

The solubility of C in solid Cu

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Abstract

The solubility of C in solid Cu was determined in the temperature range 1143–1293 K. Layers of C were vapour deposited onto high-purity Cu slices, which were annealed for 72 and 240 h at different temperatures. The C content in the samples was determined by means of combustion analysis. A Henrian behaviour for the carbon activity in the interstitial solid solution was observed.

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1. Introduction

The solubility of C in solid Cu is very small as has been well recognized since a long time. However, the value of this solubility is not well known. According to the newest assessment of the Cu–C equilibrium phase diagram [1] the smoothed solubility values reported in Ref. [2] should be regarded as of tentative, preliminary nature. Precise knowledge of the solubility of C is of great practical importance. For example, if even only minute amounts of C are dissolved during the production of high-purity noble metals exhibiting very small carbon solubilities, as a consequence of using graphite moulds, carbon-oxide gases could be formed when such metals are cast under oxidizing conditions. This could cause gas porosity in e.g. copper-base casting products.

For high-temperature applications matrix-embedded C fibres provide stiffness and prevent failure [3]. The stability of such Cu matrix composites was investigated to check the possibility of replacing electronic contacts of Ag by Cu [4]. In the case of the Cu–C system, the very low mutual solubility and the extremely poor wetting of the C fibres by Cu make the production of such graphite composites difficult. Knowledge of the amount of C which can be dissolved in Cu, upon inward diffusion

from the Cu/C interface and thereby establish the desired diffusion bonding, is of cardinal importance for the fabrication and performance of these composites.

The available data on the Cu–C equilibrium phase diagram were summarized in Ref. [1]; no carbide phases were reported. The solubility of C in liquid Cu was extensively studied [5,6]. In contrast with the agreement observed between the data reported by different authors for the solubility of C in liquid Cu for a wide range of high temperatures (1673–2123 K), the data published on solubility of C in solid Cu are contradicting [2,7]. In the first investigation [2], the equilibrium solubility of C in solid Cu was measured between 1058 and 1314 K by a vapour transport technique. Foils of Cu were equilibrated with graphite in presence of a small amount of air. The introduction of C into Cu occurred through vapour transport in the CO/CO₂ gas atmosphere in contact with the Cu foil. The determination of the C content in Cu was performed by combustion analysis. The solubility data obtained near the melting point of Cu, indicating more than 250 at. ppm at 1273 K, are two orders of magnitude higher than the solubility of C in liquid Cu. The data as reviewed in Ref. [1] are shown in Fig. 1. Later, it was speculated that these solubility values were too high, which could have been caused by adsorbed C, CO and CO₂, or trapped intergranular C [6]. For this reason these solubility data are regarded as tentative in Ref. [1]. In contrast with Ref. [2], it followed from other research that the solubility of C in solid Cu is smaller than 0.5 at. ppm at 1173 K, as determined by

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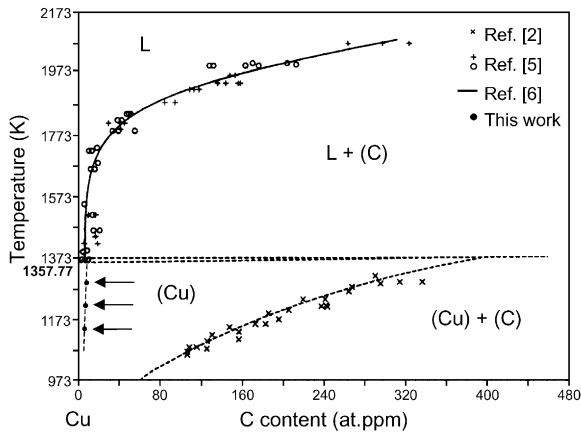


Fig. 1. Cu–C equilibrium phase diagram at the Cu-rich side according to Ref. [1]; L = liquid.

using a radiochemical technique [7]. In this investigation, the Cu specimens had been saturated with C by holding the Cu specimens at 1173 K for 20 days in the presence of a millicurie of ethylene or glucose, both marked with C^{14} . These data were not incorporated in the newest assessment of the Cu–C equilibrium phase diagram [1].

In the past, combustion analysis has been employed successfully for the determination of very low C contents (≥ 1 wt. ppm) in metals, especially in low-carbon steels. Nowadays, metals with extremely low C contents are applied in technological applications, especially in electric and electronic applications. In order to reach high accuracy in the C content determination, a modified combustion method has been developed at the end of the eighties and subsequently improved [8,9]. Thus, paying special attention to reducing the influence of systematic errors inherent to the commonly applied combustion method, a detection limit of 0.5 wt. ppm has been attained. Modern CO_2 -gas detectors, mostly high-sensitive infrared cells with a low level of electronic noise, are now available in carbon analysers.

Against the background presented above, in this work a precise determination of the solubility of C in solid Cu has been performed. The high-precision combustion technique as developed in Refs. [8,9] was employed to determine the C content in the annealed Cu samples.

2. Experimental details

2.1. Specimen preparation

Cylindrical slices of very pure Cu (99.9998 wt.%) with a diameter of 12 mm and a thickness of 4 mm were ground using 1200 grit SiC paper. A layer of 400 nm of graphite (EK 506 high-purity, Ringsdorf-Werke Germany) was deposited onto the surface of the Cu speci-

mens by physical vapour deposition. In this way, intimate contact was assured between Cu and C. Before vapour deposition of C, the Cu samples were cleaned ultrasonically in acetone for 15 min and subsequently were dried by blowing with a CO_2 -snow jet. The pressure in the deposition chamber was 1×10^{-4} Pa before sputter cleaning. The target was then sputter-cleaned with Ar^+ ions for 15 min under a pressure of 7×10^{-1} Pa and a power of 100 W (direct current), thereby eliminating a possible oxide layer on the Cu surface. Then the physical vapour deposition of C onto the Cu slice was performed at room temperature under an argon pressure of 7×10^{-1} Pa and a power of 100 W for 90 min. With respect to the mass of the Cu slice substrate, the amount of C deposited was more than enough to attain the large value of saturation solubility reported in Ref. [2].

Several C-layered Cu samples were encapsulated in glass ampoules under a final vacuum of 5×10^{-7} Pa at room temperature. The ampoules were turbo-pumped for 12 h before closing to reach this vacuum. Subsequently, the ampoules were annealed at three different temperatures: 1143, 1223 and 1293 K, for 72 and 240 h. For these times it is expected that the equilibrium solubility of C in Cu has been reached throughout the slice. The annealing temperature was maintained constant with an accuracy of ± 1 K. After the annealing the samples were quenched by crushing the ampoules in water. After water quenching a dark layer, sometimes partly coloured layer, could be observed on the surface of the samples. This indicated an excess of the carbon (graphite) deposited and a possible oxide layer formed upon contact with water during quenching.

2.2. Combustion analysis

The combustion technique consists of burning a sample of material in a flowing stream of oxygen. The CO_2 produced as a result of the combustion of the C present in the sample is taken up into the flowing oxygen. Then the absorption of infrared radiation by this CO_2 is detected in a cell and used for the quantification.

For the determination by this technique of the extremely low C content in metals as Cu much care is required. Typical systematic errors, inherent to the commonly applied combustion method, are the increase in the measured value due to carbonaceous contamination on the surface of the samples and auxiliary materials (crucibles, combustion accelerator, etc.) and an insufficient detection limit of the CO_2 -detector due to a low ratio of the signal belonging to the sample and the background signal. The background signal, which is quantified through measurement of a blank value, is produced by the unavoidable contamination of the materials used during the analysis and by the electronic noise. The blank value should be as small as possible (for more details see Refs. [8,9]).

The dark layer observed on the surface of the samples after quenching was completely removed by means of grinding and chemical etching (a solution of equal volume parts of 65 wt.% nitric acid, glacial acetic acid and 85 wt.% phosphoric acid at room temperature) until metallic brightness was observed. Thereafter the Cu slice, of mass of approximately 4 g, was cut in small pieces; amounts of about 1 g were used in the combustion analysis. For every sample four determinations were done; the average results obtained are reported here.

For every set of measurements the crucibles used in the combustion analysis were degassed in a muffle furnace at 1273 K. Their residual contamination produces an unsatisfactory reproducibility of the recorded background signal. Therefore, a pre-burning of very pure Cu chips (LECO Metal Accelerator 501-263; 0.5–1 mm), which had been annealed at 1073 K for at least 5 h and then cooled under an Ar flow, was performed in the crucible concerned before the sample itself is combusted. In this way, a good reproducibility of the recorded background signal was achieved and the determined blank value is reduced. After this pre-burning and with the crucible still hot (at about 473 K) a weighed mass of the sample, which was freshly etched, together with 1 g of annealed Cu chips were combusted. The charging in the hot crucible avoided surface adsorption of carbonaceous contaminations. The added Cu chips acted as a combustion accelerator, which guaranteed complete sample combustion [8,9].

For every measurement the blank value of the accelerator/crucible system was determined upon burning only annealed pure Cu chips. This blank value was subtracted from the total C amount measured in the respective determination. The resulting C amount is then referred to the mass of the Cu sample, to determine the carbon bulk concentration. A calibration in the very low C content range was made using standard steel samples with a C content equal to 286 ± 9 wt. ppm (LECO Chemical Standard High Purity 501-501). For the calibration an amount of 30 mg of this standard sample was weighed with a microbalance (± 0.5 μ g sensitivity) to make sure that the range of calibration corresponds well with the amounts of C to be determined (total carbon amounts in the range 0.1–2 μ g). The determinations were performed employing an ELTRA

CS 800 carbon/sulphur analyser equipped with a high-frequency induction furnace. The detection of the CO₂ produced in the combustion was done by means of an infrared CO₂ cell specially designed for the determination of extremely low C contents.

3. Results and discussion

The results from the different determinations of C content at various temperatures, as determined by means of combustion analysis, are presented in Table 1. In the case of the initial, pure Cu, besides the background signal corresponding to the blank value (cf. Fig. 2), no peak was observed. For this reason, it is considered that the C content in the initial Cu is in any case not higher than 1 at. ppm (= 0.2 wt. ppm = detection limit). After annealing the Cu/C samples at the three selected temperatures for 72 h and following the steps detailed above for the combustion analyses, a significant amount of CO₂ was detected in the infrared cell. An example is shown in Fig. 2 for the sample annealed at 1293 K for 72 h; the peak area corresponds to a C content of 7.4 ± 0.5 at. ppm (1.4 ± 0.1 wt. ppm).

In order to confirm that the determined C-solubility values represent equilibrium values, the C content determinations were repeated for samples that were

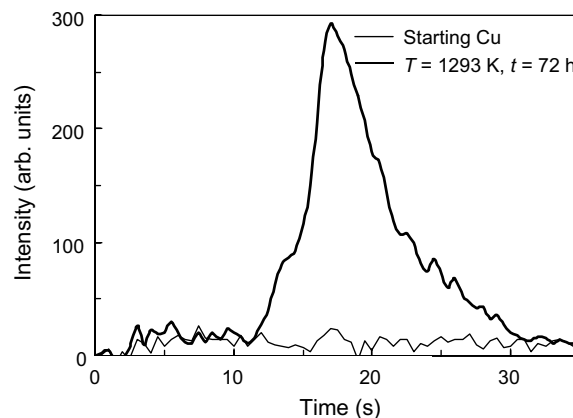


Fig. 2. Evolution of CO₂ in the combustion analyser from approximately 1 g of the starting, pure Cu and of a carbon saturated sample after annealing at 1293 K for 72 h.

Table 1
Carbon content as determined by combustion analysis; t = annealing time

Sample	C content (at. ppm/wt. ppm)	
	$t = 72$ h	$t = 240$ h
Starting Cu	No peak observed	–
Cu/C annealed at 1293 K	$7.4 \pm 0.5/1.4 \pm 0.1$	$7.4 \pm 0.5/1.4 \pm 0.1$
Cu/C annealed at 1223 K	$6.3 \pm 0.5/1.2 \pm 0.1$	$5.3 \pm 0.5/1.0 \pm 0.1$
Cu/C annealed at 1143 K	$4.8 \pm 0.5/0.9 \pm 0.1$	$4.8 \pm 0.5/0.9 \pm 0.1$
Blank value	0.2 ± 0.1 μ g	0.2 ± 0.1 μ g

annealed for a longer period of time (240 h) under the same conditions. As follow from the results gathered in Table 1, the C contents as determined after 240 h of annealing agree very well with those determined after 72 h of annealing. Therefore, it is concluded that equilibrium values for the solubilities were determined.

On average the blank value obtained in the measurements was 0.2 μg (absolute), with a maximal variation of $\pm 0.1 \mu\text{g}$. In this context it should be noted that all Cu samples were very homogeneous and the scatter in the four determinations carried out at each temperature and each annealing time was only 0.16 at. ppm (0.03 wt. ppm) in the worst case.

The results presented in Table 1 have been indicated in the equilibrium diagram (see arrows in Fig. 1). For the temperature of 1223 K the average between the values obtained for the two different annealing times has been indicated. As can be seen in Fig. 1, the new solid solubility values are significantly smaller than the previous data reported in Ref. [2]. Further, it should be noted that a significant C solid solubility has been determined here, which refutes the statement in Ref. [7] that the solubility of C in solid Cu would be smaller than 0.5 at. ppm (0.1 wt. ppm).

As already noted in Ref. [6], adsorbed C, CO and CO₂ could have contributed to the apparently high-C contents measured in Ref. [2]. With the current improvements introduced in the procedure applied for the combustion analysis (cf. Section 2) this possible influence was reduced significantly in the present work. Another explanation for overestimation of the C solubility in solid Cu could be the presence of a third element with more affinity to C than Cu. The purity of the Cu used in Ref. [2] was not indicated and determinations for the starting material were not reported. The claim of a solubility of C in solid Cu at 1173 K lower than 0.5 at. ppm (0.1 wt. ppm) in Ref. [7] could be caused by inappropriate saturation with C of the Cu specimens.

The solubility of C in solid Cu increases with increasing temperature (Table 1). The increase of the solubility of C with increasing temperature in a solid solution in equilibrium with graphite is given by the following equation if Henrian behaviour is assumed for the C activity [10]

$$\frac{x_C}{1 - 2x_C} = \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right) \quad (1)$$

where x_C is the carbon content in mole fraction, ΔH is the partial molar enthalpy of carbon in solution, ΔS is the partial molar excess entropy, R is the gas constant, and T is the absolute temperature. An Arrhenius presentation according to Eq. (1) is given in Fig. 3. The experimental data can be well fitted with a straight line, as prescribed by Eq. (1), implying validation of Henrian behaviour for the C activity in Cu. From the slope of the straight line fitted (least squares analysis) a partial molar

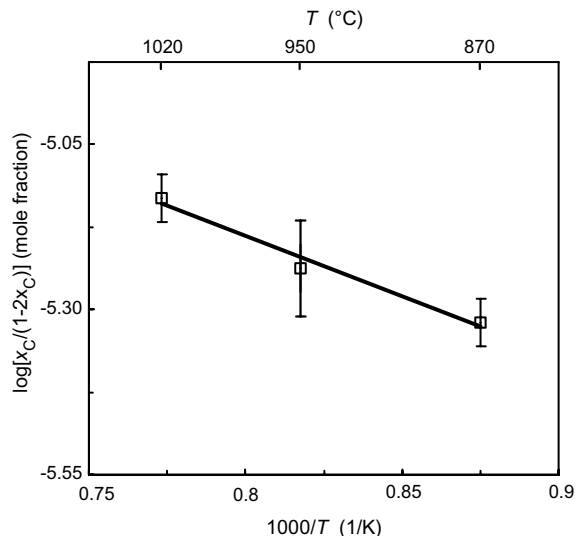


Fig. 3. The equilibrium solubility of C in solid Cu as a function of temperature. The experimental error in the C solubility has been indicated by a vertical bar.

enthalpy of dissolution of C in Cu was determined: $\Delta H = 35.1 \text{ kJ/mol}$. This value is smaller than the value 51.9 kJ/mol reported in Ref. [2] on the base of much higher (erroneous, see above) solubility data.

An additional comment will be given here on the volume diffusion coefficient of C in Cu, D . In the literature there are no data available. It has been shown that annealing for 72 h at 1143 K and at higher temperatures suffices to saturate with C the Cu substrate slices of a thickness, x , of 4 mm. Hence, an underestimate for the volume diffusion coefficient of C in Cu can be made from the relation $D \approx x^2/2t$. Thus, it follows for a temperature of 1143 K $D = 3 \times 10^{-11} \text{ m}^2/\text{s}$. This value is of the same order of magnitude as the volume diffusion coefficient of C in Ni at the same homologous temperature: $T/T_m = 0.84$, where T_m is the melting tempera-

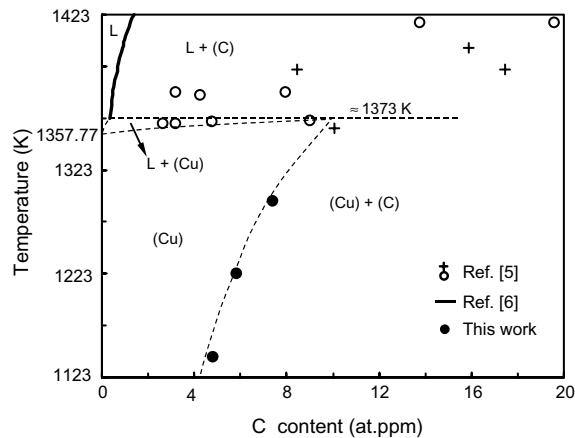


Fig. 4. Proposed equilibrium phase diagram of peritectic type for the Cu-C system at the Cu-rich side (see text).

ture: at 1450 K ($T/T_m = 0.84$) the volume diffusion coefficient of C in Ni equals 1×10^{-10} m²/s [11].

Based on the too high (see above) solubilities of C in *solid* Cu reported in Ref. [2], in comparison with the very low solubility of C in *liquid* Cu near the melting point of pure Cu, it was suggested that a peritectic type of phase diagram instead of a eutectic one would hold for the Cu–C system at the Cu-rich side (cf. Fig. 1) [1]. According to the present results, the solid solubility of C in Cu near the melting point is moderately larger than that in the liquid and, if the extrapolated liquidus line reported in Ref. [6] is adopted (solid line in Fig. 4), a peritectic type of phase diagram could be drawn indeed (Fig. 4). It should be noted that this extrapolation of the liquidus line is based on recent experimental data obtained at high temperatures (above 1823 K; see Fig. 1). The experimental data of Ref. [5] are rather old and may be affected by impurities in the starting materials. Yet, the possibility of a eutectic type of phase diagram should not be fully excluded. To make definitive conclusions about the type of the equilibrium phase diagram of the Cu–C system, further investigations on the solubility of C near the melting point of Cu are required.

4. Conclusions

The solubility of C in solid Cu was determined by means of a recently improved combustion analysis procedure. Equilibrium values varying from 4.8 ± 0.5 at.ppm (0.9 ± 0.1 wt.ppm) at 1143 K to 7.4 ± 0.5 at.ppm (1.4 ± 0.1 wt.ppm) at 1293 K were determined.

These solid solubility values are 50 times smaller than the data reported before and as included in the most recent assessment of the equilibrium phase diagram. A Henrian behaviour for the carbon activity in the interstitial solid solution was observed.

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