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Investigation of as-cast alloys in the Pt–Al–Cr system

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ABSTRACT

Platinum-based alloys are being developed which have microstructures that are analogous to the γ/γ' microstructure of the nickel-based superalloys. These Pt-based alloys have the potential to be used for high-temperature applications. The ternary Pt–Al–Cr system was investigated as part of the continued development of a thermodynamic database for the Pt–Al–Cr–Ru system. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) analyses were used to obtain phase equilibria data. The alloys were studied in the as-cast condition. A solidification projection was constructed and a liquidus surface derived. It was concluded that all phase regions were identified correctly since the results were self-consistent. Three ternary phases and 21 ternary invariant reactions were identified.

1. Introduction

Platinum alloys are being developed which have microstructures that are analogous to the γ/γ' microstructure of the nickel-based superalloys (NBSAs) [1,2]. Although the use of Pt-based alloys as a replacement for Ni-based superalloys is limited due to their higher price and higher density, it is possible that they could be used for critical components, or as corrosion resistant coatings. NBSAs can contain up to 15 alloying elements and it was envisaged that the Pt-alloys for high-temperature applications would very likely contain at least 5 elements. The potential need for a predictive thermodynamic database for Pt-containing alloys was therefore identified at the outset of the Mintek alloy development programme, but before the construction of the database could start, it was necessary to identify its major components. Experimental studies of the microstructure and mechanical and oxidation properties suggested that a thermodynamic database for the development of Pt-alloys for high-temperature applications should be based on Pt–Al–Cr–Ru [3,4]. The information required to undertake the computer assessments was either gleaned from literature, or when not available, undertaken within the project. Experimental studies of the four ternary systems have been undertaken on Al–Cr–Ru [5–8], Pt–Cr–Ru [9–11] and Pt–Al–Ru [12,13]. This paper summarises results obtained from experimental work on as-cast Pt–Al–Cr alloys.

2. Previous work

2.1. Al–Pt

The Pt–Al phase diagram (Fig. 1) is complex and although certain features had been determined reliably, other aspects of this diagram remain problematic. McAlister and Kahan reviewed the Pt–Al system in 1986 [14,15]. This most widely accepted binary phase diagram is based on the work of Huch and Klemm [16], Darling et al. [17], Chattopadhyay and Schubert [18,19], Bhan and Kudielka [20] and Piatti and Pellegrinin [21].

Pt is practically insoluble in (Al) [16]. Extrapolation of the eutectic reaction

$$L \rightarrow (Al) + Pt_5Al_{21}$$

at 657 °C [14] places the eutectic composition at 0.44 at.% Pt [21].

Pt_5Al_{21} is a complex cubic stoichiometric phase with essentially no solubility. Huch and Klemm [16] and Guex and Feschotte [22] reported a cubic $PtAl_4$ phase with ∼20 at.% Pt. However, it was suggested that the phase might actually be Pt_5Al_{21} instead. Schaller reported a hexagonal Pt_5Al_{21} phase [23], confirmed by Ellner et al. who called it $PtAl_4$ [24]. Piatti and Pellegrinin also reported a hexagonal phase, in this composition range, suggested to be Pt_6Al_{21}, but noted a transformation from hexagonal to cubic phases after treatment at 200 °C for several hours [21]. Careful analysis by McAlister and Kahan [14] of thermal arrest data by Huch and Klemm [16] confirmed the phase as Pt_5Al_{21}. Thus, cubic $PtAl_4$ has been suggested as a metastable phase in the Pt–Al system, and is not included in the generally accepted binary

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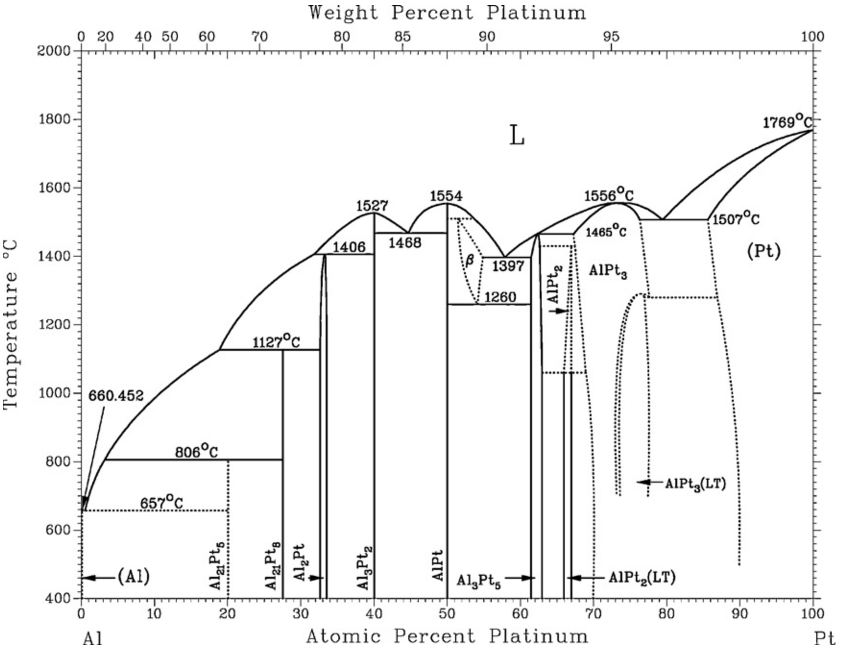

Fig. 1. Binary Al–Pt equilibrium phase diagram [15].

phase diagram given in Massalski [15], while the hexagonal phase Pt_5Al_{21} is.

The stoichiometric Pt_8Al_{21} phase at 27.5 at.% Pt has been confirmed by Edshammer [25] and Ellner et al. [24] although its structure has not been determined. The $PtAl_2$ phase has been reported as a line compound by Guex [22], while Huch and Klemm [16] and Ellner et al. [24] reported a ~1 at.% solubility range up to 850 °C. Pt_2Al_3 has a structure related to, but not isotypic with, hexagonal Ni_2Al_3 and essentially no solubility range [16,22,24].

Experimental evidence of a β-phase existing between 1260 and 1500 °C with a solubility range from 51–56 at.% Pt has been reported [18,20]. McAlister and Kahan [14] included these observations in their assessment of the Pt–Al system and proposed a peritectic reaction $L + PtAl \rightarrow \beta$. An eutectoid decomposition $\beta \rightarrow PtAl + Pt_5Al_3$ has been proposed by McAlister [14] to correspond with a thermal arrest [16]. Prins et al. [13,26] observed microstructural evidence of the $L \rightarrow \beta + Pt_5Al_3$ eutectic and $\beta \rightarrow PtAl + Pt_5Al_3$ eutectoid reactions in the ternary Pt–Al–Ru system, and microstructural evidence of a eutectoid decomposition was observed in a 53.5 at.% Pt–Al alloy [27].

Pt_5Al_3 was originally reported as a line compound, with Pt_3Al_2 being included [14,20], although Pt_5Al_3 is now believed to have a solubility range 61.5–63 at.% Pt instead of two line compounds, as reported by Ellner [24] and Oya [29].

Two crystal variants of the Pt_2Al phase have been reported. Although the low temperature form was not observed by all the researchers, and the nature of the reaction is still unknown, it is accepted that this reaction exists at 1060 °C. The reaction was observed more recently by Biggs [28].

Of very specific importance to this alloy development programme, is the Pt_3Al intermetallic phase which is responsible for the enhanced strength of the system. It forms congruently at 1556 °C [16], eutectically with (Pt) at 1507 °C [16,17], as well as eutectoidally at 1280 °C [16]. It has at least two forms: a high-temperature cubic $L1_2$ form, and at least one [14], if not two [29], lower temperature non-cubic forms. The third and lowest temperature form [29] has yet to be fully confirmed. Thus, there are two conflicting phase diagrams regarding the transformation temperatures of γ', Pt_3Al. According to McAlister and Kahan [14,15], there is a transformation of the high-temperature Pt_3Al phase from $L1_2$ to a tetragonal low-temperature variant (designated $D0_c{}'$) at ~1280 °C. However, Oya et al. [29,30] report an additional transformation at a lower temperature. The transformation temperatures given by Oya et al. are $\gamma' \rightarrow \gamma_1{}'$ at ~340 °C and $\gamma_1{}' \rightarrow \gamma_2{}'$ at 127 °C [29,30]. Biggs [28] observed two low temperature reactions at ~130 °C and ~320 °C, which coincide with the $\gamma' \rightarrow \gamma_1{}' \rightarrow \gamma_2{}'$ reactions reported by Oya at 127 and 340 °C respectively [29,30]. Investigating the transformation temperatures using in situ heating of an alloy with composition Pt_{85}:Al_{15} in a TEM [2,31], confirmed that the phase diagram for the Pt–Al system by Oya et al. [29,30] was more accurate than that of McAlister and Kahan [14,15]. Douglas et al. reported unexpected ordering of in Pt_3Al precipitates based on a modified $D0_c{}'$ unit cell [32].

2.2. Al–Cr

Murray [33] reviewed the literature up to 1988 and gave an assessed diagram based (Fig. 2) on the work of Koester et al. [34], den Broeder [35] and van Tenderloo [36]. Further investigations were performed by Ellner et al. [37], Costa Neto et al. [38], Audier et al. [39], Lee and Kwun [40], Helander and Tolochko [41] and Mahdouk and Gachon [42]. Cornish et al. reviewed the literature up to 2002 [43], and it was concluded that most authors agreed that more work needed to be done on the system.

Cr_2Al_{13} is considered the more correct composition for $CrAl_7$ [33]. Both Cr_2Al_{11}, decomposing at 785 °C [42], and $CrAl_4$ have been reported as showing metastable behaviour [33]. $CrAl_5$ has been suggested as the more correct composition for Cr_2Al_{11}.

Costa Neto et al. [38] reported no Cr_2Al_{11} in either as-cast or annealed samples, although the phase of that composition did occur in diffusion studies. Conversely, Audier et al. [39] found a peak corresponding to the peritectic formation of Cr_2Al_{11}. It was suggested that Cr_2Al_{11} formed in the solid state during slow cooling, but that nucleation was difficult. The eutectoid decomposition of Cr_2Al_{11} was reported and should not have been affected by impurities, although 99.5% starting materials were used [42]. However, an amorphous phase at 460 °C contradicted this [40].

Zhang et al. [44] established the orientation relationship between $\iota CrAl_4$ and $CrAl_7$. It was shown that the $\mu CrAl_4$ had similar icosahedral clusters to $CrAl_7$, as well as a relationship with Cr_2Al_{11}