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Some unique properties of nanocrystalline metal alloys

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The remarkable modification in physical, magnetic and other consequent properties of certain ternary alloys using two representative alloy systems eg. (Ni-Cu-Al) and (Ni-Fe-Ti) nanoparticles in different concentration ranges by correlating changes in their properties with grain size, alloying composition have been studied. A sharp decrease in ferromagnetism maintaining the higher crystalline (eg. cubic) symmetry with grain size and alloying has been observed. Both of these alloys show phase transitions, whose transition temperatures are lowered as compared to similar "bulk" compositions. Such phenomenon is attributed to reduction of effective number of spins per grain upon nanostructure formation and associated change in type of crystalline phase. Representative work on maintaining such observed nano related properties in the bulk regime as a proof of concept method is also stated. These alloys in powder form have also shown a high degree of EM radiation absorption in the GHz range, possibly as a consequence of their observed magnetic properties.

Keywords: Metal alloys, Nano-structures

1 Introduction

By analyzing different properties of luminescent nanocrsytalline[1] ZnS:Mn, it was seen that they had poor magnetic properties at room temperatures, which were quite different from properties of such bulk materials[2]. The immediate queries cropping up are if such properties are also valid for other different alloys, or if they also visible for metallic nanostructured alloys too. Among different possible metallic alloys, various Ni based alloys, having Ni with a partially filled d orbital, which 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 were considered. These are called shape-memory properties[3]. There is a critical value of such inducements for change of properties. It was earlier observed that paramagnetic properties of the nano ZnS:Mn are lowered by over an order of magnitude by reduction of their grain size[1]. Ni based alloys, which are often paramagnetic, are in that sense interesting as both phenomena, reduction in magnetic properties with grain size and shape memory properties can possibly be observed in the same Ni alloy system. Two alloy systems were considered, Ni-Cu-Al and Ni-Fe-Ti. In Ni-Cu-Al alloy, with known shape memory properties, this phenomena of magnetization reduction with grain size and reduction in value of critical temperature (phase transition temperature) was observed[4]. Ni-Fe-Ti alloy was then chosen as our system to extend our earlier knowledge about phenomena related to the grain size related change in phase transition temperature involved in Ni-Cu-Al alloys for further analysis of the interdependence between grain size, reduction in magnetization and phase transition temperatures[5]. Such a ternary Ti based alloy system was chosen as reports about only binary Fe-Ti or Ni-Ti or Cu-Ni alloys were available earlier[3]. Some reports on such ternary alloys have only theoretical predictions as may be seen from references[4,5]. An experimental study on a ternary system like Fe-Ni-Ti on a wider alloying range, as presented here, is likely to provide broader experimental information on the range of transition temperature changes possible upon ternary formation and effects in their grain size reduction, changes in defects and associated crystalline properties. The obtained data should provide additional information to corroborate the theoretical expectations reported earlier over different temperature and alloying ranges. This study was then extended to pseudo bulk system of similar Ni-Cu-Al and Ni-Fe-Ti alloy material prepared by Spark Plasma Sintering (SPS) techniques to see if such properties were maintainable on pseudo bulk form[6]. A comparison of the properties was also made. A possible practical application of such nanogranular alloys is discussed in the end in the form EM absorbing paint material based on experimental data available at hand.

2 Experimental Details

Sample preparation details of Ni-Cu-Al alloy and Ni-Fe-Ti alloy nanocrystalline powders can be found in Refs (4,5). Based on the earlier reports, the optimized time for grain size reduction was thought to have been achieved with such prolonged ball milling conditions, though it is agreed that the hardness of the Fe-Ni-Ti system can in principle be different from that of the Cu-Al-Ni ternary system. In all cases, relative miscibility of the material was estimated from the corresponding binary alloy phase diagrams[7]. Pseudo bulk sample preparation was done in the following manner by Spark Plasma Sintering (SPS) of the compacted Cu-Al-Ni and Fe-Ni-Ti ternary nano powders, where rapid heating rates of sintering resulted in maintaining the nanoscale features even post sintering. Unlike the hot-pressing technique, the extremely short sintering time cycle in SPS prohibits mass transport and hence the grain growth, allowing retention of nanostructures achieved during ball-milling as discussed[4,5]. The nanostructured alloy powders were consolidated and sintered under vacuum (~ 4 Pa) using spark plasma sintering (Make: Dr. Sinter, Japan, Model: SPS Syntex, 725) at a pressure of 60 mPa at a temperature of 600ºC for Cu-Al-Ni and 900ºC for Fe-Ni-Ti with a soaking time of 3 min. SPS heating rate of 150°C/min was maintained during sintering, where graphite die and punches were used to form a circular disk of size 12.7 mm diameter.

The phase formation details of the prepared samples were confirmed by powder X-Ray Diffraction (XRD) patterns using a Rigaku XRG 2KW Cu Kα system operated at 40 kV, with 40 mA generator current and at a data point interval of 0.025 degrees in the I versus 2θ scan. Differential Scanning Calorimetry (DSC) measurements were carried out using a Mettler Toledo Star-E TGA/DTA system. Transmission Electron Microscope (TEM) bright field images were recorded using a Tecnai-G2F30 STWIN system operated at 300 keV. Magnetic measurements were performed using a Lakeshore 7304 make Vibrating Sample Magnetometer (VSM) with a Lakeshore 340 temperature controller assembly. Electromagnetic absorption measurements of the compacted powder samples in GHz range were taken using a Agilent Technologies ENA Series E5071C Network Analyzer.

3 Results and Discussion

Summarizing the earlier XRD results for both Cu-Al-Ni and Ni-Fe-Ti alloy samples, it may be said that after ball milling, the material broadly retained the cubic pattern of that of Ni in both cases[4,5]. However, for the Ti system, there were some stress issues. In both cases, the material took a nano-granular form. Peak shifts were observed and are thought to be related to change in internal stress upon alloying, due to difference in the atomic radii of the constituents. Detailed analysis of the effects of ball milling time on the grain sizes and effect of varying the concentration rations were done[4,5].

Comparison of XRD data of SPS prepared Cu-Al-Ni alloy samples with that for the nano granular powder alloys suggest that nanogranular structures could be retained in the SPS preparation method for such alloys. No other major phase or oxide formation during SPS mode preparation was detected [Fig. 1]. Interpretation of other issues should be obvious. However, in contrast, comparison of XRD data of SPS prepared Ni-Fe-Ti alloy samples with that for the nano granular powder alloys suggest that there were nanogranular oxide peaks during SPS sample preparation, possibly due to the higher temperature of preparation required (900°C). However, the data of that is not shown here for brevity. It is surmised that the low vacuum conditions of 10^{-3} mbar during sample preparations and high temperature of preparation required resulted in sample oxidization which was not prevalent during the Cu-Al-Ni alloy samples' preparation at temperature of 600°C. Due to this issue, SPS prepared pseudo bulk Ni-Fe-Ti alloy samples were not further analyzed in detail.

Representative TEM images of these ternary alloys show that they are indeed of the nanogranular form,

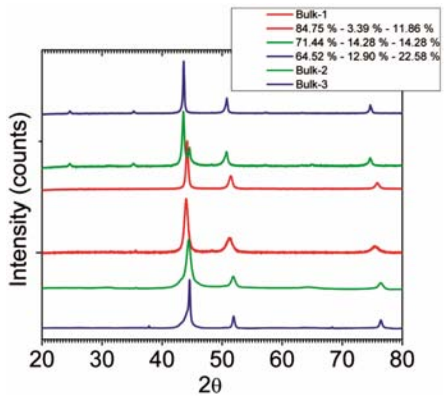

Fig. 1 — Comparison of Cu-Ni-Al nano-powders with SPS Cu-Ni-Al pseudo bulk samples

with grain sized in the range 20-50 nm. Based on high resolution images (Fig. 2), it was also surmised that in all cases, the grains were only partially crystalline. So this suggests that only a small part of the sample can be expected to have orientation or periodicity related properties like magnetic domains etc.

DSC and temperature dependent magnetic measurements were done on both Cu-Al-Ni and Ni-Fe-Ti alloy powder samples. The transition temperatures obtained from the DSC and magnetic measurement tallied – matched well[4,5]. In all cases, it was seen that the alloys showed a phase change within 130°C, which is lower than their reported phase transition temperature for similar bulk alloy materials. Such lowering of transition temperature is due to grain size dependence, lower than threshold value for grain size, which is related to the onset of the nano properties. Alloying content variation changed the extent of ferromagnetism and this is attributed to competing phenomena like (i) alloying induced change in concentration, (ii) grain size and (iii) defect induced change in magnetic (spin) ordering in such nanostructures[4,5].

If results of magnetic measurements of Cu-Al-Ni alloy powder samples and similar SPS prepared pseudo bulk samples are compared and analyzed, it is seen that the magnetic properties of SPS samples were further reduced (Fig. 3). It is suggested that this may be due to further reduction in properties of crystalline ordering of each grain upon SPS based sample preparation process, due to further demagnetization of the small magnetic nano domains at the sample preparation temperatures. An even more nano amorphous low magnetic structure is the result. Incidentally for the similar SPS prepared pseudo bulk oxidized Ni-Fe-Ti alloy samples, the magnetic properties are also similarly reduced. However, due to the oxidization, the effects of external magnetic field and inducement become much more linear (data not shown for brevity).

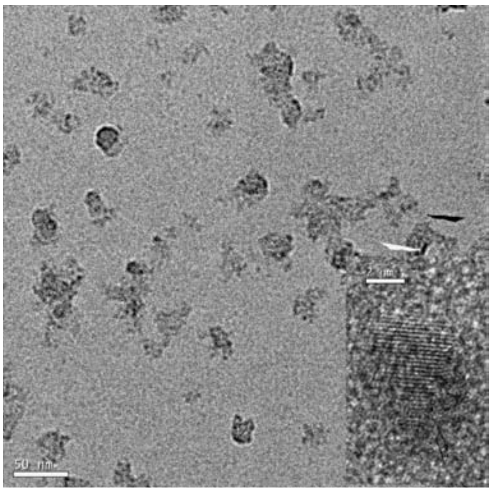

Fig. 2 — TEM image of such ternary metal alloy; the inset is an image with a higher magnification of a whole grain

Based on the results of magnetization and other data, for Cu-Al-Ni and subsequently also for Ni-Fe-Ti alloy powder samples, it was suggested that such reduction on magnetic properties and phase transition temperature are due to the parameter R, which is the Bravais lattice vector[4,5,8]. The surface to volume ratio of unit cell number is $R = 6n^2/(n - 2)^3$, where unit cubic cells of lattice constant "a" is assumed and "n" such cubes constitute each edge of a larger cuboid grain. In nanostructures, the value of R can approach 1, as half of such cells are on the surface; in large grains R can approach 0 as most unit cells are within the volume. In 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 effectively lowers the required temperature for

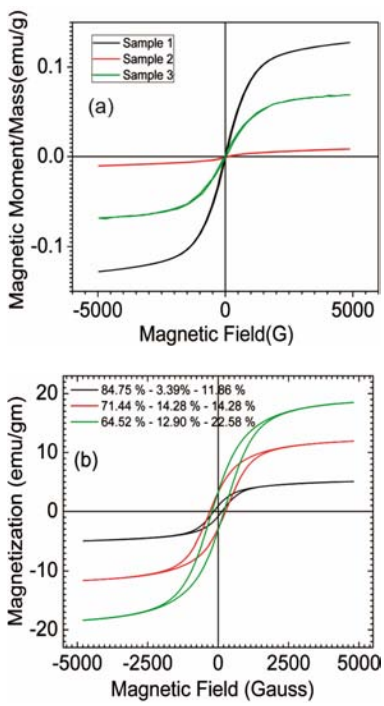

Fig. 3 — (a) Magnetization properties of SPS grown pseudo bulk Cu-Ni-Al alloy (b) Similar properties of the corresponding Cu-Ni-Al alloy nano powder[4]

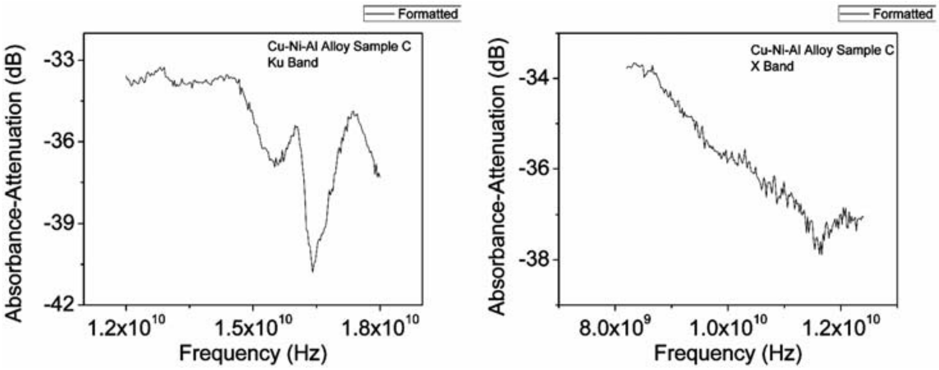

Fig. 4 — EM absorbance for compacted nano-powder Cu-Al-Ni alloy sample in Ku band and X band (GHz range)

phase transitions as was observed. In the case of SPS prepared pseudo bulk samples of both type of alloys, due to the preparation method, more amorphization was introduced leading to lowering of their magnetization even more. This effectively extrapolates continuation of the nano properties in the extended nano-island based pseudo bulk material and continuation of nano related reduction in transition temperatures.

These ternary alloys had such very low magnetic properties as above, EM absorption properties on these Cu-Al-Ni and Ni-Fe-Ti alloy powder samples were also studied in the GHz range (X band and Ku band). The spectral range was so chosen to see their response in the radar frequency ranges. It was observed that in the frequency range of 10^9-10^{10} Hz, absorption for Cu-Al-Ni alloy sample is in the 30 dB range while for Ni-Fe-Ti alloy powder samples it is in the range[9] 30-70 dB as shown in Fig. 4. Such high absorbance has EM absorbing paint related applications. The alloy grain sizes are such that they are miscible in any colour neutral paint base. Due to the nanogranular form and resultant reduction of effective number of magnetic spins in these ternary alloy granules, when the EM spectra is incident on the alloy powder or related paint material due to the small number of multi-directional spins, the incident energy is not reflected back but rather absorbed by the multi-directional spins and later it gets dissipated by thermal means.

4 Conclusions

It was shown that alloy based ternary alloy metal ‘Nano Structures’ often have some unique properties. Based on the trends observed it is suggested that such properties are grain size dependent, while some of the property changes are due to partial crystalline nature of such alloy materials. Such properties seem to be material independent and are rather dependent on grain size related extent of crystallinity. It was shown that these properties can also be almost be frozen in similar pseudo bulk material form. Such poor magnetic properties are due to reduced range of periodicity of solid state crystals, due to smaller grain sizes with only partial crystallinity. These alloys have phase change and Shape Memory properties, which can be tailored by making changes in grain size. Such ternary alloys can have EM absorption properties and their practical applications can be as GHz absorbing paint materials.

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