On the miscibility gap of Cu-Ni system

Yusuke Iguchi,1,a) Gábor Katona,1 Csaba Cserháti,1 Gábor Langer,1 and Zoltán Erdélyi1,b)

Department of Solid State Physics, University of Debrecen, Bem ter 18/b.,
Debrecen, H-4026 HUNGARY

(Dated: 29 November 2016)

The existence of the miscibility gap in the Cu-Ni system has been an issue in both computational and experimental discussions for half a century [Chakrabarti et al., Phase diagrams of binary nickel alloys, ASM, 1991]. Here we propose a new miscibility gap in the Cu-Ni system measured in nano-layered thin films by Secondary Neutral Mass Spectrometry. The maximum of the symmetrical miscibility curve is around 800 K at Cu$_{50}$Ni$_{50}$. To our best knowledge, this is the first experiment determining the miscibility from the measurement of the atomic fraction of Copper and Nickel in the whole composition range. Needless to say that Ni, Cu and its alloys are important in various fields, accordingly this result affects different areas to understand materials sciences.

PACS numbers: 81.30.Bx, 64.75.St, 82.80.Ms, 66.30.Pa

Keywords: phase diagram, thin films, secondary neutral mass spectroscopy (SNMS), diffusion

---

a)Corresponding author: iguchi.yusuke@atomki.mta.hu Present Affiliation: Institute for Nuclear Research, Hungarian Academy of Sciences, Bem ter 18/c., Debrecen, H-4026 HUNGARY

b)http://web.unideb.hu/zerdelyi

1
A phase diagram is a type of chart used to show conditions – usually temperature versus composition in the binary systems – at which thermodynamically distinct phases can exist at equilibrium. A miscibility gap is a region in a phase diagram where the mixture of components exists as two or more phases. The knowledge of phase diagrams is fundamental for example to construct interaction potentials for computer simulations and indispensable for material designing. It is not surprising than that there are still substantial efforts developing experimental and theoretical methods of establishing phase relations in multicomponent systems.

Cu-Ni alloys are very popular in various fields, e.g. corrosion-resistant structural materials, welding, soldering, resistance and magnetic devices. Cu-Ni is also frequently used as an ideal system to study the surface segregation and diffusion in completely miscible alloys. Yet, the phase equilibrium, the immiscibility in the Cu-Ni system remained a serious and unresolved issue in the past half a century. In 1957 the miscibility gap, that closes with critical point at 450 K, was predicted from thermodynamic analysis of ternary Cu-Ni-Cr system. Later, there were many reports about measurements of physical properties of Cu-Ni, such as electrical resistivity, Hall effect, specific heat, Mössbauer Effect and Nuclear Magnetic Resonance. These measurements provided some indirect information about the possible existence of the miscibility gap. Some structural measurements, such as Transmission Electron Microscopy, X-ray diffraction, Atom Probe Field Ion Microscopy and Neutron scattering also suggested a sort of phase separation, e.g. clustering. These experimental studies suggested critical temperature values. Besides these efforts, theoreticians created thermodynamic models to predict the Cu-Ni equilibrium phase diagram. Studies up to 1990s are summarized by Chakrabarti et al. They listed seven experiments and nine thermodynamic calculations suggesting critical temperature values. Five of the seven reported experiments and two of the nine thermodynamic calculations suggested critical temperature values in the “high range” (see Table 2 in; only six of the seven experiments are listed in the table as verified the results of): between 723 and 923 K. Two of the experiments and seven of the nine thermodynamic calculations of the suggested critical temperature values are in the “low range” (see Table 2 in): one 450 K, one 543 K and seven in the range of 573-667 K. Chakrabarty et al. decided to fit seven results (two experiments, five calculations) which are in the range of 573-667 K by a thermodynamic model, although altogether five experiments suggested critical temperature values in the high range and two in the low
range. They produced a miscibility curve with a closing critical temperature of 627 K, which was published in the “Phase Diagram of Binary Nickel Alloys” book by Chakrabarti\textsuperscript{16}. This curve was then used in the well-known “Binary Alloys Phase Diagrams” book by Massalski (1990)\textsuperscript{1}. From this time on, their phase diagram has been widely used for the last decades.

Although probably Chakrabarty’s phase diagram is the most widely used in the literature, researchers has continued to investigate Cu-Ni interaction due to the importance of the Cu-Ni (based) alloys and because the published data on thermodynamic mixing functions\textsuperscript{16} demonstrate substantial differences both in the absolute value and temperature dependence, moreover phase equilibrium in the immiscible region cannot be considered fully understood. For example in 2007, Turchanin et al.\textsuperscript{17} published a thorough summary about the Cu-Ni system discussing the miscibility gap and its thermodynamic properties. Recently, Kravets et al.\textsuperscript{18} wrote a detailed study about the miscibility gap with the ferromagnetic transition (Nishizawa horn\textsuperscript{19}) in this system. It is worth mentioning that the New Series of Landolt-Börnstein also addresses the question of the Cu-Ni interaction and states that “Indirect experimental evidence indicates the presence of a miscibility gap in the fcc phase at a temperature somewhere between 450 and 923 K.”\textsuperscript{20}

Although the published data show substantial differences, there is an agreement that the miscibility gap cannot be measured directly by classical metallurgical methods (separation from quenched homogeneous supersaturated alloys), since the diffusion of the atoms is so slow in this temperature range that the equilibrium cannot be achieved in reasonable time, moreover, the separation takes place in such a microscopic regions that this cannot be observed.

Unlike in previous works, this communication provides experimental results on the miscibility in the Cu-Ni system obtained by measuring the atomic fraction of the constituents. To overcome the problem of slow diffusion, hence long experimental time, we choose the so-called ”diffusion couple technique” to determine the miscibility gap. The idea to use macroscopic diffusion couples for constructing phase diagrams was suggested long time ago\textsuperscript{21}. The method is based on the assumption of local equilibrium in the diffusion zone\textsuperscript{22}. This implies that each infinitely thin layer of such a diffusion zone is in thermodynamic equilibrium with the neighboring layers. This means that the chemical potential of the different species varies continuously through the product layers of the diffusion zone. In the following we suppose that local equilibrium is maintained in the diffusion zone.
Accordingly, we used nanolayered materials instead of equilibrating homogeneous supersaturated alloys: we followed the structural and compositional changes in thin tri- and bilayers by depth profiling with Secondary Neutral Mass Spectrometry (SNMS). For details about SNMS, see Supplementary Material.

In principle, there are two ways to move a binary phase separating system across the solubility curve: i) keeping the temperature but changing the average composition; ii) changing the temperature but keeping the average composition of the system. Hence several types of polycrystalline thin film structures were synthesized by sputtering and annealed in vacuum ($5 \times 10^{-4}$ Pa) at temperatures ranging from 670 to 838 K for various durations: (a) $\text{Ni}_{30\text{nm}}/\text{Cu}_{70\text{nm}}/\text{Ni}_{30\text{nm}}/\text{SiO}_x$, (b) $\text{Ni}_{29\text{nm}}/\text{Cu}_{31\text{nm}}/\text{SiO}_x$, (c) $\text{Cu}_{31\text{nm}}/\text{Ni}_{29\text{nm}}/\text{SiO}_x$, (d) $\text{Cu}_{70\text{nm}}/\text{Ni}_{30\text{nm}}/\text{Cu}_{70\text{nm}}/\text{SiO}_x$ and (e) $\text{Cu}_{15\text{nm}}/\text{Ni}_{70\text{nm}}/\text{Cu}_{15\text{nm}}/\text{SiO}_x$. Accordingly, the Ni content of the sample is about 48 at\% for sample (a), 50 at\% for (b) and (c), moreover 18 at\% for (d) and 72 at\% for (e), respectively. The samples were analyzed by an INA-X type SNMS (SPECS GmbH) equipment with a depth resolution better than 2 nm.

As an example, Fig. 1 shows the depth profiles of a bilayered sample type (c) $\text{Cu}_{31\text{nm}}/\text{Ni}_{29\text{nm}}/\text{SiO}_x$ after an isothermal heat treatment at 722 K for 48, 168 and 336 hours together with the as-prepared one. The initially pure Cu/Ni bilayer structure transformed into a Cu-rich/Ni-rich structure keeping the initial interface positions. This result clearly shows that $\alpha_1$, $\alpha_2$ phase
separation occurred at 722K with about 40 at% (α1) and 60 at% (α2) of Nickel. Note that the equilibrium composition of the different phases which formed due to phase separation (miscibility gap) in the bilayered samples after annealing for 168h at 722K are practically the same: about 42 at% (α1) and 58 at% (α2) Nickel.

More detailed discussion about equilibrium, interface, grain size after annealing and technical issues in SNMS can be fined in Supplementary Material.

Heat treatments of samples type (a)-(c) have been performed at different temperatures (from 673 to 823 K where is completely paramagnetic region) to determine the miscibility gap. We also investigated if the free surface (surface segregation) influences the composition of the Ni- and Cu-rich layers as a function of the depth. In case of the trilayered samples, type (a), there is one Ni layer on top of the sample and another one buried under the Cu layer, accordingly we can see the effect of the free surface on the Ni composition if there is any; in bilayered samples reversing the stacking order is needed in order to investigate the same (type (b) and (c) sample).

In case of the bi- and trilayered samples, we determined the typical duration of annealing needed to reach the equilibrium was at least one week. In case of bilayered samples, we performed heat treatments of 168 to 336 hours (1 to 2 weeks). Occasionally, however, much longer heat treatments were also preformed—e.g. 42 days at 722 K—to check whether the
FIG. 3. Depth profiles recorded by means of SNMS of a sample (d) Cu$_{70}$nm/Ni$_{30}$nm/Cu$_{70}$nm/SiO$_x$ (Ni average composition 18 at%; total film thickness 170 nm) in as-prepared and annealed states (at 474°C (753K) for 24 hours). Ni contents of this thin film and annealing temperature in this experiment are far outside the miscibility gap as shown by a dot in the inset. The right shade zone is SiO$_x$ substrate.

Figure 2 shows the equilibrium composition of the Ni- and Cu-rich layers of the samples (a), (b) and (c). Accordingly, at a given temperature a trilayered sample provides three points: one from the topmost (Ni) layer, one from the middle (Cu) layer and one from the bottom (Ni) layer. A bilayered sample delivers two points—one from each layer—, however, its counterpart with reverse stacking also gives two points, therefore four points correspond to the bilayer geometry at a given temperature.

In order to check that the system can reach the homogeneous distribution of the atoms if the average composition of the sample is outside of the miscibility gap, we annealed samples type (d) and (e) at 753K just for 24 hours. A typical example of the obtained results is displayed in Fig. 3. As can be seen, the Cu$_{70}$nm/Ni$_{30}$nm/Cu$_{70}$nm/SiO$_x$ sample is almost homogeneous with sufficiently thicker diffusion length and shorter duration than previous results in Fig. 1 and 2.

Although it is difficult to be sure that we reached the equilibrium state when using the "diffusion couple technique", first and last, all of our experimental findings suggest that what we observed is really phase separation at or very close to equilibrium cause it has
enough volume diffusion length $2\sqrt{Dt}$ against that it is sufficiently thinner sample thickness with type-A grain boundary diffusion, as an example, diffusion length of Nickel in Copper is about 100nm at 722K for 168h.\textsuperscript{23}. Ni contents of separated phase are gradually converging from about 62 and 37 at% at 672 K to about 50 % at 800 K in samples type (a), (b) and (c) as shown in Fig. 2. Consequently, the miscibility gap what we obtained closes at higher temperature than Chakrabarty’s one which has been widely used nowadays. However, the critical temperature we obtained is similar to the five reported experiments which suggested critical temperature values in the high range (see Table 2 in\textsuperscript{16}). We repeat here that even Chakrabarty et al. themselves listed seven experiments of which five reported critical temperatures in the ”high range” and only two in the ”low range”. Our results support that the closing of the critical temperature is in the ”high range”. The striking result in this work is that we could measure the whole miscibility gap from direct composition measurement in Cu-Ni system. To our best knowledge, this is the first experiment determining the miscibility from the measurement of the atomic fraction of Copper and Nickel in the whole composition range.

Nevertheless, we should not forget about that these measurements were performed in nano-scaled systems which may rise two points: the possible size dependence of the miscibility and the validity of the thermodynamic calculations on the nanoscale. The size dependence of the miscibility has been predicted in the framework of the Cahn-Hilliard concept (e.g.\textsuperscript{24}). However, even Calphad\textsuperscript{25} experts pointed out the problem of the applicability of Calphad type thermodynamic calculations on the nanoscale. (e.g. nano-Calphad concept\textsuperscript{26}). According to the nano-Calphad concept “an extension of the Calphad method for systems containing at least one phase (or at least one interface film, complexion) with at least one of its dimensions being below 100 nm” is required; without attempting to be comprehensive: curvature dependence of the interfacial energies, dependence of interfacial energies on the separation between interfaces (including the problem of surface melting), role of the shapes and relative arrangement of phases, role of the substrate (if such exists), role of segregation. We should not forget about the possible change of the phase diagram\textsuperscript{27–29} with the decreasing size. Concerning these remarks, our samples are just touching the challenged dimensions for the determination of the phase diagram. The total film thickness is 100-170 nm for the tri and 60 nm for the bilayers; the individual layer thicknesses are, however, always below 100 nm (from 15 to 70 nm). As we also did some tests with thicker bilayered samples with total
film thickness up to 300 nm which, within the experimental uncertainty, resulted the same miscibility values as samples type (a) (total thickness 130 nm) we think that the results obtained for the trilayered samples give an equilibrium miscibility gap which is close to the bulk one.

Note that in principle we may also consider that stress modifies the miscibility gap. Several groups investigated this in both bulk and thin film samples\textsuperscript{30,31} and the elastic energy effect on the spinodal decomposition\textsuperscript{32,33}. The simple conclusion is that stress decreases the melting point and the critical temperature where the miscibility curve closes if there is no ordering phase (we did not observe ordering in our Cu-Ni thin films). According to these studies, however, the stress does not influence the phase diagram significantly.

Stress in our sample may originate mainly from e.g. lattice mismatch, difference in thermal expansions in bimetallic strips and net volume flux. 1) Lattice mismatch can be neglected because our samples are polycrystalline (not epitaxial) and there is very small lattice mismatches during the heating CuNi compounds. 2) Bimetallic strip effect between the film and substrate can also be negligible as Tanaka et. al\textsuperscript{34} demonstrated that there was nearly zero stress in in-situ strain measurement of Cu thin film on the SiO substrate at 300 to 500\textdegree C during the heating. This is so because Young’s modulus and linear thermal expansion coefficient of Cu and Ni are very close. 3) Atomic volumes of Cu and Ni are also very close, so net volume flux should not be very important; even if it is at the beginning of the intermixing, in equilibrium the stress should be relaxed. Summarizing these points above the miscibility gap we measured rather corresponds to the stress-free case.

Eventual conclusion of this work is that clear miscibility gap of Cu-Ni system with direct measurement of composition was determined on bi- and tri-layered thin films by means of SNMS. The measured curve closes around 800 K with almost symmetrical shape.

We also presented a method how to determine a phase diagram with nano-layered thin films using SNMS technique. It was also proved qualitatively that the miscibility gap we propose should be the same as the bulk one because there is neither obvious size nor stress effect.

These results will presumably set off huge discussions with impact not only on the Cu-Ni system but also other binary, ternary system, for example in material designing, nano materials science, phase simulation, etc.
SUPPLEMENTARY MATERIAL

See supplementary material for the detailed discussion about equilibrium, interface, structures, grain size after annealing and technical issues.

ACKNOWLEDGMENTS

This work was supported in part by the OTKA Board of Hungary (No. NF101329) and by TAMOP 4.2.2.A-11/1/KONV- 2012-0036 project (implemented through the New Hungary Development Plan co-financed by the European Social Fund, and the European Regional Development Fund). Y. I. acknowledge Hungarian Academy of Sciences Postdoctoral Fellowship Programme.

REFERENCES

1T. B. Massalski, H. Okamoto, P. Subramanian, and L. Kacprzak, Binary alloy phase diagrams, 2nd Eds. (ASM International, Materials Park, OH, 1990).
2J. Meijering, Acta Metall. 5, 257 (1957).
3W. Koster and W. Schule, Z. Metallkd. 48, 592 (1957).
4W. Schule and H. P. Kehrer, Z. Metallkd. 52, 168 (1961).
5K. P. Gupta, C. H. Cheng, and P. A. Bech, Phys. Rev. 133, A203 (1964).
6R. E. Pawel and E. E. Stansbury, J. Phys. Chem. Sol. 26, 607 (1965).
7J. C. Love, F. E. Obenshain, and G. Czjzek, Phys. Rev. B 3, 2827 (1971).
8M. T. Beal-Monod, Phys. Rev. 164, 360 (1967).
9T. Miyazaki and H. Murayama, J. Japan. Inst. Metals 38, 377 (1974).
10M. F. Ebel, Phys. Status Solidi(a) 5, 91 (1971).
11T. Tsakalakos, Scr. Metall. 15, 255 (1981).
12V. M. Lopez, T. Sakurai, and et al., Scripta. Metall. Mater. 26, 99 (1992).
13B. Mozer, D. T. Keating, and S. Moss, Phys. Rev. 175, 601 (1968).
14J. Vrijen and S. Radelaar, Phys. Rev. B 17, 409 (1978).
15W. Wagner, R. Poerschke, A. Axmann, and D. Schwahn, Phys. Rev. B 21, 3087 (1980).
16D. Chakrabarti, D. Laughlin, S. Chen, and Y. Chang., Phase Diagrams of Binary Nickel Alloys, edited by P. Nash (ASM International, Materials Park, OH, 1991) pp. 85–95.
17. M. A. Turchanin, P. G. Agraval, and et al., Powder Metall. Met. Ceram. 46, 467 (2007).
18. A. F. Kravets, A. N. Timoshevskii, and et al., J. Magn. Magn. Mater. 324, 2131 (2012).
19. T. Nishizawa, M. Hasebe, and M. Ko, Acta. Metall 27, 817 (1979).
20. P. Franke and D. Neuschütz, eds., Landolt-Börnstein, Thermodynamic Properties of Inorganic Materials: Binary Systems. (Springer Berlin Heidelberg, 2005) Chap. Group IV Physical Chemistry New Series IV/19B.
21. J. Kirkaldy, Can. J. Phys. 36, 917 (1958).
22. A. A. Kodentsov, G. Bastin, and F. van Loo, J. Alloys. Compd. 320, 207 (2001).
23. G. Neumann and V. Tölle., Philos. Mag. A 57, 621 (1988).
24. D. Burch and M. Z. Bazant, Nano Lett. 9, 3795 (2009).
25. H. L. Lukas, S. G. Fries, and B. Sundman, Computational thermodynamics. The Calphad method. (Cambridge University Press, Cambridge, 2007).
26. G. Kaptay, J. Mat. Sci. 47, 8320 (2012).
27. Q. Jiang, H. Y. Tong, and et al., Thin Solid Films 312, 357 (1998).
28. M. Ghasemi. and et al., Nanoscale 7.41, 17387 (2015).
29. A. Kroupa. and et al., PCCP 17.42, 28200 (2015).
30. H. Ohtani, K. Kobayashi, and K. Ishida, J. Phase Eq. 22, 276 (2001).
31. V. Deibuk and Y. Korolyuk, Semicond. Phys. Quantum Electron. Optoelectron. 5, 247 (2002).
32. J. Cahn, Acta.Metall. 10, 179 (1962).
33. C. M. F. Jantzen and H. Herman., Refractory Materials. Vol. 6-V. Phase Diagrams: Materials Science and Technology (Academic Press, 1978) Chap. Spinoidal Decomposition-Phase Diagram Representation and Occurrence, pp. 127–184.
34. K. Tanaka, T. Ito, and et al., J. Soc. Mat. Sci. 53, 728 (2004).