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Contribution to the study of the Ce-Zr-Au system

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Abstract. The equilibrium phase diagram of the Ce-Zr-Au system was studied by differential thermal analysis, X-ray diffraction and electron probe microanalysis along the isopletic section at 50 at. % Au. Our main result concerns the discovery of a new ternary phase and a ternary invariant. The polymorphic transitions of the ZrAu phase, previously reported, was confirmed and we precised the melting and the polymorphic transition temperatures of the CeAu phase. A schematic representation of the isopletic section is given.

1 INTRODUCTION

The study of the isopletic section ZrAu-CeAu (at 50 at. % Au) follows our previous works on the Zr-Au system [1] and the determination of the crystal structures of the equiatomic compound, ZrAu [2]. No experimental investigation of phase equilibria in the Ce-Zr-Au ternary system has been published. Assuming similarity between the Ce-Zr and Ce-Ti systems, Moffatt has first drawn a hypothetical phase diagram without any intermediate phases, as later confirmed by Harris *et al.* [3]. No phase diagram has been clearly established for the Ce-Zr system. On the contrary, the Zr-Au and Ce-Au binary systems are well known. The Zr-Au system presents height intermetallic compounds (Zr_3Au, Zr_2Au, Zr_3Au_2, ZrAu, Zr_7Au_{10}, $ZrAu_2$, $ZrAu_3$, $ZrAu_4$) and the solid-liquid equilibria has been determined by differential thermal analysis (DTA) in the whole composition range (fig. 1a). Recently, we have determined the three polymorphic forms of the congruent melting compound ZrAu by means of neutron powder diffraction [2]. At high temperature, ZrAu has a tetragonal structure (*P4/mmm*, a=4.835(2) Å and c=3.416(3) Å) related to the CsCl structure, leading to a monoclinic structure (*P2/m*, a=11.695(16) Å, b=4.828(3) Å, c=11.719(18) Å, η=107.090(17)°) at 569°C. A new transformation, which had not been detected in our previous work using DTA, leads to a triclinic structure (*P-1*, a=11.537(8) Å, b=4.841(1) Å, c=11.507(7) Å, ζ=87.42(1)°, η=104.82(1)° and ν=92.41(2)°) around 380°C. The assessed diagram for the Ce-Au system by Gschneidner *et al.* (fig. 1b, [4]) is primarily based on the work of Vogel *et al.* [5] with modifications based on the work of Mac Masters *et al.* concerning the Au-rich side [6]. Five intermetallic compounds have been identified: Ce_2Au, CeAu, $CeAu_2$, $Ce_{14}Au_{51}$, $CeAu_6$. The congruent melting compound, CeAu, presents two crystalline structures, orthorhombic with FeB-type (*Pnma*) below 480°C and orthorhombic with CrB-type (*Cmcm*) at high temperature [6].
The purpose of this study is to establish the phase equilibria along the isopletic section between the two congruent melting compounds, ZrAu and CeAu (at 50 at. % Au).

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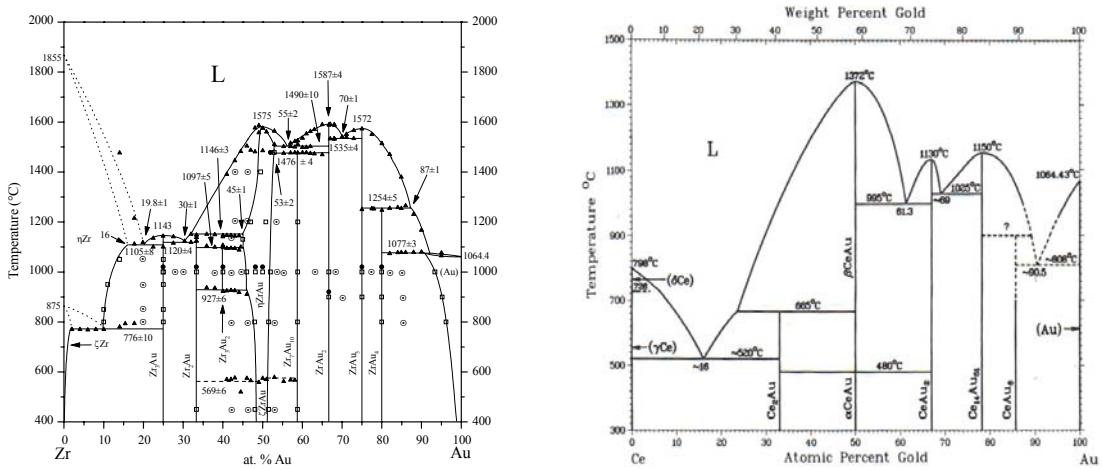

(a) From [1]

(b) From [5]

Figure 1. Equilibrium phase diagrams of Zr-Au system (a) and Ce-Au system (b).

2 EXPERIMENTAL

All samples were prepared by arc-melting under an Ar atmosphere, from zirconium and gold wires of 99.8 % and 99.99 % purity, respectively and from cerium metal pieces of 99.99% purity. Then, the ingots were annealed (for homogenisation) at 950°C under ultra-high vacuum (2.10^{-10} mbar).

Phase transitions were detected by DTA with heating and cooling rates of 10°C/min between 25°C and 1600°C. Alumina crucibles could be used up to 1000°C whereas, for higher temperatures, we preferred tungsten (W) crucibles in order to avoid reaction with the sample.

The main difficulty of this work arose from the rapid oxidation of the alloys in air at room temperature. For this reason, X-ray diffraction (XRD) measurements were performed on polished samples, for which the kinetic for oxidation is expected to be slower than that for the powder. XRD collections were conducted using a diffractometer (Co Kζ) equipped with a position sensitive detector 5°-120° (INEL-CPS 120), allowing to limit the exposure time. For the cerium-rich samples, XRD were performed under He flow.

Electron probe microanalyses (EPMA) were performed on a Cameca SX50 device using the PAP correction software [7] and pure Au, Zr_2Ni_7 and $CePO_4$ as standards with the Au(Lζ) (ς=1.28206 Å), Zr(Lζ) (ς=6.07415 Å), and Ce(Lζ) (ς=2.5615 Å) radiations. The morphology of the sample was checked by optical and electron microscopies.

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3 RESULTS AND DISCUSSION

Our main result concerns the discovery of a new ternary phase and a ternary invariant. From all equilibrium temperatures, we were able to propose a schematic representation of the isopletic section at 50 at. % Au (fig. 2), including the liquidus surface.

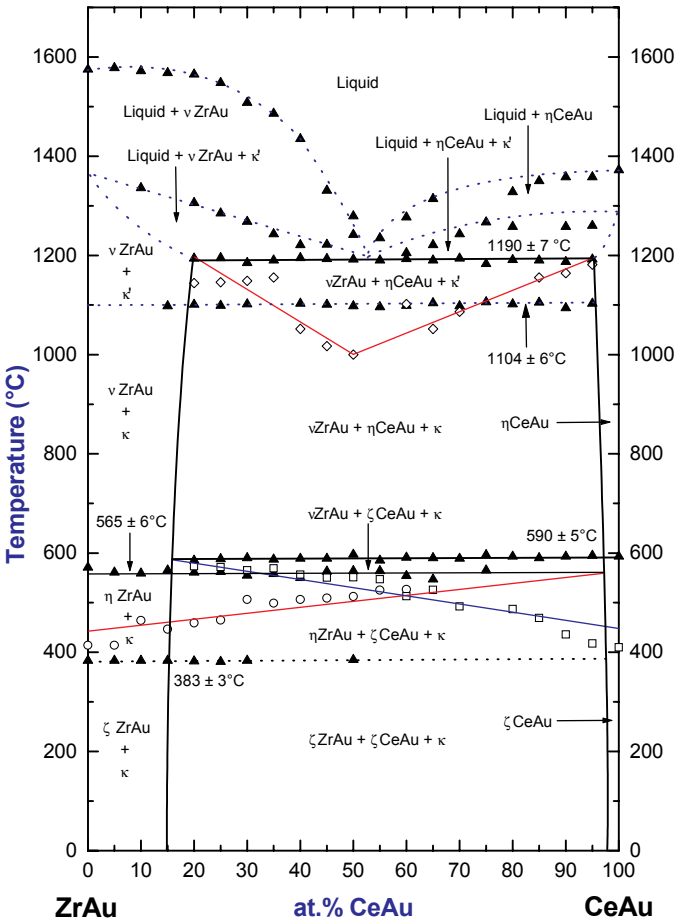

Figure 2. Schematic representation of the isopletic section at 50 at. % Au (▲ : heat effect detected by DTA ; ◇, ○, □ : Tammann analysis estimated from DTA).

3.1 Isopletic section at 50 at. % Au

No solid solution of Ce in the ZrAu phase have been found from EPMA performed on the samples annealed at 950°C. This result is coherent with regards to the respective atomic radii of Zr (1.60 Å) and Ce (1.81 Å), then the solubility of Ce in ZrAu is not expected. On the contrary, the solubility of Zr in CeAu was found to be 2 at. % at the annealing temperature (950°C). The maximum solubility of Zr in CeAu at the temperature (1190∂7°C) of the ternary eutectic do not exceed 3 at.%. Indeed, endothermic effects, associated to the invariant plateau at 1190°C, are still detected by DTA for the samples with a composition of $(ZrAu)_{0.05}(CeAu)_{0.95}$.

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DTA showed the presence of solid state reactions corresponding to the polymorphic transitions of the ZrAu and CeAu binary phases. The first one, detected at 383∂3°C, is related to the triclinic-monoclinic transition of ZrAu observed around 400°C by neutron diffraction experiments [2]. It is interesting to note that this is most probably a second-order transition as no endothermic peak is detected by DTA. Indeed, the DTA curve presents a discontinuity as consequence of the change in heat capacity associated to the triclinic-monoclinic transition. The second at 565∂6°C is related to the monoclinic-tetragonal transition of ZrAu [1]. A polymorphic transition of the CeAu phase was first detected at 480°C (on cooling) by Mc Masters *et al.* [6]. We found 590∂5°C by DTA on heating and the temperature measured on cooling was found to be 460°C, in agreement with the work of Mc Masters *et al.*

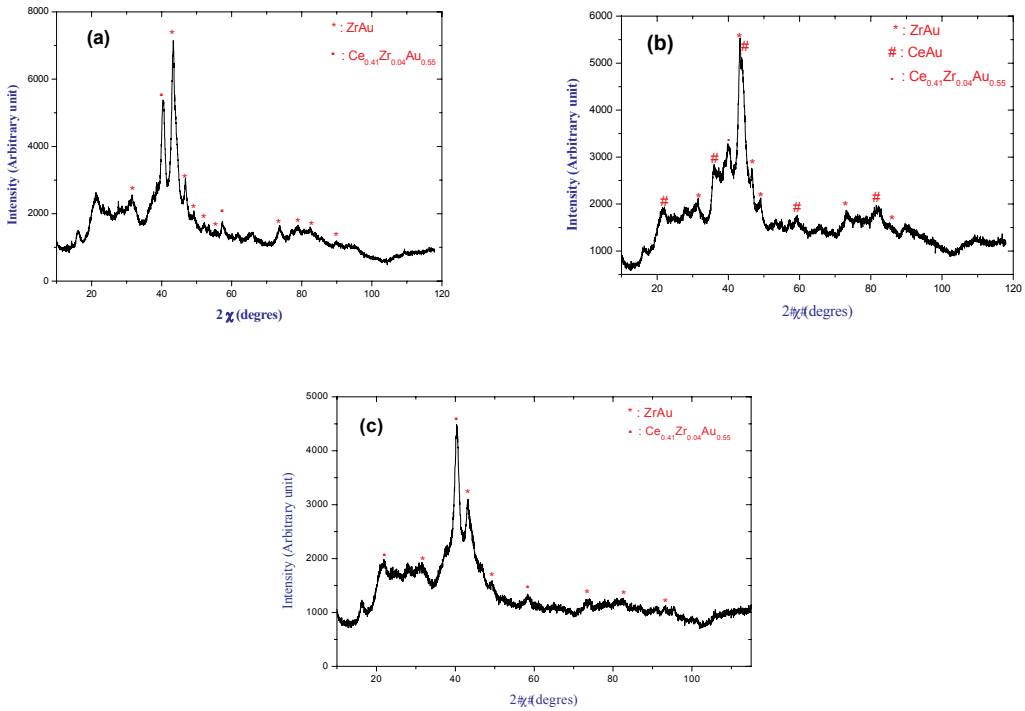

Figure 3. XRD patterns of Ce(12,5%)Zr(37,5%)Au(50%) annealed for 13 days at 1000°C (a), as cast arc-melted Ce(25%)Zr(25%)Au(50%) (b) and as cast arc-melted Ce(24%)Zr(24%)Au(52%) (c).

At higher temperatures, DTA measurements revealed the presence of two invariant plateau at 1104∂6°C and 1190∂7°C. The first one, represented as dotted lines in Figure 2, is probably due to a polymorphic transition of a new ternary phase (composition close to $Ce_{41}Zr_4Au_{55}$) with regards to DTA experiments performed on several ternary samples. We observed that the peak area associated to this transition is clearly related to the amount of the new phase (κ). The thermodynamic properties of the later are still under investigations. The invariant reaction, occurring at 1190°C, unambiguously implies ZrAu, CeAu and κ. Indeed, XRD of the Ce(25%)Zr(25%)Au(50%) sample annealed under ultra-high vacuum at 950°C (fig. 3b) revealed an equilibrium between $Zr_{48}Au_{52}$, $Ce_{48}Zr_2Au_{50}$ and κ. Figure 4 shows a schematic representation of the phase equilibria counted in the proximity of the ZrAu-CeAu section at 950°C. From the liquidus surface (fig.2), we suggest that the invariant may be a ternary eutectic. However, more work has to be done in order to precise the nature of this invariant which depends on the formation type of κ, still unknown. Details in the ternary phase field will be published elsewhere.

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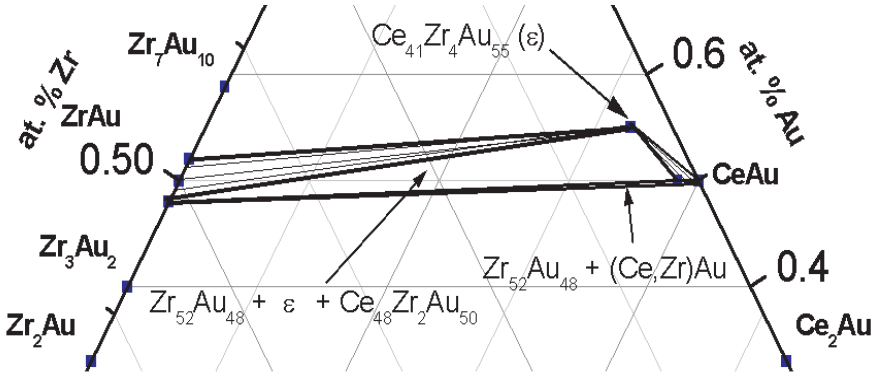

Figure 4. Equilibria at 950°C in the proximity of the ZrAu-CeAu section.

In spite of the determination of the liquidus curves thanks to the use of W crucibles, the phase equilibria implying the liquid phase are not yet clearly established and appear as dotted lines in the isopletic section. Heat treatments performed in a high-frequency furnace followed by argon jet quenching are still under work in the laboratory, in order to precise the phase equilibria at high temperature.

3.2 The new ternary phase κ

The presence of κ has been observed in samples annealed under ultra-high vacuum (2.10^{-10} mbar) at 950°C during 15 days. The composition of κ was estimated from EPMA and we obtained $Ce_{41}Zr_4Au_{55}$. In order to characterise the structural and thermodynamic properties of the new phase, we have prepared several samples with a composition close to that measured by EPMA. Figure 5 shows a optical micrograph of as cast arc-melted $Ce_{39}Zr_4Au_{57}$, which reveals the primary crystallisation of κ (grey). The XRD pattern of as cast $Ce_{39}Zr_4Au_{57}$ (fig. 6) reveals a characteristic diffraction peak (2χ=40°) which can not be attributed to ZrAu and CeAu nor to the neighbouring binary phases. The determination of the crystal structure of κ is still under work.

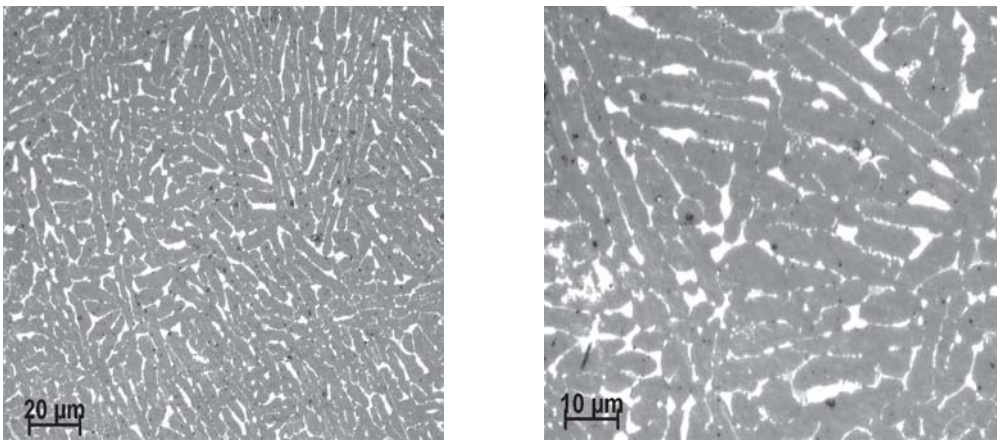

Figure 5. Micrographs of as cast arc-melted Ce(39%)Zr(4%)Au(57%) sample.

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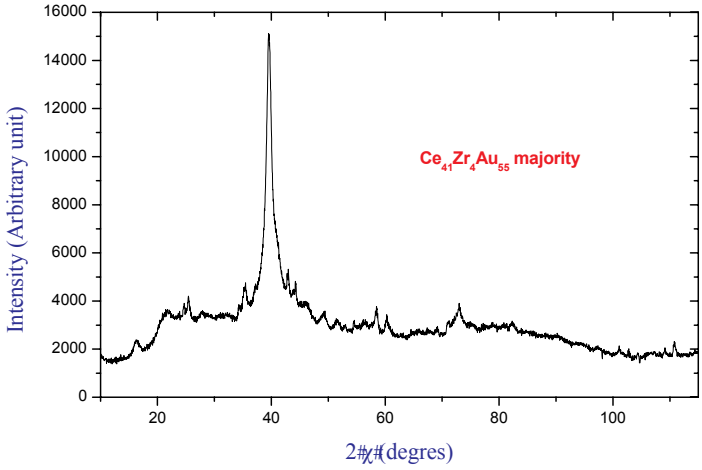

Figure 6. XRD pattern of as cast arc-melted Ce(39%)Zr(04%)Au(57%).

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