Thermal annealing effects on the structural and magnetic properties of Fe/V multilayers

2000 J. Phys.: Condens. Matter 12 5617

(http://iopscience.iop.org/0953-8984/12/26/308)

J. Phys.: Condens. Matter **12** (2000) 5617–5622. Printed in the UK PII: S0953-8984(00)09547-3

Thermal annealing effects on the structural and magnetic properties of Fe/V multilayers

J F M Borges, M I da Costa Jr and J B M da Cunha†

Instituto de Física, UFRGS, CP 15051, Campus do Vale, 91501-970 Porto Alegre, RS, Brazil

E-mail: jbat@if.ufrgs.br

Received 15 November 1999, in final form 26 April 2000

Abstract. We report a study on the structural and magnetic properties of iron–vanadium thin films grown in multilayer form and mixed by thermal treatment. The multilayer was composed of 30 Å Fe layers alternated by 30 Å of V. This typical bilayer was repeated 15 times. The samples were structurally characterized by x-ray diffraction (XRD) in the (θ–2θ) geometry. The magnetic characterization was made using a conventional alternate gradient magnetometer (AGM) with the magnetic field applied along the plane of the film, and by conversion electron Mössbauer spectroscopy (CEMS). This multilayer was annealed at temperatures between 550 and 670 °C for 60 minutes. The XRD result for the as-deposited multilayer shows a high-degree crystallinity, while CEMS suggests an abrupt interface, since no significant contribution from vanadium in iron is observed. After the thermal treatment, the results from XRD show a phase transformation of the bcc-disordered structure (α phase) into a tetragonal structure (σ phase). CEMS results show a magnetic moment reduction for temperatures above 640 °C and an order–disorder transition. The magnetic measurements suggest also a phase transformation.

1. Introduction

The Fe–V system presents a complete range of solid solubility in a bcc structure (α phase) at high temperature. At the equiatomic composition region (37–57 at.% V) a tetragonal FeCr-like phase (σ phase) occurs that is dissolved in the bcc solid solution around 1200 °C. At this concentration the α phase may be retained by quenching from temperatures above 1200 °C. For thermal treatments around 600 °C the transformation into σ phase is complete for annealing times over 100 hours. This metastable α phase form a CsCl-type ordered structure (α' phase) by short time annealing at 600 °C [1].

The phase diagram and magnetic properties of the Fe–V system have been studied mainly in relation to the order–disorder transition [2], the critical temperature for this transition as a function of concentration [3] and the distribution density of the local magnetic moments for disordered alloys [4]. Seki *et al* [3] have determined the critical temperature of the order–disorder transformation (T_c) as a function of concentration ranging from 30 at.% V to 70 at.% V and the σ phase transition. Graphically T_c shows a behaviour that approaches a parabolic symmetry centred in the area of equiatomic concentration. Sanchez *et al* [2] have shown that it is possible to retain the bcc solid solution at low temperature by forming a metastable solid solution that has the tendency of ordering as the α' phase. In this sense, Mössbauer spectroscopy results from Preston *et al* [5] can be understood only if a CsCl-like ordering exists over the range of compositions near 15–50 at.% Fe. Nevitt and Aldred [6] report that in

† Corresponding author.

0953-8984/00/265617+06$30.00

the region 30–60 at.% Fe there are weak CsCl superlattice reflections in the x-ray diffraction (XRD) with Cr Kα radiation after the sample is annealed for half an hour at 625 °C. Philip and Beck [7] report weak CsCl superlattice reflections in the XRD with Cr Kα radiation for a 50 at.% Fe sample quenched from high temperature and an enhancement of these reflections after the sample was annealed at 625 °C for a short time. Experimental results have indicated a considerable decrease of magnetic moment of Fe in the Fe–V system when a transformation of the disordered bcc phase into σ phase occurs through thermal treatment [8]. It is known that in the Fe–V system a variation of the magnetization is observed when the number as well as the configuration in the neighbourhood of Fe atoms is altered by changes in the crystalline structure and in the atomic order. The formation of Fe magnetic moments in the α phase begins around 30 at.% Fe but in the σ phase it begins around 45 at.% Fe [8]. In disordered bcc structure more V atoms surround Fe atoms as nearest neighbours. This leads together with a small volumetric concentration in the σ phase to a reduction of the iron magnetic moment. A band structure calculation for 50 at.% Fe shows a vanishing magnetic moment at Fe sites [9]. Studies done by Maksymowicz [10] concerning the dependence of the local magnetic moment have shown a linear decrease of the magnetic moment with increasing V concentration. The rate of decrease of the Fe moment with the introduction of V atoms as nearest neighbours is shown to be around 0.21 μ_B theoretically [11]. Other calculations [12] give 0.18 μ_B while the experimental result is around 0.10 μ_B [4]. The study of formation of Fe–V alloys through thermal treatment of Fe/V multilayers is still a field to be explored.

In this work we report the results of conversion electron Mössbauer spectroscopy (CEMS), XRD and magnetization measurements for Fe–V alloys obtained from thermal treatments in the range 550–670 °C of multilayers of Fe/V grown on Si substrate.

2. Experiment

The [Fe (30 Å)/V (30 Å)]$_{15}$ multilayer was prepared at room temperature by alternate deposition in ultra-high vacuum on commercial oxidized Si(111) substrate. This was achieved using the electron beam technique in a Balzers UMS-500P system with a deposition rate of 1 Å s^{-1} monitored by a quartz microbalance. The total thickness of the film was 900 Å and the thickness of the layers was chosen to give the concentration of 50–50. The multilayer was annealed at 10^{-6} mbar for 60 minutes at temperatures ranging from 550–670 °C. After the thermal treatments the films were cooled down to room temperature in vacuum.

The XRD was performed in a θ–2θ Bragg–Brentano geometry using Cu Kα radiation ($\lambda = 1.5406$ Å) in a conventional Rigaku DM 200 diffractometer. A scan step of 0.1° in the 2θ range from 30 to 50° was carried out under a fixed counting time of 40 s. CEMS measurements were performed at room temperature using a constant acceleration electromechanical drive system with a multichannel analyser for collecting and storing the data. The detector was a homemade He–CH_4 proportional counter and a ^{57}Co in Rh matrix was used as the source at room temperature. The hyperfine parameters were obtained by a least-squares fitting procedure of the data using Lorentzian line shapes. The magnetization measurements were performed at room temperature using a conventional alternate gradient magnetometer (AGM) with the applied field always parallel to the film surface.

3. Results and discussions

The XRD patterns for the as-deposited multilayer and annealed samples are shown in figure 1. The satellite structure for the as-deposited sample is typical of multilayer modulation and

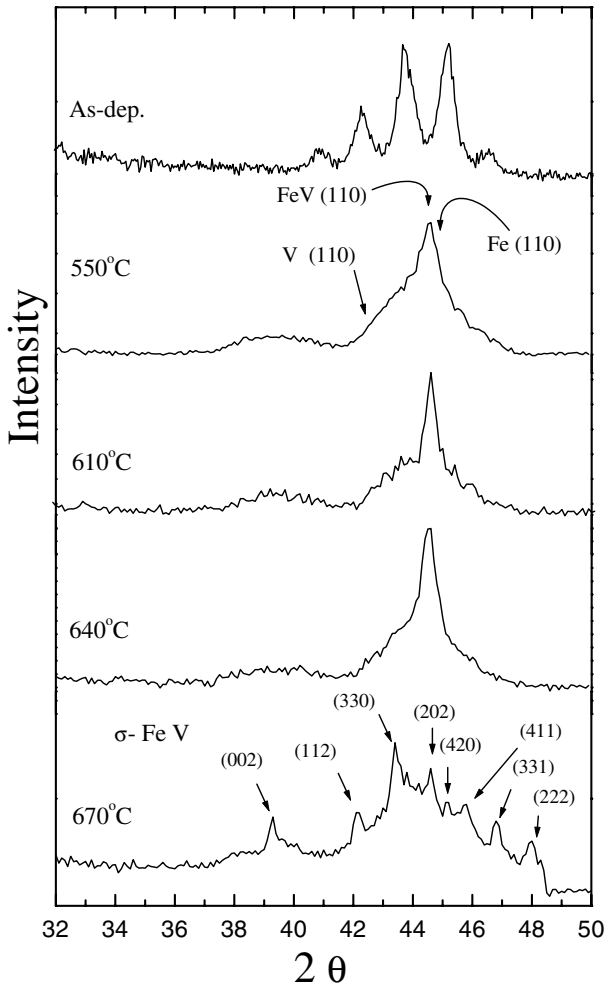

Figure 1. Representative parts of x-ray diffraction patterns for Fe/V multilayer as deposited and for some annealing temperatures. FeV, V and Fe bcc (110) reflections and various tetragonal FeV reflections are indicated.

indicates an abrupt interface. At an annealing temperature (T_A) above 550 °C the multilayer structure is destroyed and we observe the formation of an Fe–V alloy. The diffraction peak in $2\theta = 44.55^\circ$ ($d = 2.032$ Å) is an indication that we have a bcc disordered α phase or an ordered α' phase. The determination of ordering in Fe–V by x-ray measurement is very difficult because the atomic scattering factors of vanadium and iron are very similar and we do not observe the presence of superstructure lines. For 670 °C the XRD pattern was indexed to the space group $P4_2/mnm$ that corresponds to the tetragonal σ phase. An indication of this phase is also seen for all the annealed samples by the large peak in the 40° region and one superimposed with the 44.55° peak.

The CEMS spectra are shown in figure 2. Atomically disordered crystalline alloys often display wide ranges of probe local environments leading to effectively continuous distributions of hyperfine parameters. We have used the model of Wivel and Mørup [13] to fit all the spectra with hyperfine field distributions (HFDs). The $P(H)$ distribution is also shown in

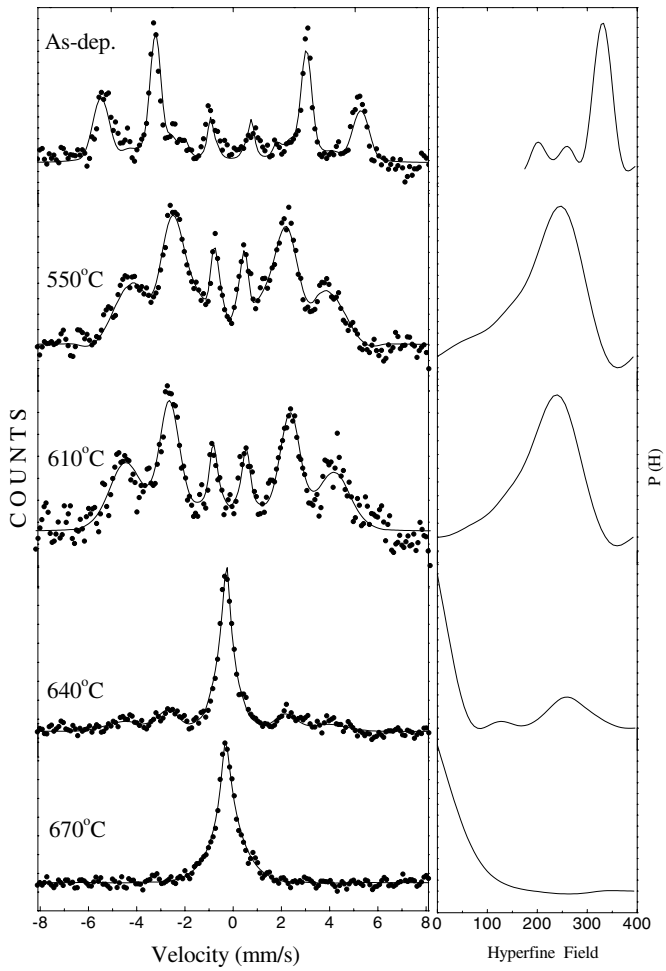

Figure 2. Room temperature CEMS spectra for Fe/V multilayer as deposited and different annealing temperatures as fitted by the hyperfine field distributions shown.

figure 2 for each spectrum. For the multilayer we observe a spectrum with an HFD profile centred around 330 kOe that is typical of bcc α-Fe. In this case the field range for the HFD was limited at 175 to 400 kOe, to avoid meaningless small field oscillations due the large background of the spectrum. The small amplitude oscillations around 200–250 kOe can be ascribed to the interface. For $640\,^{\circ}\mathrm{C} > T_A \geqslant 550\,^{\circ}\mathrm{C}$ the spectra show large HFD profiles with an average hyperfine field around 250 kOe. This is an indication that we have a disordered $Fe_{1-x}V_x$ ($x \leqslant 0.5$) alloy with a distribution of V atoms in the vicinity of the Fe atoms. Shiga and Nakamura [14] ascribed this peak in the HFD to the iron atoms that occupy the V sites in Fe–V bulk alloys. This also indicates that we have destroyed completely the multilayer structure for $T_A \geqslant 550\,^{\circ}\mathrm{C}$. For $T_A < 640\,^{\circ}\mathrm{C}$ the spectra show no significant modification with the T_A variation. For $T_A = 640\,^{\circ}\mathrm{C}$ we observe a single line spectrum that corresponds to a low field distribution and a small high field distribution, and with an isomer shift difference around 0.15 mm s^{-1} similar to that observed by Shiga and Nakamura [14]. This is attributed to an order–disorder transition in the Fe–V alloy

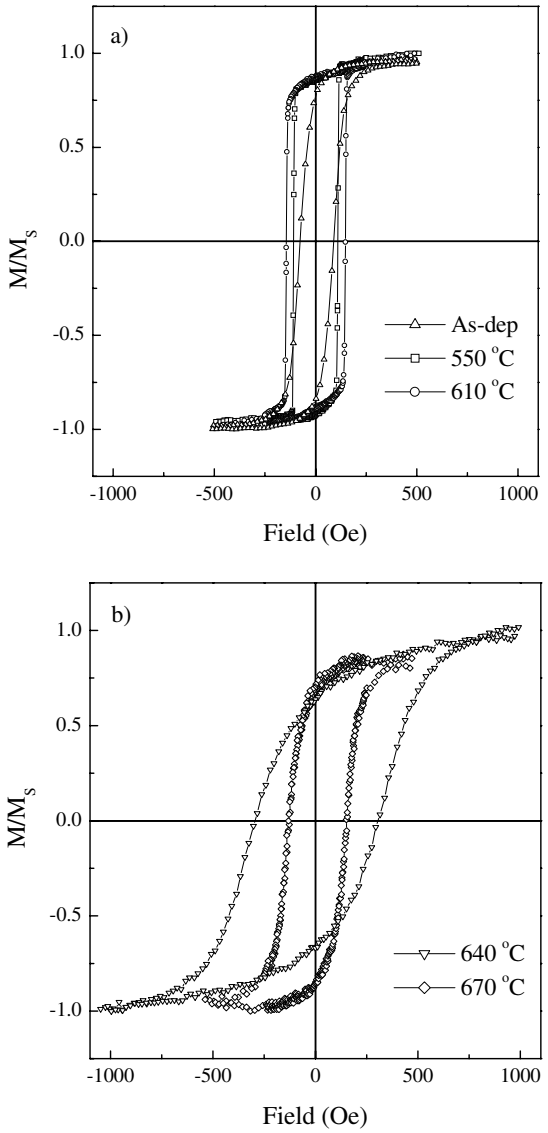

Figure 3. The in-plane magnetic hysteresis loops at room temperature for the Fe/V multilayer as-deposited, 550, 610 (a), 640 and 670 °C (b) annealing temperatures.

for the temperature region 610 °C $< T_A <$ 640 °C. This transition is not observed in the XRD pattern for $T_A = 640$ °C where we see a cubic phase and an indication of a not well crystallized tetragonal phase. For the $T_A = 670$ °C Mössbauer spectrum we only note a low field distribution in accordance with the XRD result. The iron magnetic moment reduction for the tetragonal Fe–V phase was observed by van der Kraan *et al* [8] in the bulk material. The single line in the $T_A = 640$ °C Mössbauer spectrum cannot be attributed to the tetragonal phase because it was also present in the XRD for low T_A but not detectable in the Mössbauer spectrum. These results can be understood if an ordered phase is present in the sample.

The magnetic hysteresis loops are shown in figure 3. We see a square form for the annealed samples at $T_A \leqslant 610\,^{\circ}\mathrm{C}$ that indicates a characteristic ferromagnetic curve and an increase in the coercive field with T_A (figure 3(a)). For the iron in the as-deposited multilayer we observe a small anisotropy due a stress or defects in the deposition. For $T_A > 610\,^{\circ}\mathrm{C}$ we observe a modification in the hysteresis form and an increase in the saturation and coercive fields (figure 3(b)). This increase in the crystalline anisotropy is probably due to the formation of ordered α' Fe–V alloy with a reduced magnetic moment, and consequently a decrease in the saturation magnetization. For $T_A = 670\,^{\circ}\mathrm{C}$ we see a decrease in the saturation and coercive fields in comparison with the precedent temperature. This is an indication of the σ phase formation.

4. Conclusions

Fe–V alloys in disordered bcc α, ordered CsCl-like and tetragonal phases have been obtained by thermal treatments of Fe/V multilayers. CEMS, XRD and magnetic measurements show that for temperatures up to $610\,^{\circ}\mathrm{C}$ the multilayers are destroyed and formation of a cubic ferromagnetic phase is observed. For temperatures above $610\,^{\circ}\mathrm{C}$ an ordered bcc α' phase occurs with a decrease of the iron magnetic moments. Above $640\,^{\circ}\mathrm{C}$ a tetragonal σ phase is obtained also with a decrease of the Fe magnetic moments. Our results indicate that the order–disorder transition and σ phase formation in the Fe–V system is faster when we start from a multilayer. This is because the thin layers of each different element have great relative interface with a high mobility in the vicinity of the grain boundaries and grain surface [15].

Acknowledgments

The authors wish to acknowledge the partial support of this work by CNPq, FINEP and FAPERGS, Brazilian agencies, and Mr W H Flores for technical assistance with XRD. We are indebted to Dr C A dos Santos for a critical reading of the manuscript.

References

[1] Smith J F 1999 *Binary Alloy Phase Diagrams* 2nd edn, vol 2, ed T B Massalski (Materials Park: ASM International) p 1787
[2] Sanchez J M, Cadeville M C, Pierron–Bohnes V and Inden G 1996 *Phys. Rev.* B **54** 8958
[3] Seki J, Hagiwara M and Suzuki T 1979 *J. Mater Sci.* **14** 2404
[4] Ryzhenko B V and Gel'd P V 1987 *Sov. Phys.–Solid State* **29** 108
[5] Preston R S, Lam D J, Nevitt M V, van Ostenburg D O and Kimball W 1966 *Phys. Rev.* **149** 440
[6] Nevitt M V and Aldred A T 1963 *J. Appl. Phys.* **34** 463
[7] Philip T V and Beck P A 1957 *Trans. AIME* **209** 1269
[8] van der Kraan M, de Mooij D B and Buschow K H J 1985 *Phys. Status Solidi* a **88** 231
[9] dos Santos A V 1999 private communication
[10] Maksymowicz A Z 1988 *Physica* B **149** 240
[11] Krause J C, Paduani C, Schaf J and da Costa M I Jr 1998 *Phys. Rev.* B **57** 857
[12] Hamada N and Miwa H 1978 *Prog. Theor. Phys.* **59** 1045
[13] Wivel C and Mørup S 1981 *J. Phys. E: Sci. Instrum.* **14** 605
[14] Shiga M and Nakamura Y 1978 *J. Phys. F: Met. Phys.* **8** 177
[15] Roth M 1970 *J. Appl. Phys.* **41** 1286