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Journal of Alloys and Compounds 228 (1995) 195–200

Journal of
ALLOYS
AND COMPOUNDS

Origins of paramagnetism in beryllium–copper alloys

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Received 28 November 1994; in final form 17 April 1995

Abstract

We report the magnetic susceptibility of several commercial purity and high purity grade Be–Cu-based alloys. Comparison of Curie constants with the results of chemical assay suggests that Co and Ni alloying additions form non-magnetic beryllides distributed uniformly throughout the material. Consequently, the magnetic properties of the Be–Cu alloys are found to be dominated by trace impurities such as Fe and Cr.

Keywords: Be–Cu alloys; Magnetic properties

1. Introduction

There is much interest in identifying high strength non-magnetic alloys for use at low temperatures. A typical example is coil forms for large superconducting magnets such as those used in nuclear magnetic resonance, superconducting quantum interference device (SQUID) magnetometers and magnetic resonance imaging scanners. Another use is magnetic sensor housings such as those used in oil well bore hole magnetometers to measure variations in the Earth's magnetic field. Materials with small magnetic susceptibilities are required to ensure a uniform magnetic field and maximum field penetration. We are developing a high pressure clamp for measuring magnetic susceptibility as a function of pressure. A major design consideration is the minimization of the temperature-dependent background susceptibility from the clamp itself, which can be expected to limit the ultimate precision of the measurement [1]. At the same time, we require the clamp body to be made of a high strength material, as it must contain pressures as large as 20 kbar. Since high strength steels are all unacceptably ferromagnetic, binary Be–Cu alloys are often used for this type of application. Although these alloys are not ferromagnetic, their magnetic susceptibility is still large, with a temperature dependence which complicates sensitive magnetic measurements [1,2]. Several commercial purity Be–Cu-based alloys are available, differing by heat treatment and by whether Co or Ni is used to limit grain growth. The most widely used is C17200, which contains 0.2 wt.% Co, and achieves an ultimate tensile strength of 1310 MPa, ~90% that of a high strength steel. Since the magnetic susceptibility of the binary Be–Cu alloy is much smaller than that of C17200 [1], it has been proposed that the low temperature susceptibility of the latter originates from the Co grain-precipitating agent and might consequently be reduced, albeit at the expense of alloy strength [1]. In addition, room-temperature studies of the relative permeability of Be–Cu alloys show a strong dependence of the permeability on Fe concentration [3]. This is significant because, in addition to Co, commercial purity alloy specifications allow other potentially magnetic ions such as Fe and Ni in total concentrations of up to 0.4 wt.% [4], although this limit is in actuality seldom approached. To separate the individual contributions to the susceptibility from the Co and from Fe and Ni we have measured the magnetic susceptibility of several high purity and commercial purity alloys of Be–Cu–X (X = Co or Ni). We mean by "high purity" that the total concentration of Cr, Fe and either Ni or Co is less than 0.01 wt.%. Comparison of the magnetic properties of the alloys with their chemical compositions enables us to determine the origins of their magnetic responses and perhaps suggest compositional changes to optimize strength and to minimize susceptibility.

The physical and chemical properties of the alloys studied are summarized in Table 1. C17200 is the

0925-8388/95/$09.50
SSDI 0925-8388(95)01894-8

Table 1
The weight percentages of Be, Co, Cr, Fe and Ni in the Be–Cu alloys as determined by chemical assay and the ultimate tensile strengths (UTS)

Alloy	Amount (wt.%)					UTS [3] (MPa)
	Be	Co ($\times 10^{-2}$)	Cr ($\times 10^{-3}$)	Fe ($\times 10^{-2}$)	Ni ($\times 10^{-2}$)	
Be–Cu (high purity)	1.9	<0.1	1.0	0.5	0.4	720
Be–Cu–Co, C17200 (high purity)	1.9	23	1.0	0.6	0.4	1310
Be–Cu–Co, C17200 (commercial purity)	1.9	20	3.0	10	5.0	1310
Be–Cu–Co, C17000 (commercial purity)	1.7	21	4.0	13	7.0	1240
Be–Cu–Ni, C17510 (high purity)	0.4	0.2	0.6	0.3	195	760

strongest commercial purity alloy (of composition: 1.9 wt.% Be and 0.20 wt.% Co, with impurities: 0.1 wt.% Fe, 0.05 wt.% Ni and 0.003 wt.% Cr), but substantial Fe and Co concentrations imply a potentially large magnetic susceptibility. To isolate the magnetic contribution of the Co we have measured a sample of high purity C17200 (of composition: 1.9 wt.% Be, and 0.23 wt.% Co, with impurities 0.006 wt.% Fe, 0.004 wt.% Ni and 0.001 wt.% Cr). Here, special precautions are taken to exclude impurities with the result that the Fe and Ni impurity levels are much reduced, compared with those in the commercial purity alloys. As an independent measure of the Co magnetization, we have also measured high purity C17510, a Be–Cu–Ni alloy (of composition 0.4 wt.% Be and 1.95 wt.% Ni, with impurities 0.002 wt.% Co, 0.003 wt.% Fe and 0.0006 wt.% Cr), in which the Co has been replaced by Ni. Finally, while enhanced grain size greatly reduces its ultimate strength we include high purity binary Be–Cu (of composition 1.9 wt.% Be with impurities less than 0.0005 wt.% Co, 0.005 wt.% Fe, 0.004 wt.% Ni and 0.001 wt.% Cr) to provide a baseline for the nominal non-magnetic bulk contribution from the alloy.

2. Sample preparation and measurement

Two samples of each alloy were cut from the interiors of cold-rolled precipitation-hardened plate using an electrical discharge machine: one to be chemically assayed and one for microprobe, magnetization and micrography measurements. Prior to any measurements all samples were etched with an aqueous solution of 25% sulfuric acid and 5% hydrogen peroxide at 50°C to remove any brass deposited on the sample by the brass electrode used in the machining operation. One face of each sample used in the magnetization study was polished to a 0.3 μm finish for microprobe analysis. The polished face was etched with ammonium persulfate hydroxide and wiped with a solution consisting of potassium dichromate in both sulfuric and hydrochloric acid to delineate the grain boundaries for optical and electron micrography as described in [4].

Magnetization was measured in a Quantum Design SQUID magnetometer using a 1 T field at temperatures from 300 to 4.7 K. Electron microprobe analysis was carried out in a Cambax electron microbeam analyzer using both 1 μm and 3 μm diameter electron beams. Chemical assay was performed by dissolving samples of each alloy in nitric acid and analyzing the solution using a Perkin–Elmer model 1100B atomic absorption spectrometer.

3. Results

Fig. 1 shows the magnetic susceptibility χ as a function of temperature of all five alloys between 4.75 and 300 K, measured in a 1 T field. For all the alloys except commercial purity C17200, $\chi(T)$ is well described by a Curie–Weiss law for temperatures between 4.75 and 300 K:

$$\chi(T) = \chi_{\mathrm{Curie}} + \chi_0 = \frac{C}{T - \Theta} + \chi_0 \tag{1}$$

where χ_0 is the temperature-independent part of the susceptibility, C is the Curie constant and Θ is the Curie–Weiss temperature. C, Θ and χ_0 are summarized for each alloy in Table 2. Comparison of the temperature-independent susceptibilities in Table 2 reveals that the χ_0 values are very similar for the three high purity alloys Be–Cu, Be–Cu–Co and Be–Cu–Ni, but approximately two orders of magnitude smaller than either commercial purity alloy. We observed that the susceptibility of the commercial purity C17000 alloy, which has little or no β phase Be–Cu, is always less than that of the commercial purity C17200 alloy, which does contain the β phase. This is consistent with findings of previous workers [3] who suggested that the β phase enhanced the permeability of Fe-containing Be–Cu alloys, although their measurements were only at room temperature. The Curie constants can be extracted from the slopes of the lines in Fig. 2 which plots $(\chi - \chi_0)^{-1}$ as a function of temperature between 4.75 and 300 K. Fig. 2(b) shows that the susceptibility of commercial purity C17200 cannot be described by a simple Curie–Weiss law above 50 K, suggesting that more than one magnetic species is

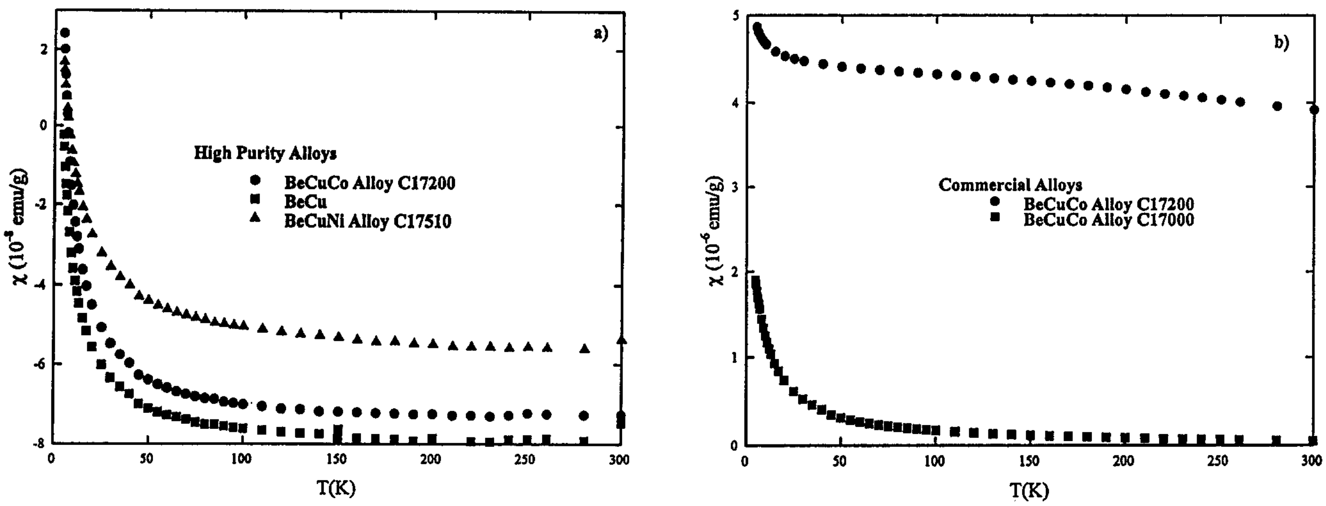

Fig. 1. The magnetic susceptibility χ as a function of temperature for (a) the high purity Be–Cu alloys (●, Be–Cu–Co, C17200; ■, Be–Cu; ▲, Be–Cu–Ni C17510(1a)) and (b) the commercial purity Be–Cu alloys (●, Be–Cu–Co, C17200; ■, Be–Cu–Co, C17000(1b)).

Table 2

The weight percentages of Co^{2+}, Cr^{2+}, Fe^{3+} and Ni^{2+} predicted to be present in the Be–Cu alloys from their Curie constants; the Curie constants C, Curie temperatures Θ_C, and temperature-independent parts of the magnetic susceptibility χ_0 are also given

Alloy	Amount (wt.%)				C ($\times10^{-7}$ emu K g^{-1})	χ_0 ($\times10^{-8}$ emu g^{-1})	Θ_C (K)
	Co^{2+} ($\times10^{-3}$)	Cr^{2+} ($\times10^{-3}$)	Fe^{3+} ($\times10^{-3}$)	Ni^{2+} ($\times10^{-2}$)			
Be–Cu (high purity)	1.1	1.0	0.7	0.25	5.5	−8.1	−2.0
Be–Cu–Co, C17200 (high purity)	1.3	1.2	0.8	0.30	6.4	−7.6	−2.2
Be–Cu–Co, C17200 (commercial purity)	9.1	8.0	5.7	2.0	44	430	−3.7
Be–Cu–Co, C17000 (commercial purity)	39.0	35.0	25.0	8.8	190	−1.2	−5.0
Be–Cu–Ni, C17510 (high purity)	1.7	1.5	1.0	0.37	7.8	−5.8	−5.8

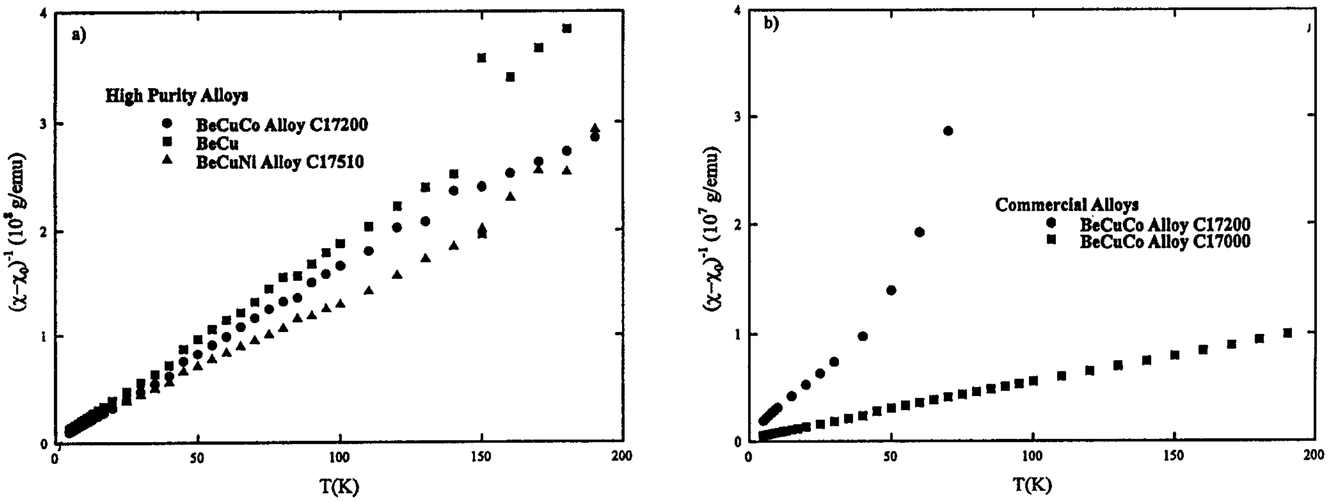

Fig. 2. The inverse of the temperature-dependent magnetic susceptibility $(\chi - \chi_0)^{-1}$ as a function of temperature for (a) the high purity Be–Cu alloys (●, Be–Cu–Co, C17200; ■, Be–Cu; ▲, Be–Cu–Ni, C17510(2a)) and (b) the commercial purity Be–Cu alloys (●, Be–Cu–Co, C17200; ■, Be–Cu–Co C170000(2b)).

present. As with the temperature-independent susceptibility, the Curie constants are approximately two orders of magnitude smaller for the three high purity alloys Be–Cu, Be–Cu–Co and Be–Cu–Ni than for either commercial purity alloy. We conclude that, since the high purity alloys have very similar magnetic properties, C17200 should be chosen for its high strength. The commercial purity alloys should be avoided for any application where magnetic inertness is required.

The volume concentration N/V of a system of interacting magnetic moments with effective magneton number p can be determined from the value of the Curie constant:

$$\chi_{\mathrm{Curie}} = \frac{1}{3}\frac{N}{V}\frac{\mu_{\mathrm{B}}^{2}p^{2}}{k_{\mathrm{B}}(T-\Theta)} = \frac{C}{T-\Theta} \tag{2}$$

Restricting our discussion here to the high purity alloys, we can develop an understanding of the magnetization of these alloys by comparing the moment concentration extracted from the Curie constant with the results of the chemical assay, listed in Table 1. With the possible exception of trace impurities such as Cr, the assay results prove that there can be a concentration of potentially magnetic species such as Co, Fe, and Ni as much as an order of magnitude higher than the Curie constants imply, indicating that the effective magnetic moments of the Co, Ni and Fe ions are much smaller than the full ionic moment for each species.

4. Discussion

We hypothesize that the absence of a ferromagnetic response from the Co in the Be–Cu–Co alloys results from the presence of paramagnetic Co beryllides. Co is completely immiscible in Cu [5] and one consequent scenario is macroscopic phase separation between Co and Be–Cu in the bulk. However, measurements of the magnetic susceptibility rule out this possibility because there is no evidence of ferromagnetic ordering which would signal the presence of bulk Co. We argue instead that the Co is incorporated into Co beryllides in the Be–Cu–Co melt [4] and further that this beryllide is paramagnetic. The effective moment per Co atom in high purity C17200 is $0.36\mu_{\mathrm{B}}$, a factor of 13 smaller than that of the full ionic Co moment, which is $4.8\mu_{\mathrm{B}}$ [6]. However, the Be–Co system is a metallic host for Co moments and, more significantly, the Co moment is reduced by the formation of covalent bonds.

It is known that both the binary series $\mathrm{Be}_{1-x}\mathrm{Co}_{x}$ and $\mathrm{Be}_{1-x}\mathrm{Ni}_{x}$ are paramagnetic for $x \leq 0.5$ [7] and we infer from the observed non-magnetic character of the Co in the Be–Cu–Co alloys and of the Ni in the Be–Cu–Ni alloy that the Co and Ni beryllides in these alloys are Be rich relative to the bulk Be concentration. This implies that the Co and Ni may be localized in Be-rich regions.

We have identified these hypothesized Be-rich regions optically and present optical micrographs of the high purity alloys in Fig. 3. In the micrographs of alloy C17200 (Fig. 3(b)) and C17510 (Fig. 3(c)) the Be-rich regions appear as uniformly dispersed dark spots and are indicated by arrows. Those in the micrograph of alloy C17200 have an average dimension of about 1 μm or smaller and are thought to be Co beryllides [4]. The dark spots in the micrograph of alloy C17510, which have an average dimension of about 5–10 μm, have been investigated by electron microbeam analysis [8] and are thought to be Ni beryllides. The binary Be–Cu exhibits the effects of unrestrained grain

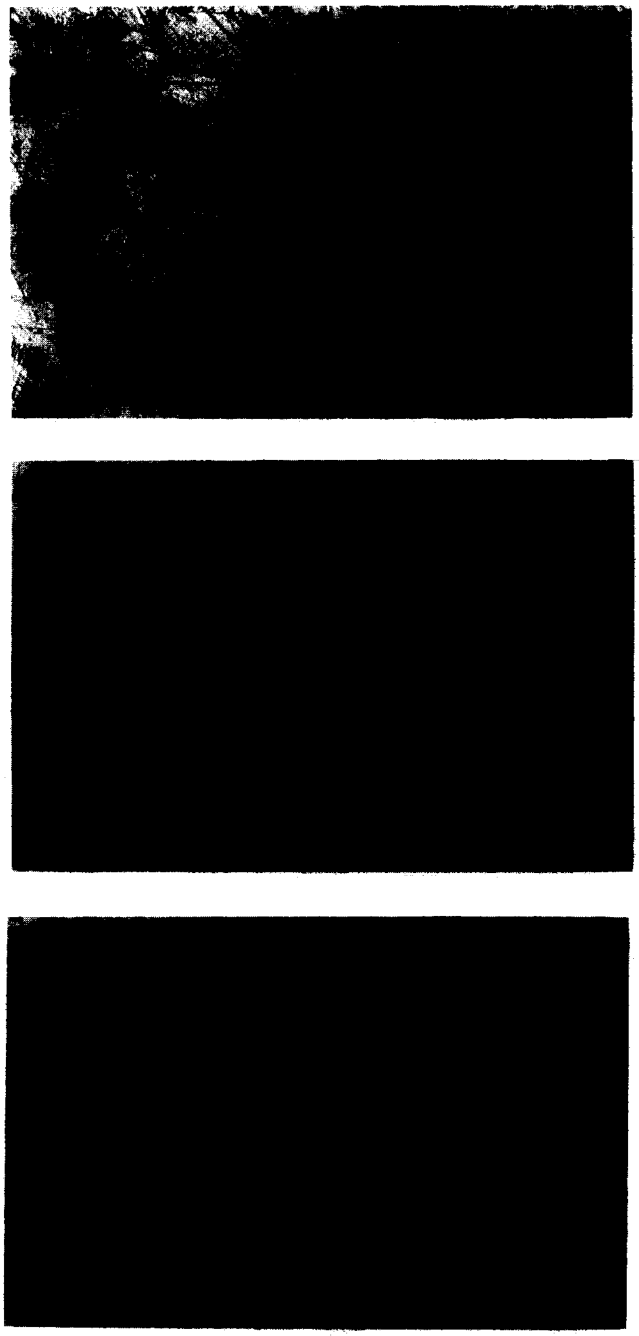

Fig. 3. Optical micrographs of the high purity Be–Cu alloys, namely binary Be–Cu (3a), Be–Cu–Co (C17200(3b)) and Be–Cu–Ni (C17510(3c)).

growth with grains of average dimension about 100–400 μm (Fig. 3(a)). In contrast, both alloy C17200 (Fig. 3(b)) and C17510 (Fig. 3(c)) exhibit a finer grain structure. As expected the stronger alloy C17200 has the finer grains, ranging in dimension from 5 to 50 μm, while C17510 has a grain size of about 10–100 μm.

We have directly imaged the inhomogeneous Co distribution in high purity C17200 using electron microprobe analysis of a single grain. The etchants used for optical micrography provide sufficient contrast to detect grain boundaries with a scanning electron microscope, as shown in Fig. 4. The electron microprobe can then be used to determine the spatial distribution of Co within a grain, provided that a sufficiently small beam diameter is used. In our case, the beam diameter, including spreading in the sample, was about 2 μm. The results of several linear scans across the central grain in Fig. 4 using 3 μm steps are presented in Fig. 5. The area of the points in this image is proportional to the local Co concentration, which ranges from the detection limit of about 0.05 wt.% to 3 wt.%. Regions of high Co concentration are uniformly distributed in this scan and are separated from one another by a length scale on the order of 10 μm. The Co concentration found in the electron microprobe scans shown in Fig. 5 ranged from an order of magnitude larger than to an order of magnitude smaller than the concentration determined by chemical assay. Taken together, the spatial non-uniformity of the Co concentration and the lack of ferromagnetic order support our proposal that the Co is primarily in the form of localized Be-rich Co beryllides. The fact that the maximum Co concentration observed, 3 wt.%, is much smaller than the 50 wt.% level of bulk BeCo indicates that the electron beam must be sampling a volume which contains both Co and Cu beryllides. The Co beryllide particles must then be smaller than the 1.5 μm penetration depth of the electron beam.

Fig. 4. Scanning electron micrograph of high purity Be–Cu–Co (C17200).

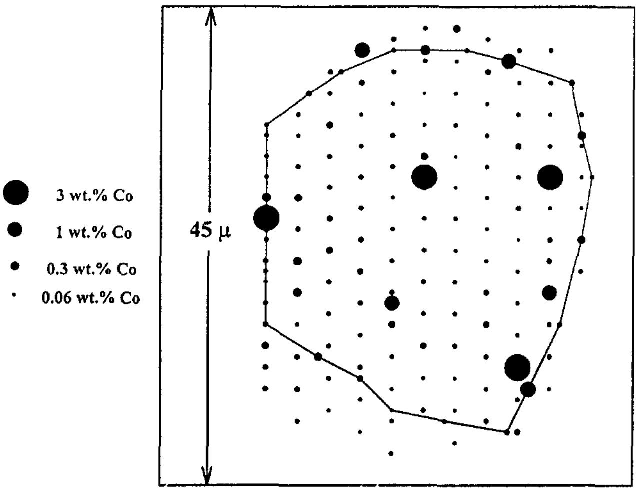

Fig. 5. A 30 μm × 45 μm raster image of the local Co concentration in a single grain of high purity Be–Cu–Co (C17200), determined by electron microprobe analysis. As indicated, the area of each symbol is proportional to Co concentration at that point. The full line indicates the grain boundary. The grain imaged is the central grain in Fig. 4.

We reach identical conclusions for the Be–Cu–Ni (C17510 alloy) because a similar study of the Ni concentration in C17510 [8] found localized Ni concentrations in this alloy as well.

In all the alloys that we studied, chemical assay reveals the presence of Fe and Cr impurities which could also form magnetic phases. Arguments similar to that used for Co apply to both of these elements, i.e. they are both immiscible [9,10] in Cu and form beryllides [7,11]. Table 1 and Table 2 reveal that Fe has a substantially reduced moment in both the high purity and the commercial purity Be–Cu alloys, since its full ionic moment is never reflected in the Curie constant, regardless of the overall Fe concentration. Since we have not observed either ferromagnetic ordering below room temperature or non-linearity in the field dependence of the magnetization at 5 K we can further constrain the beryllides not to include $FeBe_2$, $FeBe_5$ and $CrBe_{12}$, as these compounds are ferromagnetic and have Curie temperatures of 912 K, 75 K [7] and 50 K [11] respectively. Again, the greatly reduced Fe and Ni moments argues for localized Be-rich Fe and Ni beryllides. Finally, since the Curie constant in the high purity alloys is insensitive to the presence of Co or Ni, we conclude that trace impurities such as Fe or Cr dominate the magnetic properties in all cases.

The above arguments show that the magnetic properties, i.e. the Curie constants, of any of the Be–Cu alloys are not correlated with the concentrations of Co or Ni added as precipitating agents. We conclude that the magnetic properties are in every case dominated by trace magnetic impurities, which might be avoided with special processing procedures. The prospects for a magnetically neutral, high strength Be–Cu-based alloy are consequently very positive.

Acknowledgments

The authors would like to thank S. Ali, D. Krus, M. Patterson and W. Spiegelberg (Brush Wellman Inc.) for valuable discussions, and for providing the alloy samples. We are grateful for the technical assistance provided by C. Henderson of the Electron Microanalytical Laboratory at the University of Michigan. Work at the University of Michigan was supported by the US Department of Energy, Office of Basic Energy Sciences under Contract 94-ER-45526.

References

[1] D. Wohlleben and M.B. Maple, *Rev. Sci. Instrum.*, *42* (1971) 1573.

[2] H. Bernstein, *Trans. Metall. Soc. AIME*, *212* (1958) 225.

[3] B.A. Jordan, *J. Mater. Sci.*, *4* (1969) 1097.

[4] J.C. Harkness, W.D. Spiegelberg and W.R. Cribb, *Metals Handbook*, Vol. 2(10), 1990, p. 404; *Guide to Beryllium Copper*, Brush Wellman, Cleveland, OH, 1988.

[5] T. Nishizawa and K. Ishida, *Bull. Alloy Phase Diagrams*, *5*(1) (1984) 161.

[6] R. Kubo and T. Nagamiya (eds.), *Solid State Physics*, McGraw-Hill, New York, 1969, p. 453.

[7] A. Herr and A.J.P. Meyer, *C.R. Acad. Sci. Paris, Sér. B*, *265* (1967) 1165.

[8] A. Guha, in E. Ling and P.W. Taubenblat (eds.), *High Conductivity Copper and Aluminum Alloys*, Metallurgical Society of AIME, New York, 1984, p. 133.

[9] D.J. Chakrabarti and D.E. Laughlin, *Bull. Alloy Phase Diagrams*, *5*(1) (1984) 59.

[10] O. Kubaschewski, *Iron-Binary Phase Diagrams*, Springer, Berlin, 1982, p. 35.

[11] N.M. Wolcott and R.L. Falge, Jr., *Phys. Rev.*, *171* (1968) 591.