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# DETERMINATION OF SOLIDUS AND LIQUIDUS IN THE BINARY SYSTEM OF COPPER-NICKEL

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## ABSTRACT

Knowledge of solidus - liquidus phase transformation temperatures in binary as well as higher order systems finds more applications in the field of nuclear studies. Determination of solidus - liquidus temperatures of binary system Cu-Ni by using spot technique was carried out at Radio-Chemistry lab, IGCAR ( **Indhira Gandhi Centre for Atomic Research** ), Kalpakkam. The experimental results obtained by using pyrometric measurements were in good agreement with that of theoretical values (ideal solution) and feest-doherty reference values. If the same approach is extended to nuclear fuels like Uranium, Thorium etc, more relavent information may be obtained to decide the centerline temperature of the nuclear reactors case.

**Key words :** Spot Technique, Solidus & Liquidus, Pyrometer

## 1.0 INTRODUCTION

Data on the solid – liquid phase transformation (7) temperatures in binary and higher order system relevant to nuclear fuel materials are useful in estimating the upper limit of the centerline temperature(1) of the fuel. An experimental set up has been made at FChD, CG at IGCAR to measure the solid to liquid phase transition temperature in alloys at high temperature by using the spot technique. To validate the experimental technique and to calibrate the experimental setup, the solidus and the liquids boundaries in the system Cu-Ni were redetermined in this study.

The system Cu-Ni Feest and Doherty (2) studied the copper nickel binary system using DTA.

## 2.0 THEORITICAL CALCULATIONS

The Cu-Ni binary system is almost ideal. Both the components are completely soluble in solid and liquid solutions. Hence, the assumption was made that the solid and liquid solutions of the Cu-Ni were ideal.

By using this assumption the expression for mole fraction of copper in the solid and liquid solutions were derived and the values of $XCu^{1}$ and $XCu^{S}$ calculated for

$T_m^{Cu} < T. < T_m^{Ni}$ .

$$X_{Cu}^{1} = 1\text{-exp}\,(\Delta H_f^{Ni}/RT - H_f^{Ni}/RT_m^{Ni})\,/\exp(\Delta H_f^{Cu}/RT - \Delta H_f^{Cu}/RT_m^{Cu}) - \exp(\Delta H_f^{Ni}/RT - \Delta H_f^{Ni}/RT_m^{Ni})$$

$$X_{Cu}^{S} = X_{cu}^{1} * \exp(\Delta H_f^{Cu}/RT - \Delta H_f^{Cu}/RT_m^{Cu})$$

## 3.0 PRINCIPLE OF SPOT TECHNIQUE

In the method involving direct pyrometric measurements of melting point of a pure metal and the solidus and liquidus temperature of an alloy, the molten sample in an inert container forms a smooth highly reflecting surface in contrast to the rough surface of solid. When the metal is heated in an effusion cell, the reflection of the orifice from the liquid metal surface produces a well-defined circular black spot in an incandescent background. The temperature at which the black spot appears corresponds to the appearance of the liquid phase at the melting temperature (3)

## 4.0 EXPERIMENTAL ASSEMBLY

A schematic diagram of the experimental assembly is shown in Fig.1. The assembly consists of:

### 4.1 Vacuum system

A combined vacuum system consisting of a rotary pump and an oil diffusion pump was used to maintain a vacuum of $10^{-6}$mbar.

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### 4.2 RF generator

A Rf generator (370-420kHz) was used to heat the sample inductively.

### 4.3 Pyrometer

Temperatures were measured using fiber optic two color pyrometer. The pyrometer was calibrated by melting gold (m.p1336K).

### 4.4 Experimental set up

The setup mainly contains a Knudsen cell in which graphite or alumina cup is kept. The cell is supported on three tungsten legs. The entire setup is enclosed in a quartz tube.

## 5.0 EXPERIMENTAL PROCEDURE

About 400 mg copper and nickel at appropriate compositions were taken in the alumina/graphite cup. The entire assembly was evacuated to $10^{-6}$mbar. Then the sample was heated rapidly till near the melting point; after which the heating was done at a rate of 1K/min. The surface of the sample was monitored continuously using a magnifying microscope. The appearance of broken spot corresponds to the solidus temperature. A full spot corresponds to the liquidus temperature (6). This process was repeated for various compositions of Cu-Ni.

### 5.1 Chemical analysis

#### 5.1.1 Analysis for copper

The alloys were ground in a vibro-mill and portion dissolved in conc.$HNO_3$. The solution was neutralized with ammonia, a few drops of conc.$H_2SO_4$ were added to bring the pH just below 7. Then Cu was estimated by electrogravimetry by using Pt-gauze cathode.

#### 5.1.2 Analysis for Ni

To a solution of the alloy freed from copper, excess dimethyl glyoxime (1%) was added, followed by ammonia. The precipitate formed was filtered, washed and dried and weighed(4).

#### 5.1.2 Analysis for carbon

The alloys containing up to 45% Ni were analyzed for carbon by combustion of the alloy in oxygen and determination of the carbon dioxide using an IR detector (8).

## 6.0 RESULTS AND DISCUSIONS

The results of the calculation of the mole fractions of copper in the liquid and solid solutions are given in Table.1.

In Table 2 are presented the experimentally determined data for the solidus and liquidus temperatures in this study. This table also shows the results of the chemical analysis for copper, nickel and carbon.

The experimentally determined solidus and liquidus temperatures for the Cu-Ni system as a function of composition of the alloy are plotted in Fig.2. Our experimental results on the binary system Cu-Ni agree with those of Masalski et al (5). and Feest and Doherty((2).

Nickel rich regions closely match with those of Feest and Doherty. The copper rich regions agrees with the reviewed phase diagram.

The graphite contamination of the samples increased with increase in weight fraction of nickel. However, in the copper rich region, this did not significantly alter the solidus and liquidus temperatures.

**Table 1. Liquidus & Solidus temperatures of Copper-Nickel Alloy**

| Temp.(K) | $X_{Cu}^L$ | $X_{Cu}^S$ |
|---|---|---|
| 1366 | 0.9822 | 0.9754 |
| 1386 | 0.9376 | 0.9158 |
| 1406 | 0.8930 | 0.8582 |
| 1426 | 0.8447 | 0.7990 |
| 1446 | 0.7965 | 0.7420 |
| 1466 | 0.7475 | 0.6861 |
| 1486 | 0.6969 | 0.6305 |
| 1506 | 0.6451 | 0.5754 |
| 1526 | 0.5922 | 0.5209 |
| 1546 | 0.5384 | 0.4673 |
| 1566 | 0.4838 | 0.4145 |
| 1586 | 0.4274 | 3615 |
| 1606 | 0.3721 | 0.3109 |
| 1626 | 0.3127 | 2581 |
| 1646 | 0.2527 | 0.2062 |
| 1666 | 0.1934 | 0.1560 |
| 1686 | 0.1327 | 0.1058 |
| 1706 | 0.0699 | 0.0551 |
| 1726 | 0.0068 | 0.0053 |

**Table 2 . Chemical analysis of Copper-Nickel Alloy**

| Weight % Cu | Weight % Ni | Solidus K | Liquidus K | Analysed data | | |
|---|---|---|---|---|---|---|
| | | | | Cu % | Ni % | C % |
| 94.8 | 5.2 | 1359 | 1383 | 94.13 | 5.59 | 0.014 |
| 89.9 | 10.1 | 1393 | 1414 | 87.48 | 10.05 | 0.0278 |
| 84.84 | 15.16 | 1400 | 1423 | 83.17 | 15.43 | 0.0154 |
| 79.42 | 20.58 | 1494 | 1454 | 77.6 | 21.12 | 0.0131 |
| 74.29 | 25.71 | 1495 | 1510 | 75.05 | 27.97 | 0.0662 |
| 69.73 | 30.27 | 1488 | 1521 | 65.79 | 31.2 | 0.0446 |
| 65.16 | 34.84 | 1513 | 1551 | 61.36 | 36.2 | 0.011 |
| 54.71 | 45.29 | 1558 | 1575 | 53.16 | 44.4 | 0.2072 |
| 45.15 | 54.85 | 1566 | 1626 | 42.99 | 56.2 | - |
| 35.47 | 64.53 | 1613 | 1654 | 32.94 | 65.97 | |
| 25.18 | 74.82 | 1652 | 1678 | 25.6 | 75.05 | |
| 14.93 | 85.07 | 1684 | 1711 | 10.73 | 85 | |
| 6.19 | 95.81 | 1698 | 1721 | | | |

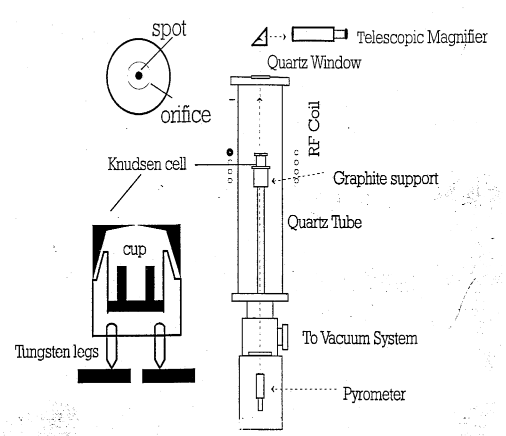
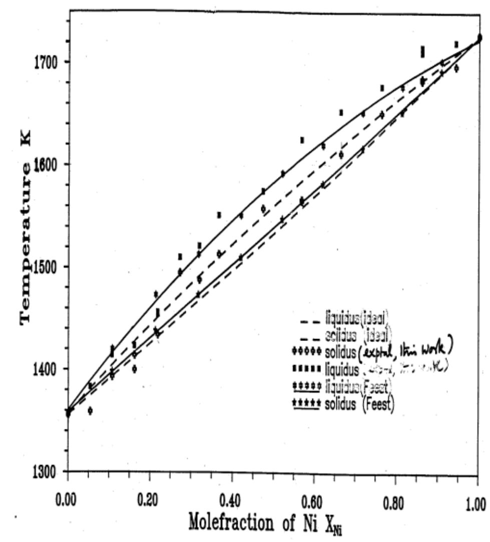
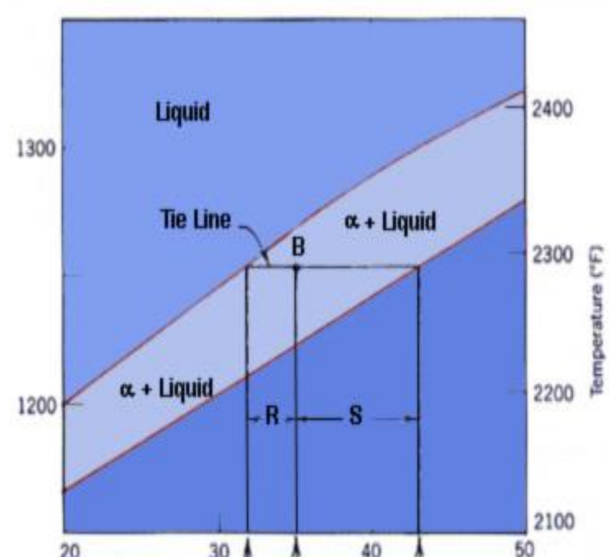



**Fig.1. Experimental Set up**




**Graph 1.Phase diagram of Copper – Nickel Binary system**

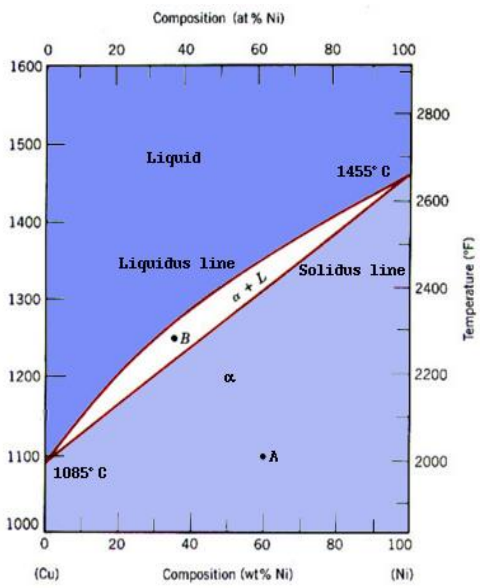



**Graph 2. Explanation of solidus – liquidus phenomena through Phase diagram**

## 7.0 CONCLUSION

(1) Determining the solidus and liquidus in the system Cu-Ni validated the experimental assembly and the technique. Values obtained in this study agreed with reviewed phase diagram data within + or – (10K).

(2) The experimental results also agreed with the theoretical values calculated




**Graph 3. Explanation of tie-line through Phase diagram**

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