd_{14}$, silver in Pd_3Gd and gadolinium in Pd (Ag) decreases steeply with increasing ruthenium content. No new Pd-Ag-Ru-Gd quaternary intermetallic phase has been found in this work.

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