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Structure and magnetism of Fe-rich nanostructured Fe–Ni metastable solid solutions

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Abstract

New futures on the physical properties of ferromagnetic FeNi alloys have been found combining in situ neutron diffraction experiments and magnetic measurements in mechanical milled Fe-rich Fe–Ni metastable solid solutions. Apart from the well-known Invar effect, on heating these materials are characterised by the existence of a first-order martensite–austenite transformation that takes place at some system-dependent temperature. On cooling, the transformation occurs at a lower temperature than on heating; for $Fe_{80}Ni_{20}$ the size of the effect being larger than 100 °C, much more than the values found in conventional FeNi alloys. These results are discussed considering intrinsic features as magnetovolume effects and/or extrinsic effects such as small grain size and the existence of defects.

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Keywords: Fe–Ni ferromagnetic alloys; Invar effect; Martensitic transformations

1. Introduction

The study of the correlation between structure and physical properties is of fundamental importance in Materials Science. All the physical and chemical properties of a material are strongly structure dependent, and the knowledge of the microstruture is of basic importance in the design and development of new materials for technological applications. A precise knowledge of the structure is of primary importance when a complete understanding of these properties is pursued [1]. Neutron diffraction is considered as a fundamental tool when the nuclear and/or magnetic structure of materials has to be determined [2]. Nowadays, large facilities as ILL in France or ISIS in UK offer the opportunity, via high flux diffractometers, to collect high-resolution diffraction patterns in short periods of time of the order of some minutes. This fact allows making in

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situ thermo-diffraction experiments in which the kinetics of the structural phase transformations and segregations can be studied in a long range of heating rates [3–6]. Furthermore, a great variety of new alloys, in amorphous or crystalline state, can be synthesised by means of modern fabrication techniques. One such technique, the high-energy ball milling, gives the possibility to obtain, massive samples in systems which are usually immiscible by other conventional synthesis procedures [7]. In concrete, a set of such types of material is the binary Fe–TM (with a transition metal (TM) element such as, Ni, Cu, Zr, Pt, Pd, Cr, Ag, …) [8]. Moreover, a number of these new phases are metastable and/or supersaturated disordered solid solutions, which present structural transformations during heating, and the structural and magnetic phase diagram of these metallic alloys is still an open question [9]. In particular, Fe–Ni alloys show a series of interesting physical properties. Among them, the well-known Invar effect is, without any doubt, the most relevant. Since their discovery at the end of the 19th Century by Guillaume [10], FeNi alloys have attracted great attention. The aim of these paper is to show how important a good knowledge of the microstructure is in order to understand the complex magnetic behaviours. In order to fulfil this goal, the case of FeNi solid solutions with either face centered cubic (FCC) or body centered cubic (BCC) structures is presented. The different scenarios that appear will be discussed in terms of the structural changes that occur during heating and their influence in the magnetic response, including magnetovolume effects and Invar behaviour.

2. Experimental details

Three metastable $Fe_{100-x}Ni_x$ solid solutions, with $x = 20, 30, 40$, were obtained in powder form by means of high-energy ball milling technique. Structural characterisation was performed using in situ neutron thermo-diffraction experiments at the POLARIS time of flight diffractometer (ISIS Facility, UK), in the temperature range from room temperature (RT) to 900 °C. The samples were heated under vacuum at a heating rate of 2 °C/min and a diffraction pattern was collected every 5 min. In addition, room temperature high-resolution X-ray diffraction was used to check the structure of the as-milled samples. The neutron diffraction patterns were collected in the d-space range between 0.35 and 3 Å, this allows us to perform high-quality fits taken into account that at least 35 reflections for each phase that appear in the mentioned d-space range. In the diffraction figures, a reduced d-space range 0.85–2.2 Å is showed in order to better appreciate the width of the diffraction peaks. Besides that, the experimental points together with the fits, the position of the reflections belonging to each crystalline phase, and the difference between the observed and calculated intensities are also included in these figures. For the fits, the Fullprof package [11] based on Rietveld method, has been used. Magnetisation vs. temperature, $M(T)$, measurements were carried out in a Faraday magnetometer under inert atmosphere between RT and 800 °C. Differential Scanning Calorimetry (DSC) was performed in all the samples between RT and 600 °C and at a rate of 10 °C/min, same as the $M(T)$ measurements.

3. Results and discussion

As it is well known, ball milling technique allows to synthesise $Fe_{100-x}Ni_x$ solid solutions in the whole compositional range, with BCC structure for $x < 20$, FCC structure for $x > 35$ and a mixture of both in between [12,13]. The FeNi alloys with initial BCC structure displays a structural change from BCC to FCC during heating, the so-called martensite–austenite (MA) transition. The temperatures at which the transition begins and finishes, T^i_{MA} and T^f_{MA}, depends on the composition, and also, $\Delta T_{MA} = T^f_{MA} - T^i_{MA}$ does not exceed 40 °C in conventional FeNi alloys [14]. Besides that, this transition presents thermal hysteresis on heating and cooling processes. Previous works, based on magnetisation measurements, X-ray diffraction and Mössbauer spectroscopy in samples annealed at different temperatures have revealed differences in magnetic behaviour which are strongly structure dependent [15–18]. However, these measurements were done