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Study the Anomaly in the Magnetic Properties of Invar Alloys by using X-ray Diffraction and Mossbauer Spectra

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Abstract: In this research, Fe $_{100\text{-}x}$Ni$_x$ nanoparticle alloys with x = 29, 32 and 37 is studied. X-ray diffraction patterns were obtained at room temperature confirmed the coexistence of both b.c.c and f.c.c phases for x = 29 and 32. However only f.c.c phase was observed for x = 37 Mossbauer Spectroscopy (MS) shows an anomaly in the occurrence of a paramagnetic structure characteristic of the low-spin (anti taenite) f.c.c phases, in addition to the magnetic materials characteristic of the b.c.c phase and the high-spin f.c.c phase obtained at high-spin f.c.c phase observed in XRD patterns. MS technique proves was an effective instrument for studying and prepared nanoparticle system. The anomaly in the nanoparticle magnetic alloys is due to competing ferromagnetic and antiferromagnetic interactions which arise as a result of fluctuations in the interatomic spacing.

Key words: Mossbauer spectra, XRD, super paramagnetic, anomaly, Invar alloy, occurrence

INTRODUCTION

Iron nickel alloys are very rich and interesting system particularly in the Invar region (65-70 at % Fe) which has a f.c.c structure. In this region anomalous behavior is observed in some physical properties such as thermal expansion, magneto-striction (Rancourt *et al*., 1987; Abd-Elmeguid *et al*., 1988; Shilfgaarde *et al*., 1999). Alloys which exhibit Invar behavior have a small Thermal Expansion Coefficient (CTE) below the Curie temperature; such alloys are of special interest to scientist and engineers. Invar alloys shows several anomalies properties such as low value for its thermal expansion coefficient at room temperature the interpretation of thermal expansion results has led to the conclusion that thermally induced spin fluctuation are responsible for the enhanced thermal coefficient in alloys, instability of force magnetism, low Curie temperature (T_C) and saturation Magnetizations (M_s), large high field magnetic susceptibilities as a function of temperature and relatively flat magnetizations versus temperature. Early studies on a serious of alloys exhibited anomalies in their atomic volume, elastic modulus and heat capacity (η). The observed anomaly in the magnetic properties of Invar alloy look like low thermal expansion and high dimensional stability under a wide range changing temperature, makes these alloys are widely used in control unit of the mechanical systems in many different industries and opto-mechanical engineering applications. The value of thermal expansion (CTE) of Invar 36 alloys at room temperature is approximately (1×10^{-6} k^{-1}). Like most mechanical properties (CTE) also varies with temperature. However, Invar's (CTE) is the lowest of any metal and varies slowly with changing temperature which makes them suitable for many applications including significant temperature changes. The low (CTE) of Invar alloys make them as a good materials for building different equipment that require temperature invariant dimensions such as laser cavities. Because of the longitudinal mode separation of a laser cavity depends on the distance therefore the sensitively on the distance must be fixed with a tolerance of the wavelength of laser between (1~0.5 µm for visible light laser radiation). Such applications demands materials with near zero thermal expansion coefficients at room temperature, properties such as magnetostriction, thermal expansion etc (Rancourt *et al*., 1987). Alloys which demonstrate Invar behavior have a small Thermal Expansion Coefficient (CTE) below the Curie Temperature (T_C), large force volume magneto-striction and shows a substantial high pressure dependence of the magnetization Curie temperature (Gallas and Jornada, 1991; Shilfgaarde *et al*., 1999). Fe-Ni alloys in the local fluctuations in compositions leads to a heterogeneous magnetization and that believed essential for the Invar effect.

MATERIALS AND METHODS

Characteristic of γ(f.c.c) at (~30 at %Ni) for Fe-Ni Invar alloys due to the connection between the average

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magnetic moment and molar volumes. They show the Invar effect for wide changing temperature range near zero thermal expansion for above concentration. This effect and anomaly of the physic properties have been subject for both theoretical and experimental research over a century. Theoretical calculations shows the atomic magnetic moment of Ni in γ(f.c.c) for Fe-Ni Invar alloys was independent of the structure of the alloys or volume but the magnetic moment of the Fe change with volume (Abd-Elmeguid *et al*., 1988). Furthermore, the atomic magnetic structure is characterized (at zero temperature rang) and that cause as continuous transition from a high moment ferromagnetic state at high volumes to a low moment disordered non-collinear form at low volumes (Abd-Elmeguid *et al*., 1988; Wassermann *et al*., 1990). For Fe-Ni alloys a-phase (b.c.c) was found in the Fe rich region but for Ni rich region exhibit the γ-phase (f.c.c) also mixture of the two kinds was observed for alloy with intermediate concentrations (Schilfgaarde *et al*., 1999; Dubrovinsky *et al*., 2001; Lehlooh *et al*., 2002).

In addition to these two Ferro magnetically ordered phases, another technique such Mossbauer Spectroscopy (MS) demonstrated the paramagnetic properties of the Invar alloys was attributed as a result of super-paramagnetic relaxations or to a low spin γ-phase (f.c.c) (Lehlooh *et al*., 2002; Schilfgaarde *et al*., 1999).

However, the structure of the alloys at which this component appears and its relative abundance for Invar were not mentioned in the literature demonstrating the sensitivity of this component depends on the preparation method. The magnetic properties anomalies for Fe-Ni alloys which prepared by chemical co-precipitation (Dubrovinsky *et al*., 2001) and by the melting (Lehlooh *et al*., 2002).

Near the Invar (36%) concentration were thus previously investigated by Mossbauer spectroscopy technique. In this concentration range, magnetic moment and structural phase transitions in that rang were observed and the low spin component also appeared. This component was attributed to super paramagnetic properties (Lehlooh *et al*., 2002) and partly to the low spin γ-phase (f.c.c) (anti-taenite) (Lehlooh *et al*., 1997).

The aim of this research is an effort to understand the magnetic behavior as a function of temperature for Fe-Ni Invar alloys region the light of differences in reported experimental results. In that procedure sensitivity of the paramagnetic phase to the method of sample preparation was appear and also the explanations measurements and the conflicting explanations concerning the appearance of such phase have enable us to conduct the present investigation. Thus, in this research, we have prepared Fe-Ni Invar alloys nanoparticles by using the chemical co-precipitation method and studied their structural and magnetic properties by using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Mossbauer Spectroscopy (MS).

Table 1: Properties of the f.c.c alloys at 290°K

Properties	$Fe_{68}Ni_{32}$	$Fe_{63}Ni_{37}$	$Fe_{71}Ni_{29}$
Average atomic unit (amu)	57.28	56.31	57.89
Lattice constant (A)	3.586±0.01	b.c.c (2.85±0.1) f.c.c (3.55±0.01)	3.586±0.01
Melting temperature (K)	1710	1735	1745
Saturation magnetic moment (μ_B/atom)	1.68	1.25	1.34
Curie temperature (K)	790	340	440
Debye temperature (K)	407.8	315	298
Structure	f.c.c	b.c.c f.c.c	γf.c.c

Experimental: Investigate the morphology of the samples and measured the particle size distribution had been done by using Scanning Electron Microscopy (SEM). The Invar alloys was prepared by using arc melting technique as described by Dubrovinsky *et al.* (2001). The f.c.c structure of the Invar alloys was determined by using X-ray diffraction pattern (Lattice parameter a = 3.5804 A°). X-ray diffraction for power samples is performed using a standard θ-2θ diffract meter with Co.Kα ($\lambda = 1.79025$ A°) radiation. Mossbaure Spectroscopy (MS) in transmission geometry was conducted using a standard constant acceleration Mossbaure Spectrometer and the spectra of that procedure were collected over 512 channels. According α-Fe spectrum at room temperature Isomer shifts had been measured relative to it also the spectra were fitted using a software based on least squares analysis. The magnetic properties for different samples are listed in Table 1.

RESULTS AND DISCUSSION

The morphology of the Invar alloy (Fe-Ni) and their precursors were determine by means of a CamScan Model of the Oxford S range of Scanning Electron Microscopes (SEM) technique. The measurement of grain size distribution of the sample had been done by using (SEM). The range of the grain size of the Fe-Ni alloys is in (~100 - 500 nm). Figure 1 shows the particle size with (x = 29, x = 32 and x = 37). Figure 2 shows XRD patterns which indicate that alloys with (x = 29 at % Ni) consists of two kinds of phases, i.e, the a-b.c.c Fe-Ni phase and the α-f.c.c phase. The α-phase (b.c.c) increases with the increasing of Ni concentration until (x = 37 at % Ni) where

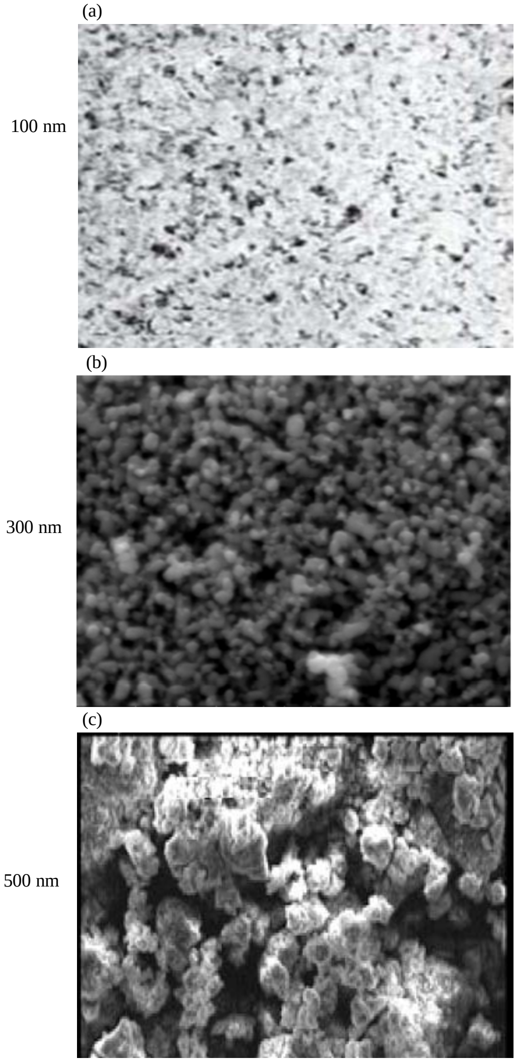

Fig. 1: SEM image for $Fe_{100-x}Ni_x$ with: a) (x = 29); b) (x = 32) and c) (x = 37)

the samples become a pure f.c.c structure. The lattice parameter of the b.c.c phase is around (2.85±0.01) A° while that of the f.c.c phase (3.5804±0.01) A°. These values are only slightly lower and higher than the lattice parameter of b.c.c Fe (2.87A°) and f.c.c Ni (3.52 A°), respectively. The small difference in the lattice parameters could be a result of the fact that Ni atom has a smaller size than Fe atom, in the range of concentration of this research. Any way the difference in lattice parameters for the three alloys are within experimental errors. The crystallite size is measured by using the broadening of diffraction lines of Scherer equation:

$$\upsilon = \frac{k\lambda}{\beta(\mathrm{Cos}\theta)}$$

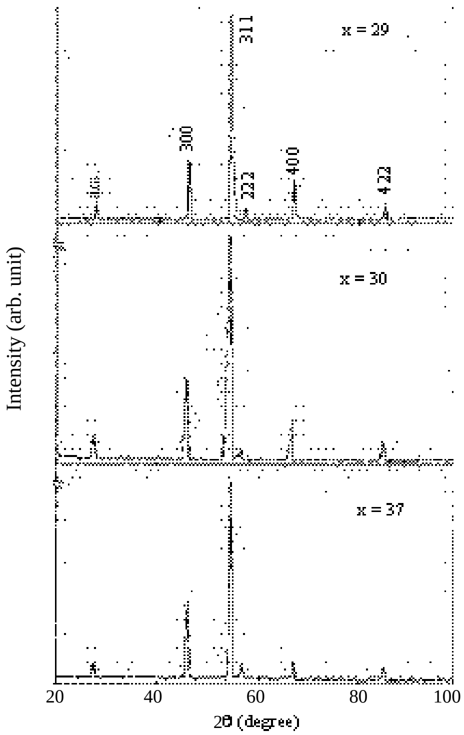

Fig. 2: Typical X-ray diffraction pattern for $Fe_{100-x}Ni_x$ (x = 29, x = 32, x = 37)

Where k is a constant (0.94) while e is the wave length of X-ray (1.79 A°) and a is a constant of the width of the diffraction peak at half maximum (FWHM). The value of the crystallite size for the $Fe_{71}Ni_{29}$ sample is (3.5±5) nm. The crystallinity size of this sample does not depend on the Ni concentration that indicates the entrance of Ni atom into the b.c.c lattice of Fe atom or that of the Fe into f.c.c lattice of Ni atom, does not influence the structure crystal appreciably. Figure 3 shows the Mossbauer Spectra pattern for three samples the hyperfine parameters (β_{hf}) had been obtained by fitting of the spectra with the suitable components are listed in (Table 2). The spectrum for the sample with concentration (x = 29 at % Ni) was fitted with two magnetic sextet components and a central singlet. The component with β_{hf}= 34.3 T is associated with the b.c.c Fe-Ni Invar alloys and that with β_{hf} = 29.2 T is associated with the f.c.c Fe-Ni lattice. These values are compared with those measured earlier of these phases in alloys with (x = 30 at % Ni) which prepared by the arc melting method (Lehlooh *et al*., 2002) and by chemical co-precipitation method (Lehlooh *et al*., 2002). Also, the central singlet components with width of (0.82 mm/sec) and relative intensity of 15% is concluded that observed for the alloy with (x = 30 at Ni %) prepared by using arc melting method (Lehlooh *et al*., 2002). However, this

Table 2: The physical properties for the $Fe_{100-x}Ni_x$ and it conclude the following Isomer Shift (IS) in mm/sec, hyperfine magnetic field (β_{hf}) in Tesla (T), relative Intensity (I) and Width (W) of the inner lines in mm/sec of Mossbauer Spectra (MS) for the $Fe_{100-x}Ni_x$ alloys

Isomer shift	x = 29	x = 32	x = 37
IS_1	0.01	0.02	0.07
IS_2	0.00	0.02	0.06
IS_3 (Singlet)	-0.05	0.04	-0.03
Hyperfine magnetic field			
β_{1hf}	34.3	34.2	30.0
β_{2hf}	29.0	29.7	16.3
Relative intensity			
I_1	0.53	0.35	0.57
I_2	0.32	0.58	0.32
I_3 (Singlet)	0.15	0.07	0.13
Width of inner lines			
W_1	0.27	0.25	0.34
W_2	0.71	0.43	0.58
W_3 (Singlet)	0.82	0.74	0.49

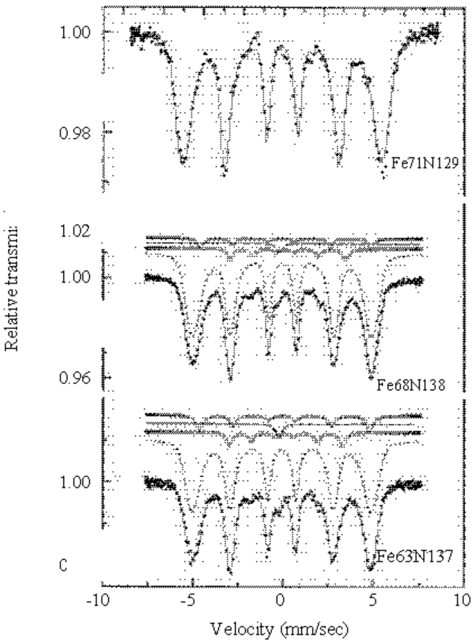

Fig. 3: Mossbauer spectra for the $Fe_{100-x}Ni_x$ system (x = 29, x = 32 and x = 37)

singlet with width of (0.82 mm/sec) is appreciably broader than that with width of (0.40 mm/sec) observed in the Invar alloy which prepared by using co-precipitation method. The reason of the broadening due to associated with super paramagnetic relaxation in a small particles, such the relaxation in super-paramagnetic is a result to broadening of the central singlet component which was mention earlier (Lehlooh *et al*., 2002 ; Ok and Han, 1973).

The spectrum pattern for the alloy with (x = 32 at Ni%) was also fitted with two sextets components corresponding to the b.c.c and f.c.c structure, the broad central singlet component could be associated with super paramagnetic relaxation.

Table 2 shows the relative intensity corresponding to f.c.c lattice grows as the expense of the b.c.c lattice also it is consistent the behavior of the relative intensities of two phases as shows in Fig. 1 for X-ray diffraction. However, the relative intensity of the singlet components drops down to about half its value for the previous alloys, which could be a result to a reduction of the proportion of the small super-paramagnetic particles in this alloys.

The spectrum of the sample with concentration (x = 37 at Ni%) was fitted with two sextets components with hyperfine filed (β_{hf}) of (30.0 and 16.3 T) in addition to a relatively narrow central singlet components with width of (0.49 mm/sec). The two filed sextets were previously mentioned for the alloy with (x = 35 at Ni%) prepared by melting arc method (Lehlooh *et al*., 2002), and were assigned to f.c.c lattice. This determinant is consistent with the pure phase observed in the X-ray diffraction pattern for this alloys. The peaks of the magnetic moment component with (β_{hf} = 16.3 T) coalesce into a broad magnetic sextet.

The preparation $Fe_{100-x}Ni_x$ at different concentration by using chemical co-precipitation method and that Invar alloy studied by using the following techniques, i.e, (Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Mossbauer Spectroscopy (MS)). The results have shown the formation of a single component of f.c.c lattice structure of γ(f.c.c) phase. The Mossbauer Spectroscope (MS) analysis has confirmed that (Fe and Ni) addition favor the formation of the disordered f.c.c lattice rather than the b.c.c lattice. The (anti taenite) phase developed in the concentration region around the Invar stoichiometry (36 at Ni%) and super-paramagnetic relaxation associated with the nanoparticle were shows to that concentration while such behavior of the super-paramagnetic relaxations were not observed in alloy with (X>30 at Ni%) prepared by using arc melting method. The variations of the magnetic moment phases and their relative proportions at different values of (X concentration) could indicate the sensitivity of these phases depends on the preparation method and the particle size distribution. In the research the magnetic properties, thermal expansion and Mossbauer spectra of the Invar alloys $Fe_{100-x}Ni_x$ have been studied on one and the same specimen. This enables main elements of the magnetic structure determining the anomaly in bulk magnetostriction to be revealed and quantitative relationships to established. The Invar anomaly in the alloy studied is produced by competing positive and negative exchange interactions between Fe atoms which arise as a result of fluctuations in the interatomic spacing. The existence of two forms of interactions in concentrated alloys requires further investigations. Amorphous alloys are the most suitable materials for an experimental verification of theoretical calculations of the magnitude of the magnetic moment and its dependence on atomic volume.

CONCLUSION

This study connects the Invar characterization of $Fe_{100-x}Ni_x$ with the method of chemical co-precipitation proved to be suitable preparation of Invar nanoparticles with approximately uniform particle size distribution, the results showed the Fe-Ni Invar alloys which prepared in that method have a good physical properties making it is using for some applications involving significant temperature change such as laser and opto-mechanical applications. The prepared nanoparticle system demonstrated anomalous structural and magnetic phase transitions in a narrow range of elemental concentrations around the Invar stoichiometry. The (anti-taenite) phase developed in the concentration region around the Invar stoichiometry (36 at Ni%) and super paramagnetic relaxations associated with the nanoparticles were observed up to that concentration. The prepared Fe-Ni nanoparticles by the above method demonstrated different magnetic properties and phase transitions than the bulk system prepared by arc melting method. Such relaxations were not observe. In alloys with x>30 prepared by arc melting. The variations of the magnetic moment phase and their relative proportions at different values of (X concentration of Fe-Ni) could indicate the sensitivity of the phase to the preparation procedure and the particle size distribution. The thermal and magnetic properties of some Invar alloys were studied using the X-ray diffraction and Mossbauer Spectroscopy technique which indicate there are in fact two types of Invar alloy phase structure, γ-phase (f.c.c) in the Fe rich region and α-phase (b.c.c) in the Ni rich Ni. The Invar phase represents a simple crystallographic arrangement in which to study the stability of the Nickel moment.

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