Interdependence of nano grain size, alloying effects and magnetic properties of Ni-Cu-Al alloys

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The remarkable modification in physical and magnetic properties of ternary Ni, Cu and Al based ensemble of ball milled nanoparticle alloys and their crystalline shape with grain size and composition has been studied in the present paper. The onset of crystalline changes have been correlated to grain size and alloying content. A sharp decrease in ferromagnetism maintaining the cubic symmetry with grain size and alloying was also revealed. These alloys show two phase transitions, one near room temperature and the other near 80°C compared to 200°C for similar bulk compositions. Such observations have been explained and their possible usage is being explored.

Keywords: Alloys, Nanostructures, Magnetic properties, Phase transitions

1 Introduction

Dimensional and crystalline changes upon grain size reduction of materials lead to modifications in their physical properties. As a corollary effect, alloying variation in nano form leads to enhanced changes in hardness, elasticity, crystalline phases, expansion coefficients, conductivity, magnetic effects etc. Nano metallic alloys[1], nano medical markers[2], optical light emission[3], nanostructured dielectrics[4], ultra-fine electrical contacts[5] are a few implementations of material property alterations in nanostructures. Among different possible nano materials, metallic alloys and their change in properties with alloying are now considered. In traditional preparation processes, metallic alloys are synthesized in bulk form inside arc furnaces at high temperatures[6]. Similar materials in nanogranular form may be prepared by high speed planetary ball milling at room temperatures in different compositions or grain sizes. Production of metallic nanogranular alloys by other techniques or using bulk metallurgical methods is not easy[7].

Among different possible metallic alloys, certain systems, including Ni based alloys, having a partially filled d orbital, change their physical shape and crystalline form with external inducements like temperature, pressure or magnetic field and can regain their old form upon removal of the external inducement or heat treatments[8,9]. It was, recently, observed that paramagnetic properties of certain materials are lowered by over an order of magnitude by grain size reduction[10]. Ni based alloys, which are expected to be paramagnetic, are in that sense interesting[11,12]. Ni based alloys in nanogranular form will be all the more interesting if they change crystalline shape with temperature. We chose Ni-Cu-Al alloy as our test system. During the discussion of results, other reports on such Cu-Al-Ni system have also been quoted. If the grain size of such a Ni based alloy system is reduced, it is postulated that their phase transition temperature will also be reduced. It will be an interesting study to know the extent of this temperature reduction with alteration in grain size. They also hold promise of being used in switching applications, if the above changes are substantial. Ni-Cu-Al based nanostructured ball-milled alloys have been used here as a test case for an analysis of the interdependence between grain size, internal stress and associated defects like stacking faults, magnetization and with alloying composition.

2 Experimental Details

2.1 Sample preparation

Elemental powdered Ni, Cu, Al (Sigma Aldrich Co Ltd) of 99.5% purity were alloyed using a Retsch PM 200 planetary ball mill at a rotation rate of 450 rpm[7] within solid solubility limits using Retsch made 250 mL cylindrical shaped tungsten carbide grinding jars and 10 mm diameter spherical shaped tungsten carbide grinding balls[13]. Spectroscopic grade hexane was used for creating an inert ambiance. The hexane was allowed and evaporated after completion of ball milling. The powder mixture to ball ratio used was 1:10. Ball milling time was varied to get different

particle sizes. The minimum time used was twelve hours and the maximum time used was twenty eight hours. Two sets of experiments were performed. In the first set, the effect of grain size on the material properties has been studied. Here, samples with three different grain sizes were obtained having the same composition of 84.75% Ni, 11.86% Cu, and 3.39% Al. Results of Fig 1(a and b) have shown that grain sizes could be changed by varying the ball milling time. The alloying compositions were chosen in keeping with the expected solid solubility limits as per individual binary alloy phase diagrams. In the second set of experiments, the alloy fraction was varied to investigate the alloying effects in the nanostructured regime. In this experimentation, all samples were ball milled for the same number of hours (twenty eight) and at the same milling speed. Such long milling hours also ensured that there were no transient states to confuse results. The compositions used for this were (i) 84.75% Ni, 11.86% Cu, and 3.39% Al, (ii) 71.44% Ni, 14.28% Cu, and 14.28% Al, (iii) 64.52% Ni, 22.58% Cu and 12.90% Al, respectively.

2.2 Instrumental characterization

The phase formation details of the prepared samples were confirmed by powder X-Ray Diffraction (XRD) patterns using a Philips Xpert Pro Cu Kα system operated at 40 kV, with 40 mA generator current and at a data point interval of
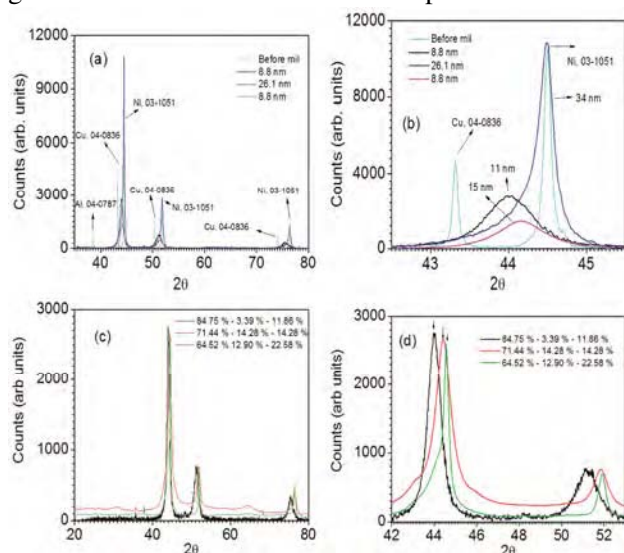

Fig. 1 — (a) Powder X-ray diffraction patterns for Ni-Cu-Al under different ball milled conditions, (b) the magnified image of the major peak of (a); (c) the XRD pattern for different composition variations; (d) the magnified image of the major peak of (c)

0.025 degrees in the I versus 2 θ scan. High Resolution Transmission Electron Micrographs (HR-TEM) in the form of bright field images were recorded using a Tecnai-G2F30 STWIN system operated at 300 keV. Differential Scanning Calorimetry (DSC) measurements were carried out using a Mettler Toledo TGA/DTA 851E system. Magnetic measurements were performed using a Lakeshore 7304 make Vibrating Sample Magnetometer (VSM) with a Lakeshore 340 temperature controller assembly.

3 Results and Discussion

3.1 X-ray and HR-TEM analysis

Figure 1(a) shows the X-Ray diffraction patterns for elemental un-milled Ni, [cubic, JCPDS No. 03-1051], Cu [cubic, JCPDS No. 04-0836], Al [cubic, JCPDS No. 04-0787] powder mixture as well as the different ball milled alloys of the first set. After ball milling, the peaks for elemental Ni, Cu or Al disappeared and a new pattern with broad primary XRD peak profile appeared [Fig. 1(b)] due to the small particle sizes[14]. It does not correspond to any known JCPDS profile, though it broadly matched with that of the main constituent, cubic[14] Ni. It is seen that the major peaks are asymmetric and related to defect induced stress. A Rietveld analysis suggested that the material is cubic with an unit cell of about 3.56Å. This is expected since nanostructures have a higher symmetry factor. The peak shifts are related to change in the internal stress. As a representative example, in crystalline alloy systems with different possible crystalline structures like cubic and hexagonal, where the alloy is hexagonal in higher alloy concentrations, upon reduction in grain size to nanocrystalline form, they take the cubic form with higher symmetry rather than the hexagonal structure[15]. As stated above, the minimum and maximum times of ball milling used was between twelve and twenty eight hours. It was observed that after fifteen hours of ball milling, there was very little reduction in the grain size, as calculated from Scherrer formula and considering effects of all peak profiles (Table1) and a steady state condition is then achieved. So any milling time, higher than 15 h was considered as leading to the terminal particle size", in the first part of the experiment. In that respect, the first part of the experiment is essential. A shift in unit cell dimension from 3.52Å in pure Ni to 3.56Å in these samples is due to alloying effects. The phenomena of grain size reduction and alloy

Time (h)	Grain size (nm)	"*d*" value (Å)	Coercity (G)
10	26.1	2.04	178
15	8.8	2.05	256
28	8.8	2.05	125

Table1 — Effect of ball milling time on grain size variation of Ni-Al-Cu nano-structures (84.75% Ni, 3.39% Al, 11.86% Cu)

Alloy Content	"d" (Å)	Grain Size (nm)	Coercivity (Gauss)
84.75%Ni, 3.39%Al, 11.86%Cu	2.05	8.8	125
71.44%Ni, 14.28%Al, 14.28%Cu	2.04	10.7	271
64.52%Ni, 12.90%Al, 22.58%Cu	2.03	22.8	211

Table 2 — Effect of alloying on the XRD patterns of Ni-Al-Cu nano-structures

formation in planetary ball milling are based on the direct interaction and the effective rate of such interactions of the metal balls with the powder grains. The probability of a direct impact/interaction of the balls with the metal grains of Ni-Cu-Al reduces with the change in grain cross-section. As the grain size reduces, this probability of an interaction also reduces drastically. So for an interaction to happen, the number of milling hours have to be increased as the grain size of the powders gets further reduced. After a certain grain size is obtained, this probability does not significantly change. Hence, after a while, the grain sizes do not get reduced appreciably. That leads to a limiting grain size. Hence, a non-linear change in grain size with milling time was observed. The extent of such size reduction with time also depends on the hardness of the powder in question. As an example, the binary alloy phase diagram for Cu-Ni alloy shows that doubling the Cu content can shift the formation temperature by 40°C or for Al-Ni by as much[13] as 200°C. Controlled variation in alloying content may lead to higher stacking fault density and associated deformed/stressed cubic structure which leads to alloy hardening[16]. This suggests that alloying fraction variation can improve alloy hardening even in nanostructures. A practical aspect is that such stressed nanomaterials may be used to reinforce other matrices. In case of Ni-Cu-Al content ratio variation during alloying (in the second set of experiments), hardness of the material and formation temperatures also change and thereby the extent of grain size reduction with time also got changed[13]. So the terminal grain size values obtained in each case as presented in Table 2 are also different, though, all of them were milled under the same conditions and for the same number of hours. In this experiment, on alloy fraction variation, primarily changing Ni-Cu content ratio, due to Cu with a larger atomic radii, also led to (i) reduction in the peak full width at half maximum (FWHM) values [Fig. 1c] and (ii) only a certain peak [111] became asymmetric, possibly due to increased internal stress and alloy hardening

effect[14] [Fig. 1d]. As only one peak showed a major asymmetry, possibility of trace quantities of other binary phase formations was ruled out[17]. All this suggests stressed crystalline structure formation with changing Ni-Cu content ratio[18]. It is possible that along this [111] direction, defects like stacking faults lead to the observed stress in such cubic systems[18].

Figure 2 shows representative High Resolution Transmission Electron Micrographs (HR-TEM) of these samples under different ball milled conditions. In general, increasing ball milling time decreased the particle sizes in the alloy [Fig. 2(a-c)]. There was a crystalline and an amorphous content in the grains as observed in all these particles at atomic scale resolution. Inset in all these micrographs shows the corresponding low magnification electron micrographs of the samples, elucidating the uniform microstructure of the powder particles. It was also observed that change in alloying content/constituent ratio also alters the grain sizes even with identical ball milling conditions. A detailed electron microscopy characterization also infers that with progressive increase in grain size the relative crystallinity i.e. the extent of crystallinity within the grains also increases. Hence, HR-TEM images and their analysis broadly corroborate the XRD data and its analysis. The images suggest that the samples are in part crystalline with an amorphous component and sample *d* spacing values calculated from HR-TEM results are close to that of the data obtained from XRD (approximately 0.21 nm).

3.2 Calorimetry and magnetization analysis
The DSC data plotted in Fig. 3 shows an inflection at about 27°C and another at 85°C, as compared to 200°C for similar bulk samples[19]. This inflection point changed systematically with grain size and alloying composition [Fig. 3(a and b)]. They are marked with arrows in Fig. 3. Such grain size dependent phenomena have also been reported recently for Ni-Cu-Al systems by other groups[20]. On comparison with magnetism related results, it is suggested that the first
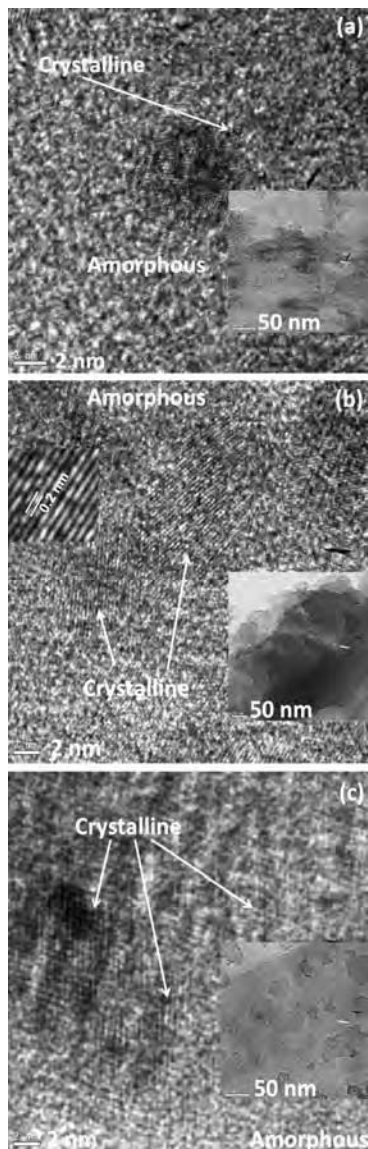
Fig. 2 — Representative HR-TEM micrographs of Ni-Cu-Al alloy (84.74% Ni, 11.86% Cu, 3.39% Al); results suggested progressively smaller sized particles with increased milling times as represented by (a) 28 h, (b) 15 h to (c) 10 h, respectively; images in the inset are of lower magnification with crystalline pockets within an amorphous background. The images were used to verify the grain sizes obtained from Scherrer's formula

inflection is due to crystalline shape change while the second at 85°C represents magnetization rotation[21]. Some metal alloys have the property that upon external inducements like temperature, pressure etc. their crystalline properties change; by applying another external inducement, this change can be reversed. Such a transformation is called a martensitic phase transition. Moreover, this martensitic phase transition does not change the composition. Ni-Cu-Al
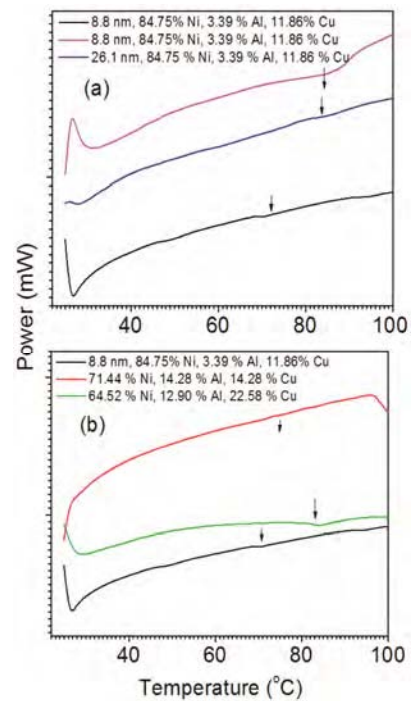

Fig. 3 — DSC profile of the different Ni-Cu-Al nanostructured samples of different (a) grain sizes and (b) alloying compositions showing the effect of grain size and alloying variation

alloy system under study is thought to have this property[8]. In other metallic nanostructures, a similar change in phase transition temperature with grain size was attributed to the increased surface area[20]. Room temperature magnetic measurements (24C) suggest that all the metallic nanostructures were ferromagnetic [Fig. 4]. Reduction in grain size, from 26.1 nm to 8.8 nm (Fig. 4a) reduced the magnetization saturation values almost by an order of magnitude from ~31 emu/gm to ~4 emu/gm. These values were very similar to data from Cu-Ni nanostructured films[22]. Grain size dependence of magnetic properties was observed in these films as well. A magnetization dependence on grain size was also observed for ZnS:Mn nanostructures by the authors[10], where the magnetic properties were lower (susceptibility per gm was 4 μ) by more than an order of magnitude w r t similar bulk material (susceptibility per gm was 300 μ). Changing alloying content was also observed to increase the magnetic saturation values almost up to an order of magnitude (Fig. 4b). Change in the relative ratio of Ni, Al and Cu changed the material hardness of the alloy formed. Increasing the Ni content, relatively reduces the hardness. Earlier, we showed how the grain size and defects in a similar Ni-Al-Cu ternary control the
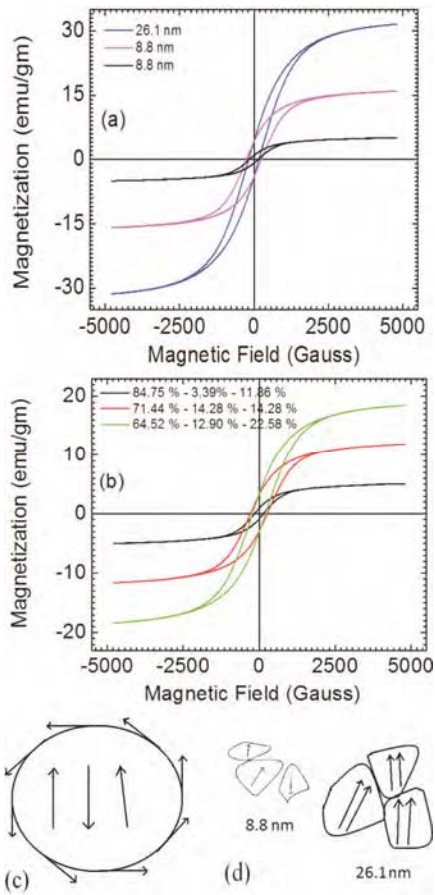
Fig. 4 — Room temperature (24ºC) magnetization profile of different Ni-Cu-Al nanostructured samples of (a) different grain sizes and (b) alloying compositions(c) A schematic showing the orientation of surface spins on a cross-section; (d) the schematic of likely orientation of different magnetic clusters
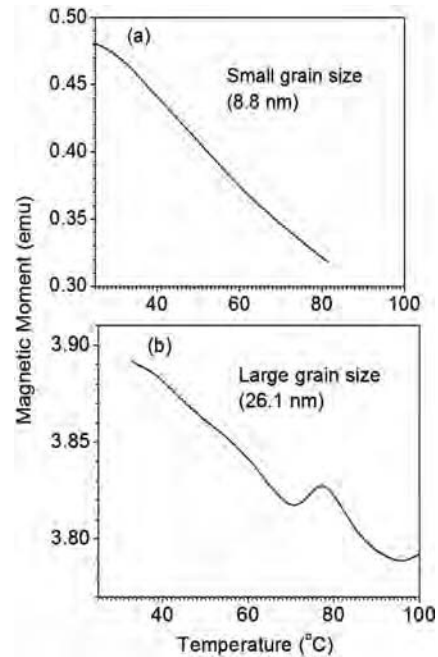

Fig. 5 — Representative graph of magnetization as a function of temperature for two Ni-Cu-Al samples of different grain sizes (a) 8.8 nm and (b) 26.1 nm (same alloy composition) showing the effect of grain size on phase transition temperature

extent of magnetization. Due to the increasing material hardness with change in alloy fraction, the limiting grain size has increased. Hence, lower Ni content alloys due to their higher grain sizes, with higher relative crystallinity paradoxically, had higher magnetization values. It is postulated that (i) increased alloying and related spin alignment, (ii) stress and defects leads to a non-cancellation of spins and increased magnetization. As the dimensionality of a physical system is reduced, a part of the material is ordered while the other part consists of non-correlated spins i.e. presence of large quantities of amorphous components within the dispersed nanogranular systems leads to randomization of magnetic spins with a few islands of ordered spins/crystalline components as were also suggested by HR-TEM images[23]. Other reports and theoretical analysis on such Ni-Cu-Al clusters[22,24] also suggest so. This non-correlated amorphous

component may increase with smaller particle size i.e. incomplete chemical and structural ordering leads to the observed phenomena.

Reports suggest that for very narrow hysteresis loops as in the present case (Fig. 4), the inter-particle interaction is small while the role of surface effects may be dominant[25]. The variation of coercivity with grain size (Table 1) may be co-related with defects and the extra energy required to anneal and remove defects and associated orientation. Larger directional stress associated with defects may lead to better orientation and higher coercivity. Table 2 also gives the coercivity values as a function of alloy content. The coercivity value analysis for the alloys is difficult competing phenomena like change in grain size, (ii) change in Ni and Cu concentration and (iii) variation of defects and stress in these alloys. The correlation of grain size and surface re-alignment of magnetic spins under external field was analyzed using a temperature dependent magnetization measurement on a representative alloy of the first set (84.75% Ni, 11.86% Cu, 3.39% Al) [Fig. 5(a and b)]. A magnetization reduction with temperature and grain size due to increasing randomization was seen, suggesting temperature related surface spin orientation fluctuations were increased and magnetic ordering was reduced in smaller grains. Only larger

grain sizes showed a magnetic phase change with temperature (Fig. 5b). It roughly corresponded to the higher temperature phase change observed in DSC (Fig. 3) at around 85°C and can be related to a magnetic reorientation/magnetic rotation at this temperature[21]. Thus, a critical size requirement in nanostructures for such phase transitions is suggested. Such materials may have usage in electromagnetic shielding applications, or for their electrical/electromagnetic response properties as sensing/switching materials based on the reduced transition temperature with grain size reduction.

3.3 Theoretical aspects

A suggested theoretical explanation for the observed phenomena[26] is that the effective crystal field in such metallic systems and the periodic potential U(R+r) = U(r) changes with reduced grain size, where **r** is a vector and **R** is the Bravais lattice vector. The metallic system compensates for the reduction in finite crystal dimension (reduced grain sizes) by increasing the d spacing with reduction in grain size. The free electrons in the metals ensure the extent of long range ordering, so a change in d spacing with grain size is more obvious in metals[26]. Hence, the systematic experimental peak shift with reduction in grain size was observed. The phenomena of phase transition temperature change with grain size may be explained by the following model: unit cubic cells of lattice constant a is assumed and n such cubes constitute each edge of a larger cuboid grain. The total number of unit cells in the volume is $(n-2)^3$ while the number of unit cells on the surface is $6n^2$. The surface to volume ratio of unit cell number is, thus

$$R = 6n^2 /(n-2)^3 \qquad \qquad ... (1)$$

In nanostructures, the value of R approaches 1, with half of such cells on the surface; in large grains R approaches 0 with most unit cells within the volume. In martensitic phase transitions, only the volume unit cells are largely involved and thus in nanostructures, only half of the normal thermal energy is required for inducing the transition. Thus, lowering of grain sizes also lowers the required temperature for martensitic phase transitions as was experimentally observed. The observed low magnetization values may be explained as: The individual magnetic spins are either in the bulk volume or on the surface. In smaller grain sizes $R \approx 1$. A representative diagram [Fig. 4(c and d)] shows that without a magnetic field, the surface spins

cancel each other, leaving only a small number of volume spins to be oriented (Fig. 4c). In the presence of external magnetic fields of a few kilo Gauss, the surface spins are not fully re-aligned and lead to the observed low magnetization in metallic nanostructures. Increased alloy content and resultant internal stresses lead to some more of the surface and volume spins in the stressed cubic system not cancelling out resulting in a higher magnetization (Fig. 4d). In the regime of $1 > R > 0$, a temperature change leads to realignment of spins within the volume of the grain. In smaller grain sizes (8.8 nm), R is less (closer to 0) while in larger grain sizes (26.1 nm), it is higher (closer to 1). Hence, a magnetic phase change for the larger grain size sample (Fig. 5b) is more likely.

4 Conclusions

Ferromagnetism in Ni-Cu-Al based nanogranular alloys showed a grain size dependence. It may be attributed to higher surface effects, dependence of internal stresses and stacking faults/defects and associated magnetic ordering with grain size. Their cubic symmetry was intact. These alloys show a phase transitions at < 26°C and < 80°C, compared to 200°C for similar bulk materials. At room temperatures, ferromagnetism in these alloys is greatly reduced w.r.t. similar bulk structures up to a critical grain size. This suggests that decrease in grain size leads to higher crystalline disordering, disordering of the spins, higher defect density and a consequent dilution in ferromagnetism. Alloying content variation enhanced the ferromagnetism and is attributed to competing phenomena like alloying induced change in concentration and grain size change and defect induced change in magnetic (spin) ordering in nanostructures.

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