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The role of in situ reactive metal getters in the determination of phase equilibrium diagram in metallic systems

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Abstract

The maintenance of high purity inert environment over the sample is necessary to carry out DTA studies on reactive metal systems for determining the phase boundaries. This paper describes how oxygen impurity present in the argon stream affects the shape of the DTA trace in the melting temperature determination of copper.

INTRODUCTION

Differential thermal analysis (DTA) is among the most versatile techniques employed in the determination of phase equilibrium diagrams in metallic systems. One of the major problems in the investigations of such systems, however, is the maintenance of highly inert atmosphere around the sample at the temperatures of the experiment. Our recent experiments on the determination of phase equilibrium diagrams in nickel based alloys have shown that the usual method of passing the dry inert gas over the bed of reactive metals could be inadequate to remove the traces of oxygen which inadvertently enter the stream of the flowing high purity inert gases [1–3]. The in situ reactive metal getters located close to the sample being investigated were found to help considerably in maintaining a clean, oxygen free gaseous atmosphere around the sample. The results on the melting point of pure copper obtained in high purity (99.9999 vol.%) flowing helium with and without the in situ metal getters, presented in this communication, demonstrate clearly the extent to which the measurements can be influenced by trace amounts of oxygen in the inert gas. The

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observations made further provide a method to check the purity of copper with respect to oxygen.

EXPERIMENTAL

The melting point of copper was determined by differential thermal analysis (DTA). The simultaneous differential thermal analyser (STA 429) supplied by Netzsch GmbH, Selb, FRG, was used to obtain the DTA curves. About 600 mg of copper chiselled from oxygen free copper block and cleaned ultrasonically with trichloroethylene and acetone was used in each experiment. Nearly the same mass of platinum foil was used as an inert reference material. The sample and the reference were taken in the special recrystallised alumina DTA cups supplied by the manufacturer. The curves were recorded in high purity (99.9999 vol.%) flowing helium (10 ml min^{-1}) at the heating and cooling rates of 10 and 5 K min^{-1}. Prior to the determination of the melting temperature of Cu, the instrument was calibrated for temperatures at the melting points of silver and gold. The temperatures were measured with a calibrated EL 18 thermocouple.

The experimental procedure for recording the DTA curves was as follows. The high purity helium gas (99.9999 vol.%) dried by passing over a bed of molecular sieves was passed through a column of calcium metal granules maintained at 550 K. The gas so purified was flushed into the DTA system to replace the air inside. The system was then isolated from the gas manifold and evacuated to a total pressure of less than 10^{-4} Pa using a turbomolecular pump backed by a rotary pump. The system was repeatedly filled with purified helium and evacuated. This operation was repeated three or four times, after which a steady gas flow of purified helium (10 ml min^{-1}.) was maintained inside the system. In some of the experiments the tantalum or zirconium foils were placed over the alumina shields of the sample holder to function as in situ oxygen getter. All-metal leak-free gas and vacuum manifolds were used in the experiment.

RESULTS

Typical DTA curves for the melting of copper obtained in the absence and presence of in situ oxygen getters are shown in Figs. 1 and 2. Single well defined melting and freezing peaks were obtained when the zirconium or tantalum foils were used as oxygen getters. The melting point of copper determined using the extrapolated onset temperature concept [4] was 1359.6 ± 1 K in the presence of in situ getters as shown in the upper DTA trace in Fig. 2. Considerable under cooling was, however, observed in the cooling cycles and the freezing point recorded in some cases was as low as 1317.4 K.

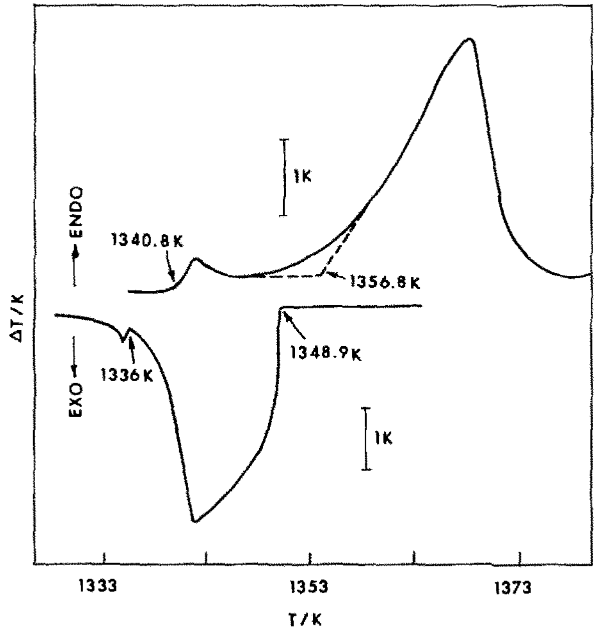

Fig. 1. DTA trace for the melting point of copper in flowing helium without an in situ getter. Quantity of copper, 600 mg; heating and cooling rates, 5 K min^{-1}.

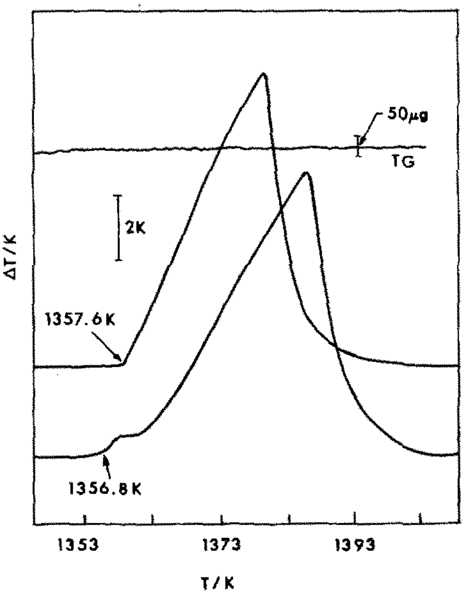

Fig. 2. DTA trace for the melting point of copper in flowing helium with in situ zirconium getter. Lower plot indicates melting point trace in the first cycle; upper trace is in the next cycle. Quantity, 600 mg; heating rate 5 K min^{-1}.

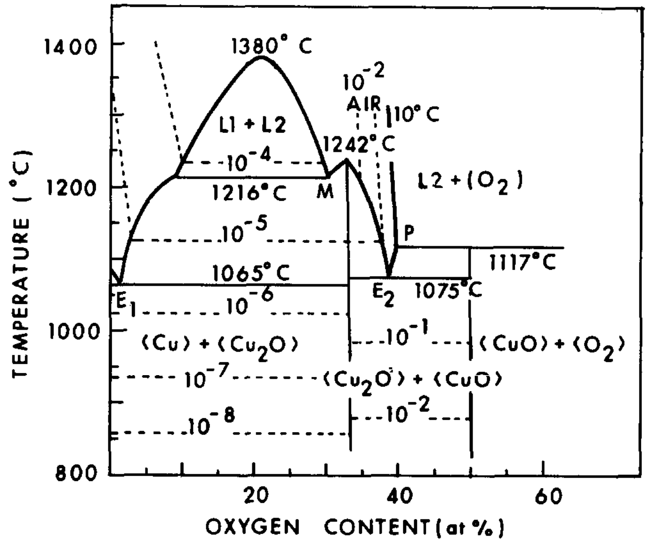

Fig. 3. Phase diagram of Cu + O system as given by ref. 5. The dotted line indicates oxygen isobars.

The DTA curves recorded in the absence of in situ getters showed two peaks both in the heating and the cooling cycles as shown in Fig. 1. A minor peak beginning at 1340.8 K was followed by a major peak whose extrapolated onset temperature was 1356.6 K. Both peaks could also be recorded in the cooling cycle but with sizeable undercooling effect. The inception temperatures of the two peaks in the cooling cycles were 1348.9 and 1336 K respectively. The height of the minor peak decreased as oxygen impurity decreased in the gas stream (lower DTA trace in Fig. 2). and eventually disappeared (upper DTA trace in Fig. 2).

DISCUSSION

The observation of the variation of melting point of copper with the introduction of in situ oxygen getter in the system can be readily understood in terms of the Cu–O phase diagram from ref. 5 reproduced in Fig. 3. It can be seen that the melting point of copper is influenced substantially for the small addition of oxygen. The phase diagram was based on the Cu + O system studied by Osterwald [6], Gerlach et al. [7] and by Kuxmann and Kurre [8]. The eutectic temperature on the copper rich side has been determined to be 1338 K at 1.54 at.% oxygen (0.39 wt.% oxygen). The initial minor peak at 1341.9 K obtained during melting could thus correspond to that of the eutectic. The subsequent peak due to melting of oxygen saturated copper at 1356.5 K is as expected lower than that reported for the melting of pure copper according to the IPTS-68 scale [9].

The reported melting point of pure copper is 1358.02 K [10]. It is obvious that the oxygen partial pressure in the carrier gas stream in excess of 10^{-6} atm above 1276 K would result in the formation of Cu_2O which would form an eutectic with the copper metal as indicated in the phase diagram.

The location of zirconium metal getter in the vicinity of copper reduced the oxygen potential in the environmental flowing gas stream by several orders of magnitude as is evident from the Ellingham diagram for the metal oxygen systems [11]. From the present observation it can be concluded that oxygen pressure prevalent over the sample is much below the dissociation pressure of Cu_2O. Since in the presence of zirconium metal getter, the nickel–aluminium melted alloys were found to remain unoxidised with bright metallic surface [1–3], it is concluded that the oxygen partial pressure in the helium gas around the sample is at least 3 to 4 orders of magnitude below that which would exist over nickel–aluminium alloys and over $Cu-Cu_2O$ mixture. The equilibrium oxygen pressure around 1273 K over Zr/ZrO_2 couple is, in fact, of the order of 10^{-34} atm and therefore would provide a really good inert gaseous environment for the determination of phase equilibrium diagrams in reactive metal systems as has been observed in our latest investigations.

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