Synthesis of FeNi tetrataenite phase by means of chemical precipitation

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Abstract

FeNi L1₀ (tetrataenite) phase has great perspectives for hard magnetic materials production. In this paper it was synthesized in chemically co-precipitated FeNi nanopowder by means of thermal treating included cycling of oxidation and reduction processes at 320 °C. The presence of FeNi L1₀ phase in the samples was confirmed by magnetic measurements and DSC analysis.

1. Introduction

Recently, a great deal of efforts has been done in order to produce new high-energy permanent magnets, caused by so-called “rare-earth crisis”, when the price of the most abundant Nd₁₋ₓFeₓB magnets sharply increased as a consequence of China’s refusal to sell the raw materials for their production worldwide. This decision has forced scientists to search new ways of stabilization of already known hard magnetic phases, as well as to try to produce new high-performance magnetic materials. Table 1 illustrates properties of the known magnetic systems without rare earth materials. It is seen that amongst all systems, FeNi L1₀ (tetrataenite) phase has the highest theoretical value of energy product (320 kJ/m³), which is the figure of merit in a hard magnetic material. Thus, this phase is considered as the most promising substitution material for permanent magnets application. However, the search for substitute materials requires creating and exploring new approaches for extreme magnetic properties formation. Thus, our work primarily aims to explore some new technique for production of the desired phase.

Since the FeNi L1₀ phase was first discovered in the 1960s [5], various methods have been attempted to obtain this thermodynamically stable structure. In laboratories, there were numerous attempts to produce tetrataenite phase, included thin film deposition [6] high-pressure torsion [7]; crystallization of as-quenched alloy with composition Fe₄₋ₓNiₓ₋₅₋ₓSiₓBₓPₓCₓ₀₋ₓ [8] and electroless nickel plating of Fe with consequent cyclic heat treatment [9] etc. The main challenge of synthesis of this phase is attributed to extremely slow diffusion rate the temperature of equilibrium chemical order-disorder Tₑq ≈ 320 °C. Above this temperature the disordered face-centered cubic A1-type structure is entropically stabilized. This is why tetrataenite was observed in nature only in meteorites, as they had plenty of time for long-range diffusion to happen. Therefore, the main goal of laboratory synthesis of tetrataenite is to increase diffusion rate at the temperature of its stability.

All aforementioned methods enhance atomic diffusion, which is controlling formation of L1₀ phase. To further increase the rate of L1₀ phase formation in FeNi alloys by 6–9 order of magnitude, some authors [10] recommend to focus the efforts on two main aspects: i) to increase the driving force for

| Phase          | Maximum energy product (BH)max, kJ/m³ | Tc, K | Ms, MA/m | K1, MJ/m³ |
|----------------|-------------------------------------|------|----------|----------|
| AlNiCo [1]     | 10 – 40                              | 1043 | 1,4      | 0,5      |
| FeN [1]        | –                                   | 810  | 1,92     | 1        |
| MnAl [1]       | 112                                 | 650  | 0,6      | 1,7      |
| MnBi [1]       | 106                                 | 633  | 0,58     | 0,9      |
| MnGa [1]       | 69                                  | 770  | 0,47     | 2,35     |
| FePt [2]       | 172                                 | 750  | 0,75     | 0,66     |
| CoCr [3]       | 20                                  | 510  | 0,4      | 0,031    |
| HfCo [4]       | 278,4                               | 751  | 1,18     | –        |
| Zr₂Co₁ [4]     | 188                                 | 783  | 0,97     | –        |
| FeNi L1₀ [1]   | 320                                 | 810  | 1,38     | 0,27     |
| (theoretical)  |                                     |      |          |          |
phase transformation, possibly through the addition of ternary alloying elements or additional stimuli that may enhance the stability of the L10 phase; ii) to increase the vacancy concentration in order to provide a large reservoir of grain boundaries and to enable atomic rearrangement, possibly through nanostructuring at low temperatures.

In this paper, we used the method of L10 FeNi synthesis by cyclic oxidation and reduction at 320 °C proposed by E. Lima et al [9, 11], which enormously enhances the local diffusion at the grain surfaces making the synthesis of Fe–Ni alloys at low temperatures possible. However, instead of nickel plated micrometer size Fe particles, we subjected Fe50Ni50 nanopowder, produced by chemical co-precipitation, to the same heat treatments. It is expected that usage of nanoparticles will further enhance the diffusion rate in the sample due to increase of surface contribution.

2. Experimental

2.1 Chemical co-precipitation

Precursors for chemical co-precipitation of FeNi were Fe(NO3)3·9H2O and Ni(NO3)2·6H2O. Concentrations of distilled water solutions were 10 %. Both solutions of the salts were pumped into the reactor, where were mixed with 10 % NaOH solution in ratio that maintained the level of pH=12. (Fe,Ni)(OH)2 hydroxide, produced at the end of reaction, was rinsed in distilled water until pH reached 7 and after that it was centrifugated and dried in air at 50 °C for 72 hours. Obtained sample was then milled and placed in a tube furnace. Reduction of hydroxide was carried out in H2 atmosphere at 320 °C for 4 hours.

During process of production FeNi nanopowders by chemical precipitation method reactions go as follows:

\[
\begin{align*}
\text{Fe(NO}_3\text{)}_3 + 3\text{NaOH} & \rightarrow \text{FeOOH} + 3\text{NaNO}_3 + \text{H}_2\text{O} \quad (1) \\
\text{Ni(NO}_3\text{)}_2 + 2\text{NaOH} & \rightarrow \text{Ni(OH)}_2 + 2\text{NaNO}_3 \\
2\text{FeOOH} + \text{H}_2 & \rightarrow 2\text{Fe} + 2\text{H}_2\text{O} \quad (3) \\
\text{Ni(OH)}_2 + \text{H}_2 & \rightarrow \text{Ni} + 2\text{H}_2\text{O} \quad (4)
\end{align*}
\]

First two reactions occur during process of precipitation in reactor. Last two proceed in a tube furnace during the reduction in H2 atmosphere.

2.2 Cyclic oxidation and reduction process

Obtained FeNi powder was subjected to heat treatments, included oxidation for 20 min under N2/O2 atmosphere with ratio of 95/5 and following reduction under H2 atmosphere during 40 min. We used 5 and 10 cycles of the treating.

3 Results and discussion

SEM images of the initial FeNi powder sample just after chemical precipitation together with the samples, subjected to 5 and 10 cycles of oxi-reduction treatments are presented in Figure 1. The chemical composition of 50:50 of all samples was clarified by means of EDX analysis. The comparative analysis of morphology of the powder samples have show, that under cyclic treatment the agglomeration and coalescence occurred. The average particles size was not significantly change and for all samples was equal to 100 nm.

Figure 2 shows XRD patterns for whole set of the samples before and after cyclic oxidation and reduction treatments. It is seen that all samples consisted of single fcc FeNi phase. XRD analysis revealed that there were no essential changes in phase composition of the samples and their lattice parameters. It is worth mentioning, that since diffraction peaks of FeNi L10 phase have very low intensity (fct tetrahtenite forms superlattice), it is impossible to validate the presence of tetrahtenite in the samples.

In order to confirm the presence of FeNi L10 phase in the powders, we used DSC analysis. Recently N. Bordeaux et al [10] reported that depending on heating rate DSC curves for
the slices of meteorite, that consisted of almost pure FeNi L1₀ phase (approximately 92 %), have small endothermic peak (enthalpy is 4.4 kJ/mole) in temperature range from 550 to 600 °C, which is attributed to chemical disordering process of the tetrataenite phase.

The DSC curves for all samples presented in Figure 3. The temperature rapping rate during experiments was fixed at 10 °C/min. The heat flow temperature dependence for all sample shows identical behavior with two anomalies at 480 °C and 730 °C. The endothermic peak at 730 °C is corresponded to formation of nickel ferrite from Ni and Fe oxides on the surface of the particles [12, 13], which in turn were synthesized during chemical precipitation due to nanopowders’ pyrophorosity. Oxide phases are absent on XRD patterns, which is attributed to inability of this method to register low content phases (less than 5 %). The endothermic peak at 480 °C is associated with Curie temperature of the fcc FeNi [14]. The small misfit with the literature data is explained by the fact that at nanoscale size magnetic materials reveal lower value of Tc due to surface effect [15, 16].

It should be mentioned, that data, obtained for the sample after 10 cycles of oxi-reduction treatment, shows additional endothermic peak at 530 °C. Temperature value of the peak lies in the range, corresponding to disordering process of L1₀ FeNi phase. Thus, by means of DSC method we confirm the possibility of the tetrataenite phase formation in nanoparticle samples under cyclic oxidation and reduction treatments. The quantitative analysis of the DSC data by means of calculating the enthalpy of the reaction, allowed us to estimate the volume fraction of the desired phase, which was equal to ~ 10 wt. %.

According to the literature data, FeNi L1₀ phase reveals high values of magnetocrystalline anisotropy field of Hₐ=20 kOe [17]. In order to evaluate anisotropy field in the powder sample with L1₀ phase we carried out magnetic measurements. All powder samples were previously textured in the magnetic field and then compacted with paraffin in Al capsule. Figure 4 shows the results of magnetization investigation for the FeNi samples before and after heat treatment. The field was applied perpendicular to the texture direction. As it is shown on the graphs the sample subjected to 10 cycles of oxi-reduction treatments revealed the coercitive field of Hc = 700 Oe, that is approved the presence of the L1₀ phase in the specimen. Two other samples have shown the typical soft magnetic behavior of magnetization. However, the magnetization study did not show matter anisotropy. It is explained by two reasons: (i) according to DSC results it was found that the volume fraction of L1₀ phase in our samples is not sufficient to observe significant anisotropy on magnetization curves, (ii) the challenges with assembling nanoparticles in an aligned structure. The latter is a common problem with the measurements of magnetic properties of nanoparticle clusters, caused by the trend of nanoparticles to aggregate in clusters. Magnetic moment orientation in that clusters sums up from average magnetic moment orientations of constituent particles.

To solve these problems and evaluate the anisotropy field in the literature [18, 19] it was proposed to use Singular Point Detection (SPD) technique. It is very powerful technique for the study of magnetization in polycrystalline samples. In this method Hₐ can be estimated from second derivative graphs of magnetization curves. On these curves a peak, corresponded to orientation of some crystallites with the hard axis lay parallel to applied external magnetic field, can be observed. The SPD plots for whole set of the samples are present in Figure 5. The first main peak in all graphs associated with reaching the
saturation magnetization of the majority of the fcc FeNi grains. It should be mentioned that only in the sample subjected to 10 cycles of oxidation/reduction treatments the second peak attributed with FeNi L1₀ grains reversal is observed. An anisotropy field \( H_A \) for this sample can be calculated as a difference between two peaks observed on SPD curves. The estimated value of \( H_A = 18 \) kOe in the FeNi sample after 10 cycles of thermal treatment is in a good agreement with previous experimental data.

4. Conclusions

By using cyclic oxidation and reduction at 320 °C we synthesized FeNi L1₀ (tetrataenite) phase in chemically co-precipitated FeNi nanopowder. Successful production of tetrataenite phase in the samples was confirmed by DSC analysis and magnetic measurements. DSC curves show endothermic peak at temperature of 530 °C, which is corresponding to chemical disorder transformation of tetrataenite in the sample, subjected to 10 cycles of oxidation / reduction treatments. Evaluated value of \( H_A = 18 \) kOe by means of SPD method is close to experimental data for FeNi L1₀ phase. To enhance the anisotropy field, which in turn is a key factor for permanent magnets application, and to produce textured material it is proposed to modify shape of the particles and bring it to the anisotropic form, for instance we proposed to use nanorods or nanotubes. The approach developed in our work enhance the diffusion rate in solid state and can be used for stabilization of ‘new’ compounds in the low-temperature region (below 320 °C) of phase diagrams of materials with high melting temperature (above 1500 °C). Some of these low temperature phases could become new replacement phases with extreme magnetic characteristics and low production costs.

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