



Evaluation of the Stable and Metastable Cu-Co-Fe Phase Diagrams

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(Received March 14, 2002)

Abstract. The thermodynamic description of the Cu-Co-Fe system was modified on the basis of experimental data obtained by electromagnetic levitation. Using the modified database, the solidus and liquidus temperatures were calculated. Very good agreement was obtained between the calculated and experimental data. The compositions of the metastable miscibility gap in the liquid were found to agree well with the observed values.

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Introduction

There has been recent growing interest in the extension of the solid solubility of alloys exhibiting metastable miscibility gaps in magnetic systems such as Cu-Co. Such materials are known to exhibit giant magneto resistance (GMR), corresponding to a large drop in electrical resistance under the influence of a magnetic field. For example, a supersaturated Cu₉₀Co₁₀ solid solution annealed at 440°C for different times exhibits an increased GMR of 11% at room temperature. It is believed that the heat treatment caused solid-state spinodal decomposition of fine Co precipitates responsible for the enhanced GMR.

Previous studies showed that supercooling of Cu-Fe, Cu-Co and Cu-Co-Fe alloys below a certain temperature, called T_{SEP} , resulted in metastable separation of the liquid into Cu-rich (L2) and Co or Fe-rich (L1) liquids [3-6]. T_{SEP} was found to depend on the alloy composition. Liquid phase separations and formation of metastable phases were also observed during rapid cooling of these alloys. Recent combination of the binary phase diagram data for the Fe-Cu [7,8], Fe-Co, Co-Cu [8,9] were used to construct approximate ternary sections for the Cu-Co-Fe system [10] by using experimental melting data for ternary alloys [11]. More recently, additional experiments were conducted by the present authors [12] to fully determine the phase boundaries in the ternary alloys.

The present effort is directed at obtaining a reliable thermodynamic description for the Cu-Co-Fe system and to perform consistent calculations of the ternary phase diagrams.

Experimental Procedures

High purity copper (99.99%), cobalt (99.99%) and iron (99.99%) were used to prepare Cu-Co-Fe alloys containing up to 85% Cu and weighing approximately 1.5 grams. The specimens were alloyed by arc melting in Argon environment using a non-consumable tungsten electrode. For each arc-melted sample, the individual

alloy components were weighed with an accuracy of ± 0.01 grams to fabricate the desired compositions. The arc-melting period was kept brief, normally a few seconds, to allow only for the melting of the copper to form a single button. Each arc-melted button was then levitated and processed using an electromagnetic (EM) levitation apparatus described elsewhere [3-5]. The typical sample processing cycle during EM levitation consisted of melting, superheating by about 200K, and then cooling. The heating or cooling is accomplished by changing the ratio He/Ar gas mixture and/or the gas flow rate. The sample temperature was monitored continuously by two-color optical pyrometer connected to a data acquisition system.

The stable phase boundaries were determined by cycling samples through the melting and freezing cycles several times. Subsequently the specimens were quenched on a copper chill plate from various predetermined degrees of superheating or supercooling. The microstructure and phase compositions of the samples were then determined. The full description of microstructural characterization is beyond the scope of the current paper and will be given elsewhere [12].

Thermo-Chemical Modeling of the Co-Cu-Fe System

The thermochemical description of the Co-Cu-Fe system used to model the experimental results was that employed by the software developed by Thermo-Calc AB of Stockholm, Sweden. The description of the fcc, bcc and Liquid phases is used is based on the SSOL database. The pure element data is that given by Dinsdale [13], with magnetic contributions added to the bcc and fcc phases as detailed by Hillert and Jarl [14]. The excess Gibbs energies for these phases is provided using the Redlich-Kister format. Thus the excess Gibbs energy, E_G^L is given by the following equation:

$$(1) \quad E_G^L = x_{Co}x_{Cu}(L_{CoCu}^0 + (x_{Co}-x_{Cu})L_{CoCu}^1 + (x_{Co}-x_{Cu})^2L_{CoCu}^2) + x_{Co}x_{Fe}(L_{CoFe}^0 + (x_{Co}-x_{Fe})L_{CoFe}^1 + (x_{Co}-x_{Fe})^2L_{CoFe}^2) + x_{Cu}x_{Fe}(L_{CuFe}^0 + (x_{Cu}-x_{Fe})L_{CuFe}^1 + (x_{Cu}-x_{Fe})^2L_{CuFe}^2)$$

where the elements are arranged in alphabetical order and x_{Co} , x_{Cu} and x_{Fe} are the mol fractions of Co, Cu and Fe, respectively. The nine Redlich-Kister(R-K) coefficients L_{CoCu}^0 ...through... L_{CoFe}^2 can be temperature dependent, positive, negative or zero. In addition to Eq(1) similar equations apply for the fcc and bcc phases and the Co-Fe and Cu-Fe systems as well. As a consequence a total of 27 excess parameters are required to set the R-K formalism for the Co-Cu-Fe ternary. For the fcc phase the L_{CoCu}^0 term and its' eight companions in Eq(1) are replaced by A_{CoCu}^0 A_{CuFe}^2 . Similarly for the bcc phase B_{CoCu}^0 designates the nine R-K coefficients..... B_{CuFe}^2 . This description assumes that ALL ternary interactions are zero. The R-K coefficients are often unknown. Normally only the first and second order (R-K) i.e. L_{CoCu}^0 and L_{CoCu}^1 for the liquid phase of the Co-Cu binary system can be determined from experimental or reliable theoretical information. Assessment of the other second and higher order coefficients are problematic which in many cases precludes the application of the R-K model.

The values used in the present calculations are as follows. The Co-Fe binary values used were those given in SSOL and are due to Fernandez-Guillermet [15]. These values are given for liquid, fcc and bcc phases in Joules/g.at. (which means Joules per mol of atoms) and temperature, T, in Kelvin. The specific values are: $L_{CoFe}^0 = -9312$, $L_{CoFe}^1 = -1752$ for the liquid, $A_{CoFe}^0 = -8471$, $A_{CoFe}^1 = 1181-1.65T$ for the fcc phase and $B_{CoFe}^0 = -23669+104T-12.79T \ln T$ for the bcc phase. All other R-K terms for bcc, fcc and liquid phases in Co-Fe are zero. There are many R-K formulations of the Cu-Fe System. The description used here in Thermo-Calc, which includes the abovementioned magnetic term, is due to Jansson [16]. In this description $L_{CuFe}^0 = 36088-$

2.33T, $L_{CuFe}^1 = 325 - 0.033T$ and $L_{CuFe}^2 = 10355 - 3.6T$ for the liquid. The bcc phase was described with $B_{CuFe}^0 = 39258 - 4.15T$, while the fcc was defined with $A_{CuFe}^0 = 48233 - 8.61T$ and $A_{CuFe}^1 = 8862 - 5.29T$. All of the remaining R-K terms for the bcc, fcc and liquid phases in Co-Fe are zero.

There are several other R-K descriptions of the Cu-Fe system [17-19], which were reviewed by Kaufman [20]. These descriptions were based on the observed and submerged miscibility gaps in the liquid and fcc phases of the Cu-Fe system. As disclosed in [20], the values of A_{CuFe}^0 and A_{CuFe}^1 reported by three group of investigators [17,18 and -19] are respectively as follows: A_{CuFe}^0 , 48206-8.446T, 49704-9.412T and 39719-2.13T, and A_{CuFe}^1 , -5918+5.017T, 8585-5.047T and 2090. When these parameters are evaluated at 1250K, it is found that A_{CuFe}^0 is 37648, 37939 and 37056. These values not only are in remarkable agreement with each other, they also agree well with the Thermo-Calc value given above as 37471. The A_{CuFe}^1 values at 1250K are 353, 2276 and 2090 respectively. Thus the second R-K term is much smaller than the first order term and the three independent analyses are in relative agreement in the center of the temperature range of interest. The comparable value for A_{CuFe}^1 from Thermo-Calc is 2250 J/g.at, again in good agreement with the results of [17-20].

A similar consideration of the liquid parameters yield comparable results. Thus the differences in excess Gibbs energies (after multiplication by the appropriate mole fraction is quite small! In addition it is apparent that the magnetic contributions in this system) is quite small since the R-K coefficients derived in [17-19] do not make an explicit allowance for magnetic factors. The R-K coefficients for the Co-Cu system are not contained in the Thermo-Calc Database. Only the magnetic terms are included based on the above-mentioned Hillert- Jarl [14] formulation. Accordingly the values derived some 25 years ago [20] were adapted to complete Eq(1). These are $L_{CoCu}^0 = 46860 - 13.05T$, $L_{CoCu}^1 = -6695 + 4.68T$ for the liquid, $A_{CoCu}^0 = 28700$, $A_{CoCu}^1 = 1255$ for the fcc phase and $B_{CoCu}^0 = 35000$ for the bcc phase. Recently, Kubitsa and Vrestal [21] performed a combined experimental and Thermo-Calc based assessment of the R-K coefficients of the Co-Cu system by performing Knudsen-cell mass spectrometry and calculating the phase diagram. Their R-K parameters are $L_{CoCu}^0 = 35200 - 4.95T$ and $L_{CoCu}^1 = -1000 + 0.083T$ for the liquid and $A_{CoCu}^0 = 40900$, $A_{CoCu}^1 = -1600$ and $A_{CoCu}^2 = -6900$ for the fcc phase [21]. These values compare quite well at 1250K.

Figure 1 shows the binary phase diagrams for the Co-Fe, Co-Cu and Cu-Fe binary systems and the ternary Co-Cu-Fe system based on the above-mentioned parameters at 1450°C. The diagrams agree fairly well with experimental observations, except for one major exception. The calculated ternary diagram shows the existence of a stable two-phase liquid region in central portion. Such stable melt separation has not been observed in the ternary liquids investigated so far. For example, if one uses the unmodified database to calculate the phase formation during cooling of a Cu-20 wt.% Co- 20 wt.% Fe alloy, the formation of two stable liquids can be clearly seen. This separation could not be confirmed experimentally [11,12]. On the other hand, metastable liquid phase separation has been observed upon supercooling of certain binary Cu-Co and Cu-Fe as well as ternary Cu-Co-Fe alloys.

Modification of the Database

In order to eliminate the two-liquid separation from the diagram without affecting the solidification temperatures or the binary-edge diagrams, a small ternary correction term given by Eq(2) was added to both the fcc and liquid phases as given in the following equation:

$$(2) \quad E_G^L \text{ (ternary)} = x_{Co}x_{Cu}x_{Fe} ((5000x_{Co} - 80000x_{Cu} + 10000 x_{Fe})$$

The resulting ternary section at 1450°C is shown in Figure 2. This small ternary term is enough to suppress the miscibility gap and provide a means for calculating the solidification behavior observed as shown below! The maximum size of this correction is approximately $-65000/81 = -802$ J/g.at. The slight differences between these two sets of Gibbs free energies can hardly be discernible, but this modification is sufficient to yield results, that are closer to reality than those drawn from the unmodified data set.

An important aspect of the modified diagram is that it now correctly predicts the sequence of phase formation during solidification. For example, for the Cu-20 wt.% Co- 20 wt.% Fe alloy mentioned above, the modified database gives only one liquid is at equilibrium at high temperatures (1390-1500°C), see Figure 3. The calculated melting temperatures of the ternary alloys are compared with the experimental results in Table 1, which also includes some of the melting temperatures reported in [11]. As can be seen, in most cases, the discrepancy between the measured and calculated values is smaller than approximately 3%, but much larger for those measured in [11].

The same modified set of data was used to calculate the metastable equilibrium, which exists during supercooling, by suppression of all solid phases. The metastable equilibrium between two liquid phases is shown in Figure 4, for the alloy whose equilibrium phases are shown in Figure 3. The two-liquid phase separation takes place at 1120°C. In addition, the composition of each liquid phase as a function of temperature was calculated and shown in Figures 5 & 6. These figures suggest the formation of two liquids at 1120°C, of the following compositions:

L1 : 40 Wt.% Co – 42 Wt.% Fe – 18 Wt.% Cu;

L2 : 8 Wt.% Co -7 Wt.% Fe – 85 Wt% Cu.

Experimentally it was found, that the separation temperature is 1220°C, and the compositions of the two liquids are:

L1 : 35 Wt.% Co - 41 Wt. % Fe - 24 Wt.% Cu;

L2 : 9 Wt.% Co -7 Wt.% Fe -84 Wt.% Cu.

The calculated compositions agree very well with the measured ones. The discrepancy in the separation temperature might be attributed to minor impurities, which might affect the stability of the supercooled melt. Hence the formation of the metastable liquids L1 and L2 would take place at a temperature that is higher than the calculated one.

Summary and conclusions

Database for Cu-Co-Fe ternary alloys, which is based on commercially available sources, was slightly modified. Using the modified database, the liquidus temperatures were calculated. An excellent agreement between the calculated and experimental result was obtained. In most cases, the discrepancy between the measured and calculated values is smaller than approximately 3%. In addition, the modified database was used to predict the metastable miscibility gap and the phase boundaries. A very good agreement was obtained as well.

Acknowledgement

The authors wish to thank Mr. C. Cotler for his technical assistance.

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Table 1: Summary of Cu-Co-Fe Melting Temperatures Calculated and Measured Through EM Levitation.

Alloy No	Composition in Wt. %			Melting Temperature [°C]		
	Cu	Co	Fe	Measured		Calculated
				Ref. 11	This work	Calculated
1	96	2	2		1000	1090
2	90	5	5		1143	1210
3	84	8	9		1230	1245
4	80	10	10	1322	1240	1250
5	80	5	15		1300	1310
6	75	10	15		1280	1270
7	72	5	23		1315	1350
8	65	25	10		1290	1280
9	64	18	18		1280	1280
10	60	30	10	1386	1280	1295
11	60	20	20	1392	1300	1290
12	55	30	15		1330	1300
13	55	10	35	~1386*	1355	1360
14	49	16	36		1340	1360
15	45	37	18		1325	1330
16	38	20	42	~1392**	1300	1390

* The presented temperature was taken as the mean value of 1384°C given for Cu-10 wt.% Co-30 wt.% Fe and 1388°C given for Cu-10 wt.% Co-40 wt.% Fe.

** This value was reported for alloy Cu-20 wt.% Co-40 wt.% Fe

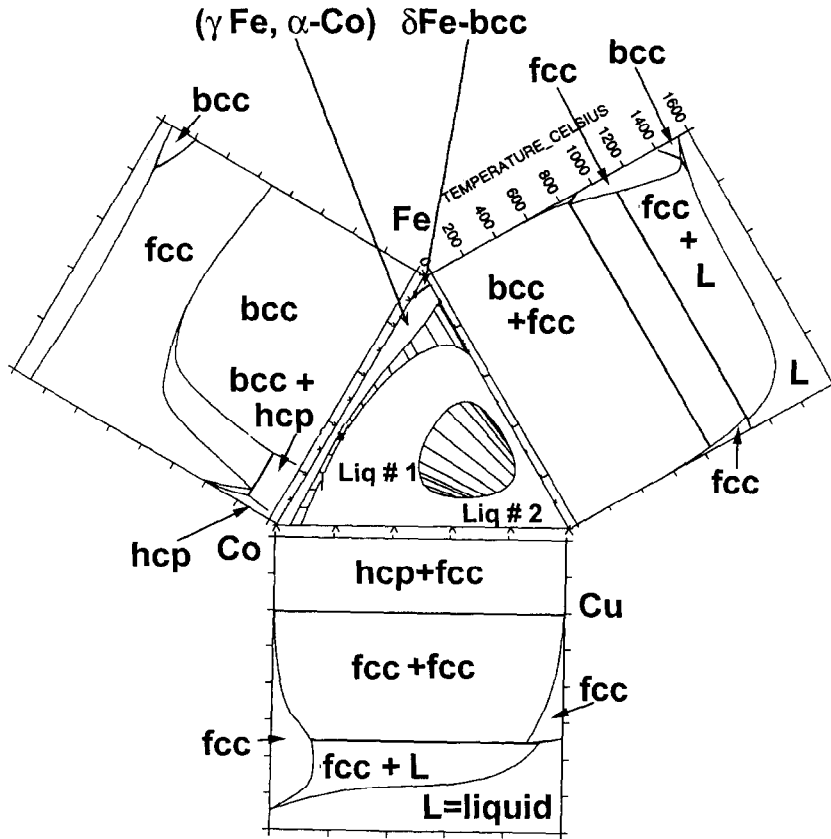


Figure 1. Calculated Binary Phase diagrams for the Co-Fe, Co-Cu and Cu-Fe Systems and the Co-Cu-Fe Ternary System at 1450 °C without the ternary term added to the Gibbs Energy.

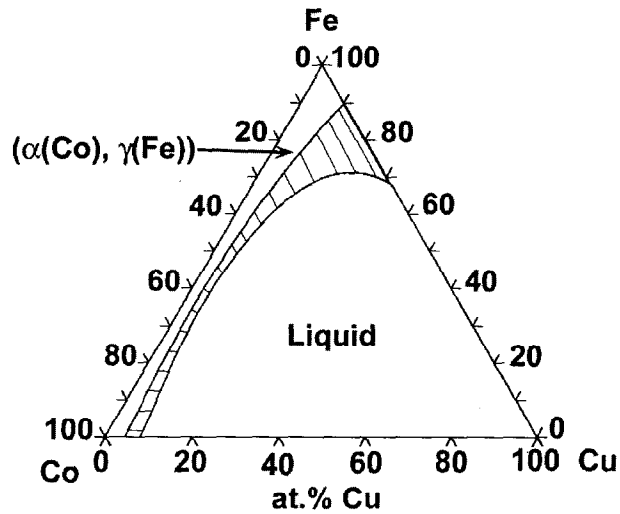


Figure 2) Computed Isothermal section at 1450°C in the Co-Cu-Fe system using the modified database.

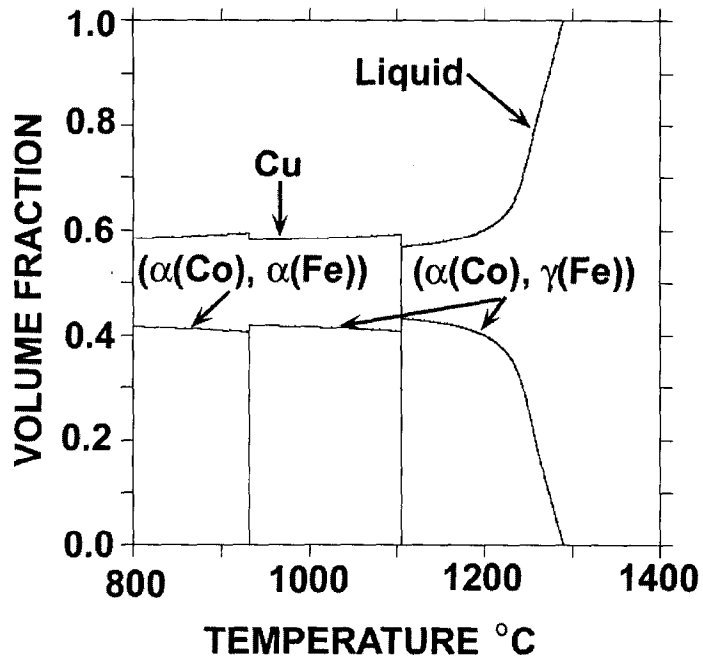


Figure 3) Computed phase formation in a Cu 20 wt.% Co-20 wt.% Fe alloy using the modified database.

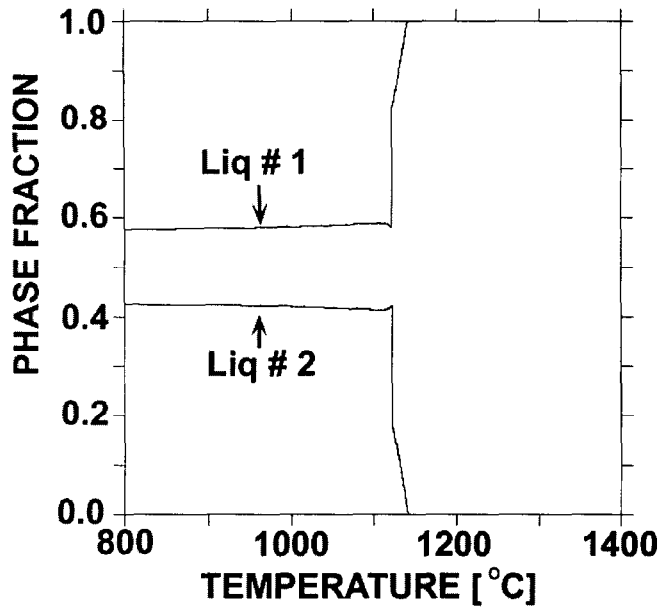


Figure 4) Formation of metastable melt separation during supercooling of Cu-20 wt.% Co-20 wt.% Fe alloy using the modified database.

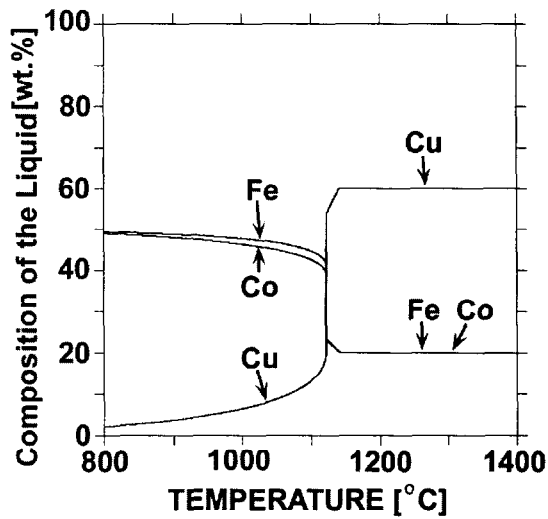


Figure 5) Composition of metastable (Co+Fe)-rich liquid phase (L1) during supercooling of Cu-20 wt.% Co-20 wt.% Fe alloy using the modified database as a function of temperature.

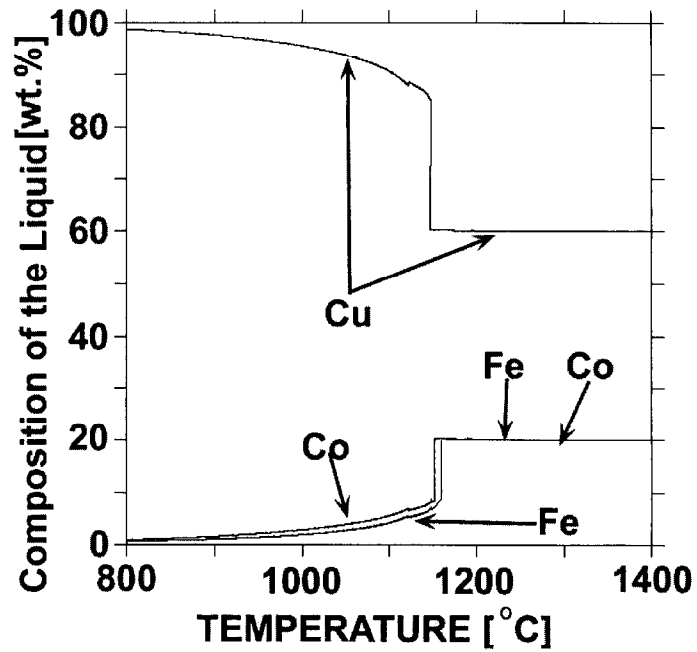


Figure 6) Composition of metastable Cu-rich liquid phase (L2) during supercooling of Cu 20 wt.%Co-20 wt.% Fe alloy using the modified database as a function of temperature.