

MAGNETIC PROPERTIES OF FINE PARTICLES OF COPPER-BASED ALLOYS

K.V. CHUISTOV, A.E. PEREKOS, T.V. EFIMOVA,
T.V. RUZHITSKAYA, I.V. ZOLOTAREVSKIY¹

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G.V. Kurdyumov Institute for Metal Physics, Nat. Acad. Sci. of Ukraine
(36, Academician Vernadsky Blvd., Kyiv 03142, Ukraine),

¹Zaporizhzhya State University
(66, Zhukovskiy Str., Zaporizhzhya 69063, Ukraine)

Evolution of structure and magnetic properties of fine particles of Cu–Ni–Fe and Cu–Ni–Co alloys in the process of isothermal annealing have been investigated using the methods of X-ray structure analysis and magnetic measurements. Peculiarities of magnetic properties have been specified, which are governed by phase and chemical composition of particles, their diminutive size, and the presence of concentration inhomogeneities.

Since the 1970s, and especially for the last two decades, a new extensive branch of the physics of magnetic phenomena – physics of disordered magnetics – has been intensely developed. On the one hand, close attention to such systems is caused by a wealth of their physical properties, which eventually result in practical applications. On the other hand, it is brought about by the necessity to deepen theoretical views on magnetism, since a large amount of them, being developed for ordered systems, has turned out to be unable to describe the behavior of more complicated objects such as disordered magnetics.

A numerous class of disordered magnetics includes, among others, a large group of alloys (Cu–Ni–Co, Cu–Ni–Fe, Cu–Co, Cu–Mn–Al, Fe–Cr, Fe–Ni–Cr and others), in which fine ferromagnetic particles are formed in a nonmagnetic matrix as a result of decomposition of supersaturated solid solutions (SSS). Solid solutions of such a kind, which contain particulates of ferromagnetic phases, display unusual physical properties. This reflects the fact that physical properties of small particles of metals essentially differ in most cases from those of their bulk counterparts. Moreover, in the systems of ferromagnetic particles dispersed in nonmagnetic metallic matrices, various collective effects often arise, which are caused by an interparticle interaction. The interaction between the particles can be elastic, magnetic, exchange, and of other types. For example, if one particle creates elastic strain around itself, another

one will “feel” this strain and, thus, elastic interaction of the particles will occur. Interaction of such a kind may lead to a corrected distribution of the particles [1, 2].

Ferromagnetic particles dispersed in a nonmagnetic matrix can interact as magnetic dipoles. Sometimes, the dipole-dipole magnetic interaction in a system of superparamagnetic particles may lead to the appearance of new magnetic state – macrospin glass [3, 4]. There is also the interaction through conduction electrons (of RKKY-type). In the ensemble of superparamagnetic particles, it may give rise to another interesting magnetic phenomenon – superferromagnetism [5].

Of early experimental works, which disclosed peculiarities of the magnetic properties resulted from the dipole-dipole interparticle interaction in the ensembles of superparamagnetic particles, especially noteworthy are papers [3, 4]. The work [3] is devoted to studying alloys of the Cu–Ni–Fe system, whereas [4] – to the investigation of Co–Cu alloys, in which either Ni + Fe or Co magnetic particles with a size about 10 – 20 nm were formed after quenching and further decomposition. For both the systems, the curves of the temperature dependence of magnetic susceptibility (TDMS) displayed maxima, the appearance of which cannot be explained on the basis of known magnetization mechanisms. Taking into account the whole multitude of experimental results, the authors concluded that, in the process of the decomposition of these alloys, a bound magnetic state was formed in the system of small superparamagnetic particles. The dipole mechanism of interaction between the magnetic moments of particles was suggested to contribute to the occurrence of this magnetic state as well. Later on, a similar magnetic state was also found in other copper-based alloys: Cu–Ni–Co, Cu–Mn–Al, and others [5–11].

It should be noted that all the above papers focused on the features of the magnetic behavior of ensembles of magnetic particulates in nonmagnetic matrices, dimensions of which considerably (by 6 – 7

orders) exceeded those of particulates. It is interesting to study the magnetic properties of such systems when the process of SSS decomposition occurs in specimens with restricted dimensions, for example, in fine particles (FPs).

As the objects of investigation, we chose FPs of Cu-(13%)Ni-(7%)Fe and Cu-(30%)Ni-(10%)Co (atomic percentage) alloys obtained by electric-spark dispersion technique in distilled water and ethanol [12]. The alloys were prepared from electrolytic copper, nickel, cobalt (99.9%) and carbonyl iron (99.95%). After melting under argon atmosphere in an induction furnace, ingots were cast in a copper mould. Then, with a purpose of homogenization, they were subjected to thermomechanical treatment and long-term (for 10 hours) annealing at 1273 K. Bulk specimens for magnetic and X-ray investigations had the form of parallelepipeds ($3 \times 3 \times 15$ mm) and disks (\varnothing 10 mm, thickness 1 mm). X-ray studies were carried out using a general-duty DRON-3.0 X-ray diffractometer with Fe $K\alpha$ radiation. Magnetic investigations were performed in the temperature range 77 – 300 K and in fields up to 800 kA/m with the use of a ballistic magnetometer. Inaccuracy of magnetic measurements was 1 %. Both the size and shape of particles were studied by means of a JEM-100 transmission electron microscope with employment of the carbon replica method, whereas particles' size distribution – using an optical laser granulometer "Analizette-22". Electron microscopy and granulometer studies showed that, for the most part, powders consisted of two fractions – fine and coarsegrained. FPs were found to be in the form of a sphere and have a size between 0.05 and 0.5 μm [13]. TDMS measurements were performed by means of the induction method with a frequency and amplitude of the probing field 50 Hz and 400 A/m, respectively. Annealing treatments were carried out at 873 K with the durations at each temperature up to 30 and 5 h, respectively. The results of these studies are accumulated in Figs. 1, 2 and Tables 1, 2.

Shown in Fig. 1 are TDMS curves for both the bulk specimen and FPs of Cu-Ni-Fe alloy, with each curve corresponding to a different duration of annealing at 873 K. It is seen that, at a certain stage of decomposition, a maximum emerges on TDMS. Its position depends on the duration of heat treatment, and it shifts towards higher temperatures as the annealing time increases. As is shown in [3–4, 8–9], such TDMS behavior originates from the magnetostatic dipole interaction between particulates, and a temperature of TDMS maximum

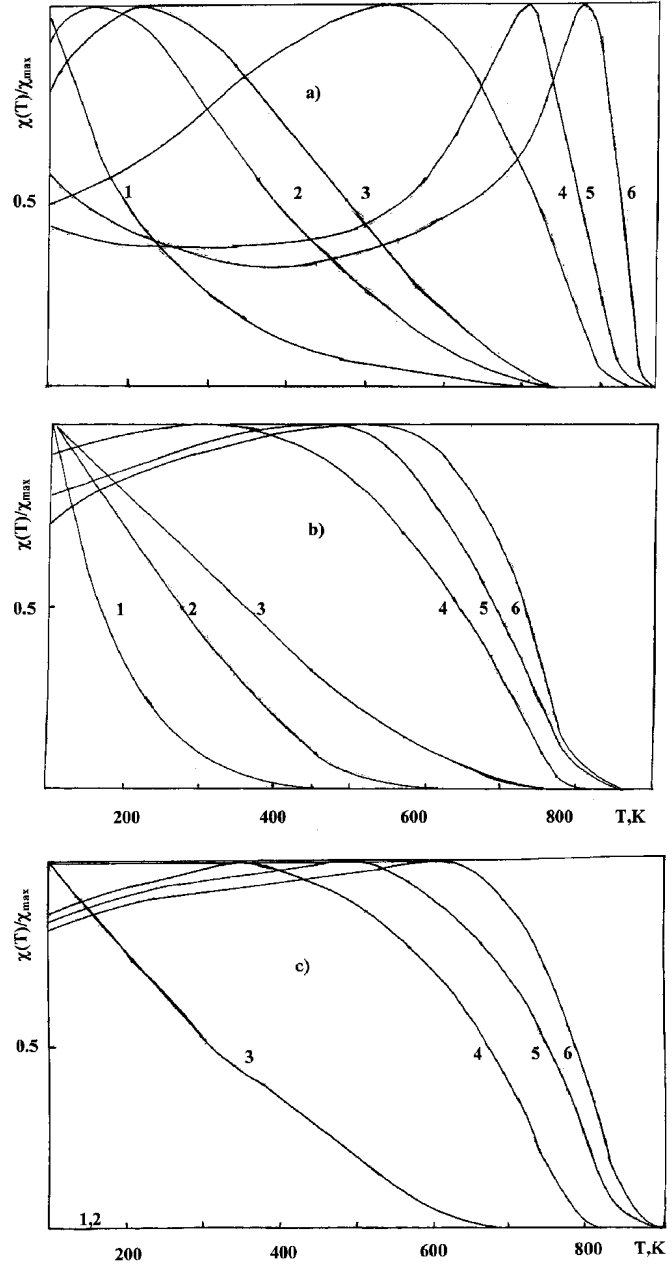


Fig. 1. Temperature dependences of magnetic susceptibility of the bulk specimen of Cu-Ni-Fe (a) and FPs obtained in ethanol (b) as well as in water (c): initial state (1), after annealing at 873 K for 10 min (2), 30 min (3), 5 h (4), 15 h (5), and 30 h (6)

(T_L) can be determined using the formula

$$T_L = (4\pi/9k) nM^2, \quad (1)$$

where k is the Boltzmann constant, M – magnetic moment of a particulate, and n – the number of particulates in a unit volume.

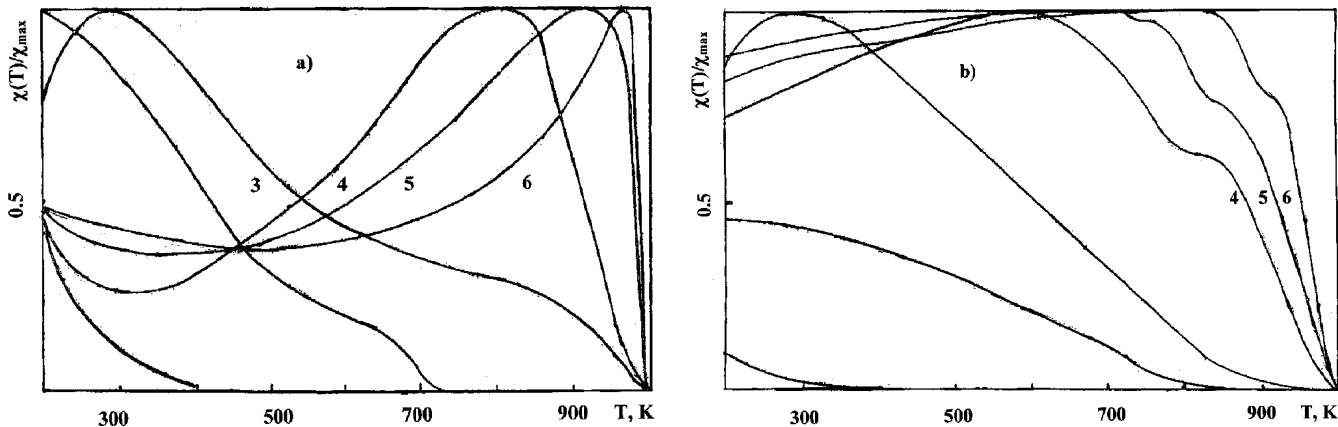


Fig. 2. The same as in Fig. 1 for Cu-Ni-Co alloy

Furthermore, it is seen from Fig. 1 that magnetic susceptibility of FPs in the initial state is far smaller than that of the bulk specimen, and it equals to zero at all in FPs obtained in water. For FPs obtained in ethanol, the peculiarities of the behavior can result from the higher cooling rates, while, in the latter case, an additional factor, namely, oxidation of ferromagnetic iron and nickel should be taken into account. So, the data of Table 1 indicate that the annealing treatment of FPs at 873 K gives rise to decomposition of oxides followed by reduction of iron and nickel. By dissolving then in copper, Fe and Ni form a solid solution unstable against a further decomposition [14]. On $\chi(T)$ curves, this corresponds to the appearance of a noticeable magnetic susceptibility (Fig. 1, curve β), and, at further treatments – to the emergence of maxima on TDMS (Fig. 1, curves 4 – 6).

It should be noted that the kinetics of T_L change is also slower in FPs than in the bulk specimen. According to the results of work [14], the peculiar behavior of $\chi(T)$ curves for the former specimens may be explained by a smaller rate of particulates growth, the size of which determines the value of T_L shift. This may follow from

the fact that the particulate magnetic moment M , which is included in (1), is determined as

$$M = I_S V, \tag{2}$$

where I_S is the saturation magnetization of the magnetic phase, and V – the volume of a particulate.

What is more difficult is to explain a fuzzier character of maxima on TDMS observed in FPs, as compared with the bulk specimen. It was shown in [14, 15] that, both in the initial state and in the process of heat treatment, magnetization as a function of temperature changes much slower in FPs of Cu-Ni-Fe alloy than in the bulk specimen which displays the sharpest magnetization changes just near the Curie temperature T_C . According to the results of [17], the main reason for such a character of magnetization vs temperature dependences may lie in the compositional inhomogeneities, which cause the magnetic phase transition from ferromagnetic to paramagnetic state to occur within a certain interval of temperatures, rather than at a fixed one. Compositional inhomogeneities in the bulk specimen may arise because the coherent boundary between the matrix phase and a

Table 1. Phase composition of $\text{Cu}_{80}\text{Ni}_{13}\text{Fe}_7$ specimens in the process of decomposition resulted from heat treatment at 873 K

| Heat treatment duration, min | Bulk specimen | FPs (ethanol) | FPs (water) |
|------------------------------|-------------------------------------|-------------------------------------|--|
| initial state | solid solution Cu-Ni-Fe | solid solution Cu-Ni-Fe | solid solution Cu-Ni-Fe, Cu_2O |
| 5 | solid solution Cu-Ni-Fe | solid solution Cu-Ni-Fe | solid solution Cu-Ni-Fe, Fe_3O_4 , Cu_2O |
| 10 | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, Cu, Cu_2O , Fe_3O_4 |
| 30 | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, Cu, Cu_2O , Fe_3O_4 |
| 60 | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, Cu_2O , Fe_3O_4 |
| 300 | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, Fe_3O_4 |
| 600 | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe, satellites | solid solution Cu-Ni-Fe |

particulate is not sharp, and the composition gradually changes as a function of distance. In FPs, additional factors associated with surface segregation and oxidation may operate. More detailed studies are necessary to disclose the genuine origin of the broadening of maxima on TDMS in FPs, as compared with the bulk specimen.

An additional peculiarity has been revealed on the examination of TDMS of the Cu–Ni–Co bulk specimen and FPs obtained in ethanol. It consists in the fact that, on a certain stage of decomposition, an inflection arises on TDMS, which can be clearly seen from the $\chi(T)$ dependences presented in Fig. 2. This feature emerges on both the curves corresponding to the bulk specimen (after annealing for more than 10 min, see Fig. 2, *a*, curves 2, 3) and to the FPs obtained in ethanol (after annealing for more than 5 h, see Fig. 2, *b*, curves 4–6). There might be several reasons for the peculiar behavior of the TDMS curves. One of them might consist in the formation, as a result of FPs decomposition, of two ferromagnetic phases with different chemical compositions and, consequently, Curie temperatures. This explanation, however, should be rejected, since, according to the results of X-ray structure analysis, a single equilibrium magnetic phase enriched with Ni and Co is formed in the process of SSS decomposition.

Other, more likely reason may be associated with the existence of a size distribution of particulates and the transition of the larger ones from superparamagnetic

to ferromagnetic state in the process of their growth. A considerable increase in coercivity H_c observed in both the bulk specimen and FPs upon a growth of annealing time is in compliance with this assumption (see Table 2). Apparently, the emergence and growth of H_c are associated just with the presence of ferromagnetic particulates, for which TDMS displays different character from those in superparamagnetic state: for the former ones, coercivity first scarcely changes with temperature and then sharply falls in the vicinity of T_C [18]. From our point of view, it is this phenomenon that may lead to the appearance of peculiarities observed on the TDMS curves presented in Fig. 2.

Thus, based on the investigations carried out, we conclude that the peculiarities of magnetic properties of FPs obtained by electric-spark dispersion technique are determined by a chemical and phase composition of powders, diminutive dimensions of ferromagnetic particulates formed in the process of SSS decomposition, magnetic interaction between them, as well as the presence of compositional inhomogeneities.

Table 2. Change of the saturation magnetization σ_S and coercivity H_c of the specimens under study in the process of the heat treatment at 873 K

| Heat treatment duration, min | Bulk specimen | | FPs (ethanol) | | FPs (water) | |
|------------------------------|-----------------------------------|--------------|-----------------------------------|--------------|-----------------------------------|--------------|
| | σ_S , A·m ² /kg | H_c , kA/m | σ_S , A·m ² /kg | H_c , kA/m | σ_S , A·m ² /kg | H_c , kA/m |
| | Cu–Ni–Fe | | | | | |
| initial state | 11.3 | 2.2 | 4 | 2.0 | 17 | — |
| 10 | 18 | 1.6 | 12.5 | 0.8 | 9.0 | 0.9 |
| 30 | 18.5 | 2.4 | 13.5 | 0.8 | 8.0 | 1.0 |
| 300 | 19 | 1.6 | 14.1 | 1.9 | 7.0 | 2.9 |
| 900 | 19 | 4.6 | 13.8 | 2.4 | 6.7 | 3.4 |
| 1800 | 20 | 4.8 | 13.8 | 3.6 | 7.0 | 4.0 |
| | Cu–Ni–Co | | | | | |
| initial state | 10.6 | 0.2 | 1.2 | — | 1.3 | — |
| 10 | 19 | 4.2 | 15.7 | 0.7 | 3.7 | 0.2 |
| 30 | 20 | 4.4 | 17.6 | 1.0 | 4.0 | 0.5 |
| 300 | 19 | 12.5 | 17.3 | 1.75 | 4.3 | 0.75 |
| 900 | 19.2 | 19.2 | 18.1 | 3.0 | 4.3 | 2.2 |
| 1800 | 19 | 11.6 | 17 | 4.0 | 10.7 | 5.6 |

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МАГНІТНІ ВЛАСТИВОСТІ ВИСОКОДИСПЕРСНИХ ЧАСТИНОК СПЛАВІВ НА ОСНОВІ МІДІ

К.В.Чуїстов, А.О.Перекос, Т.В.Єфімова, Т.В.Ружицька, І.В.Золотаревський

Резюме

Методами рентгеноструктурного аналізу і магнітних вимірювань досліджено структуру та магнітні властивості високодисперсних частинок сплавів Cu–Ni–Fe та Cu–Ni–Co в процесі їх ізотермічного відпаду. Виявлено особливості магнітних властивостей, котрі зумовлені фазовим та хімічним складом частинок, їх малими розмірами та наявністю в них концентраційних неоднорідностей.