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Thermodynamically driven migration of nitrogen implanted into iron.

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Abstract

A redistribution of nitrogen atoms towards a buried carbon-rich layer is observed for thin iron films implanted at 250°C. The effect is attributed to the formation of ε-$Fe_{3-x}(C,N)$ iron carbonitride. Above 300°C the ε-carbonitride phase becomes unstable and consequently the redistribution effect vanishes leading to well separated profiles of nitrogen and carbon atoms.

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I. INTRODUCTION

The problem of nitrogen migration in iron is of great importance for practical applications of ion implantation into metals. Today available high current ion implanters yield high beam power density, which leads to a temperature increase during implantation process. This temperature rise may induce impurity redistribution, unfavourably affecting properties of the metal. The migration of implanted nitrogen in iron is a rather complex phenomenon. It has been shown that when implanted at temperatures from 80°C up to 200°C nitrogen atoms migrate towards the surface [1-3]. Recent experiments allowed to identify the mechanism of this migration as a radiation induced segregation of nitrogen-defect complexes [4]. When implantation temperature exceeds 200°C the in-bulk diffusion of nitrogen results in the almost complete loss of nitrogen from the near-surface layer of bulk samples [5]. In contrast, in thin iron films the loss of nitrogen can only result from the outdiffusion of nitrogen atoms through the surface. This requires temperature as high as about 400°C [6].

The presence of alloying elements in steels may affect significantly migration of nitrogen atoms. For example the annealing experiments performed on nitrogen implanted AISI 316 steel revealed the presence of diffusion tails, never observed after annealing of pure iron samples [7]. It should be noted, however, that the results obtained when using highly alloyed steels with numerous alloying elements are rather difficult to analyse. Therefore it was decided to use in the present study a simple model system made of pure iron implanted with impurity atoms prior to nitrogen implantation. It was thus possible to analyze the role of a given alloying element, without any interference due to the presence of other elements or complicated structure characteristic of thermally treated steels. Another advantage of such a system is the possibility to introduce the impurity atoms at a well defined depth, making the nitrogen redistribution analysis much easier. This study is focused on the role of carbon for several reasons: (i) this impurity is present in all types of steel, (ii) contamination of surface layer with carbon atoms often occurs during implantation

and (iii) some ambiguities still persist about the role of carbon on nitrogen redistribution during the implantation process. In order to avoid the loss of nitrogen during high temperature implantations due to the in-bulk diffusion the samples were thin (about 130 nm thick) iron layers deposited on polycrystalline alumina substrates. In such a case nitrogen atoms are trapped between two close surfaces of iron up to ~400°C [6] and their redistribution may be easily determined by using the resonant nuclear reaction $^{15}N(p,\alpha\gamma)^{12}C$ at 429 keV.

II. EXPERIMENTAL

In the experiment 130 nm thin iron films deposited by ion beam sputtering onto polycrystalline Al_2O_3 were prepared. To prevent any possible carbon contamination during implantation process the iron films were then coated with a ~30 nm thick Al_2O_3 layer. Such sandwich samples were pre-implanted at room temperature (RT) with 110 keV $^{12}C^+$ ions up to a dose of 1.6×10^{17} ions/cm^2. The next step was a 55 keV $^{15}N^+$ implantation up to a dose of 1×10^{17} ions/cm^2. The nitrogen implantations were performed at RT, 150°C, 250°C and 300°C. The implantation parameters were chosen so as to obtain a carbon-rich layer located deeper than the projected range of 55 keV nitrogen ions. The nitrogen and carbon depth distribution profiles were measured by means of the resonant nuclear reaction $^{15}N(p,\alpha\gamma)^{12}C$ (E_p~429 keV) and nuclear backscattering reaction $^{12}C(\alpha,\alpha)^{12}C$ at 5.7 MeV. Structure of the implanted layers was determined by means of Conversion Electron Mössbauer Spectroscopy (CEMS) and Grazing Incidence X-ray Diffraction (GIXD). The CEMS measurements were performed at RT by using a He-6%CH_4 gas flow electron counter. The Mössbauer source was about 100 mCi ^{57}Co in a Rh matrix. All isomer shift data are referred to metallic iron.

III. RESULTS AND DISCUSSION

The first part of the experiment was devoted to study the nitrogen profile evolution in the presence of the buried carbon-rich layer after implantations performed at elevated temperatures. The results are shown in Fig. 1. Completely different nitrogen profiles were measured. When implanted at RT the nitrogen profile corresponded to a Gaussian-like distribution, in agreement with the results obtained by simulation with the TRIM code [8]. After implantation performed at 150°C a second peak close to the outer Al_2O_3/Fe interface was clearly evidenced. The increase of implantation temperature up to 250°C resulted in the formation of a second nitrogen peak located deeper than the projected range of nitrogen ions. Carbon analysis presented in fig. 2 revealed that its position corresponded to the initial carbon distribution. As well at 250°C a redistribution of carbon atoms towards the initial location of nitrogen atoms was observed. At 300°C the nitrogen profile was less modified and rather similar to that observed after RT implantation .

The results presented in Fig. 1 demonstrate that in a rather narrow temperature range (from 150°C to 250°C) two different mechanisms of nitrogen migration are observed: migration towards the surface occurring at 150°C and migration towards the carbon-rich layer which was observed for temperatures around 250°C and disappearing at ~300°C. Redistribution towards the surface at 150°C has been recently studied and was identified as a radiation induced segregation (RIS) process [4]. During RIS process (well described by Rehn et al. [9]and Lam et al.[10]) nitrogen atoms form complexes with defects (in the case of nitrogen in iron most probably with vacancies forming so called Miller pairs [11]) and are dragged by defects towards a defect sink. In the case of implantation the strongest sink for defects is the sample surface (or as in our experiment the Fe/Al_2O_3 interface) where defects annihilate after a rearrangement of atoms in the outermost atomic layer. As a result of a RIS process a second nitrogen peak was formed in the vicinity of the sample surface. In order to interpret the results obtained at 250°C and 300°C CEMS and GIXD experiments were performed. The CEMS spectra recorded for the samples implanted with 55 keV N^+ ions at 250°C and 300°C are shown in Fig. 3a and 3b. The spectra were analyzed by fitting

the spectral components to the experimental data with the use of the parameters obtained by various authors for nitrogen-containing phases. The set of these parameters can be found in Refs. 12 and 13. The spectrum obtained for the sample implanted at 250°C was fitted with components corresponding to three phases: α-Fe (sextet with B=33.1 T), ε-$Fe_{3-x}N$ (sextets with B~27.8 T and 19.2 T) and ε-$Fe_{3-x}(C,N)$ (two sextets with B~21.6 T and B~12.0 T). In the case of the sample implanted at 300°C two main phases were detected: α-Fe and γ'-Fe_4N (two sextets with B~34.0 Tand 21.4 T) and a third sextet with B~20.5 T which could be attributed to Fe_3C . These results were confirmed by GIXD experiments where γ'-Fe_4N was detected only after 300°C implantation (Fig. 4).

The major conclusion from the structural analysis of the implanted samples is that in the case of irradiation performed at 250°C the ε-$Fe_{3-x}(C,N)$ iron carbonitride phase is formed, whereas at 300°C the nitrogen is mainly included in γ'-Fe_4N iron nitride which does not contain carbon atoms. This result is consistent with the work of Vredenberg who has shown that after implantation performed above ~310°C only γ'-Fe_4N phase was formed [14].

Before discussing the possible mechanisms of nitrogen redistribution it should be reminded that above 200°C nitrogen atoms are mobile in iron matrix in both hot implanted and annealed samples [5] and may thus easily migrate until they are trapped in nitride or carbonitride precipitates. Moreover a previous work [5] has shown that in a sample nitrogen implanted at 250°C without carbon, nitrogen only migrates towards the surface. In contrast in the present experiment nitrogen migrates also towards the carbon rich deeper layer. The local concentration of free nitrogen atoms is lower in the precipitate zones, creating a concentration gradient towards the grains of ε-$Fe_{3-x}(C,N)$ (for 250°C implantations) or γ'-Fe_4N (for 300°C implantations). Taking into account that the enthalpy of formation of carbonitrides is higher than that of nitrides, it is expected that nitrogen atoms will be trapped preferentially in the regions of high carbon concentration which leads to the observed redistribution of nitrogen atoms. From the results presented in Fig. 2 it can be concluded also that at 250°C the carbon atoms migrate towards the nitrogen-rich zone. At this temperature the behaviour of nitrogen and carbon atoms is thus essentially the same, both

impurities migrate to the zones where carbonitride phase may be formed. Such an observation is consistent with the mechanism proposed by N. Millard and co-workers [15] in which the formation of strongly bounded phases (e.g. carbonitride) diminishes the concentration of freely migrating impurity atoms. In consequence a concentration gradient of freely migrating atoms is created leading to their migration towards the precipitates of the new phase. The essential point of this mechanism is the separation of the total number of impurity atoms into two components: the fraction of fixed atoms bounded in the precipitates and the fraction of unbounded atoms migrating freely in the sample. The concentration gradient which becomes the driving force of impurity redistribution towards the precipitates is active only for this mobile fraction. It is very likely that the formation of carbonitrides modifies the distribution of carbon atoms through exactly the same mechanism as it is the case for nitrogen.

Above 300°C the ε-Fe_{3-x}(C,N) phase becomes unstable and the only stable nitride phase is γ'-Fe_4N which cannot contain carbon atoms. This phase is formed in the region of the highest nitrogen concentration. Therefore the driving force for carbon and nitrogen redistribution due to the formation of carbonitrides which was observed at 250°C disappears, and nitrogen and carbon profiles remain almost unperturbed.

The results presented above provide an experimental confirmation for the model proposed by Millard et. al. [15]. In this model, developed for bulk iron, nitrogen migration towards the surface was explained by the presence of carbon in the surface layer leading to the formation of a carbonitride phase.

IV. CONCLUSION

Nitrogen implantation into thin iron films pre-implanted with carbon ions allowed to evidence a nitrogen and carbon redistribution driven by the formation of carbonitrides. The effect was observed in a ~130 nm thick iron film at temperature around 250°C and was related to the formation of ε-$Fe_{3-x}(C,N)$ carbonitride. At 300°C ε-$Fe_{3-x}(C,N)$ is unstable: the only stable nitride, γ'-Fe_4N, cannot contain carbon atoms so the carbonitride phase cannot be formed. As a consequence the redistribution of nitrogen was not observed at 300°C.

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FIGURE CAPTIONS

Fig. 1. Nitrogen depth distribution profiles measured on nitrogen implanted samples at room temperature (RT), 150°C , 250°C or 300°C .

Fig. 2. Nitrogen and carbon profiles measured after nitrogen implantation at 250°C.

Fig. 3. CEMS spectra obtained for the sample implanted at 250°C (a) and 300°C (b). The phases detected in the samples are listed in the insets in both figures. α, ε, ε', γ', θ, correspond to the iron, ε-$Fe_{3-x}N$, ε-$Fe_{3-x}(C,N)$, γ'-Fe_4N, Fe_3C phases respectively.

Fig. 4. The GIXD spectra obtained for the samples implanted with N^+ ions at 250°C and 300°C .

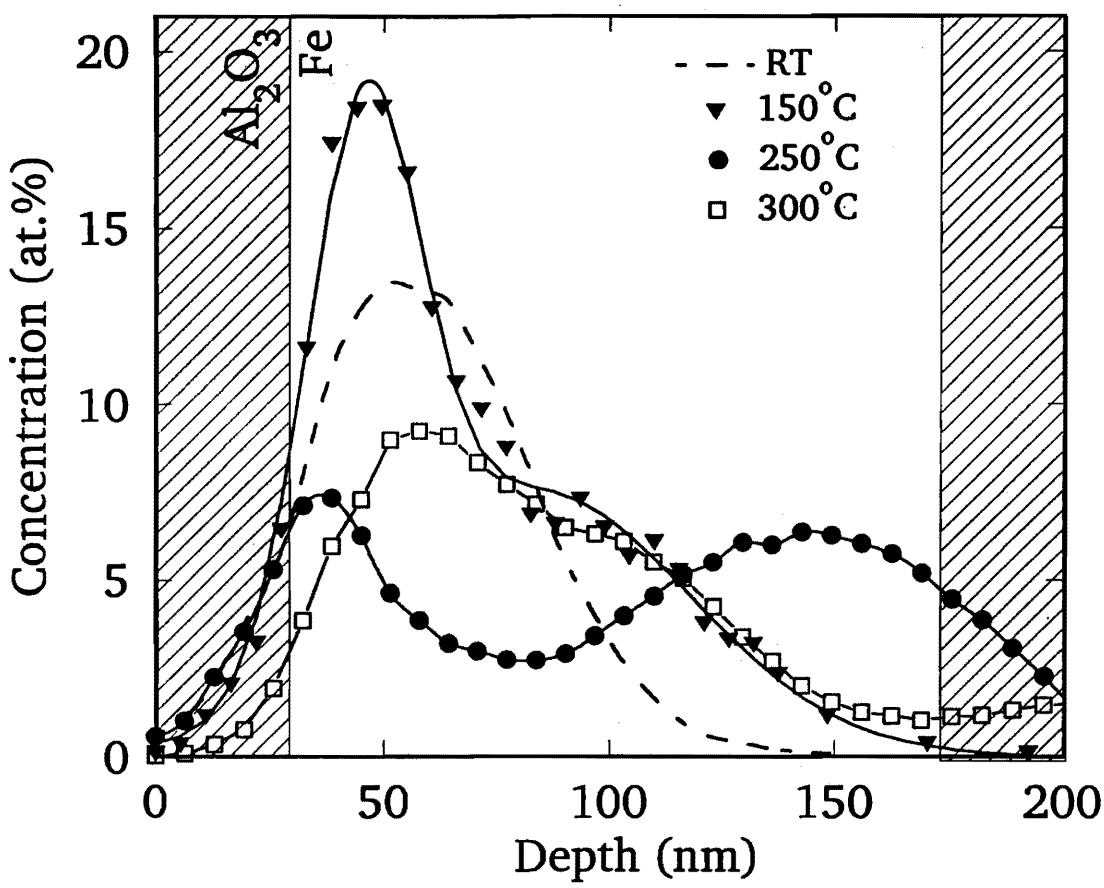
Concentration (at.%)
Depth (nm)
Al_2O_3
Fe
RT
150°C
250°C
300°C
0
5
10
15
20
0
50
100
150
200

FIG. 1

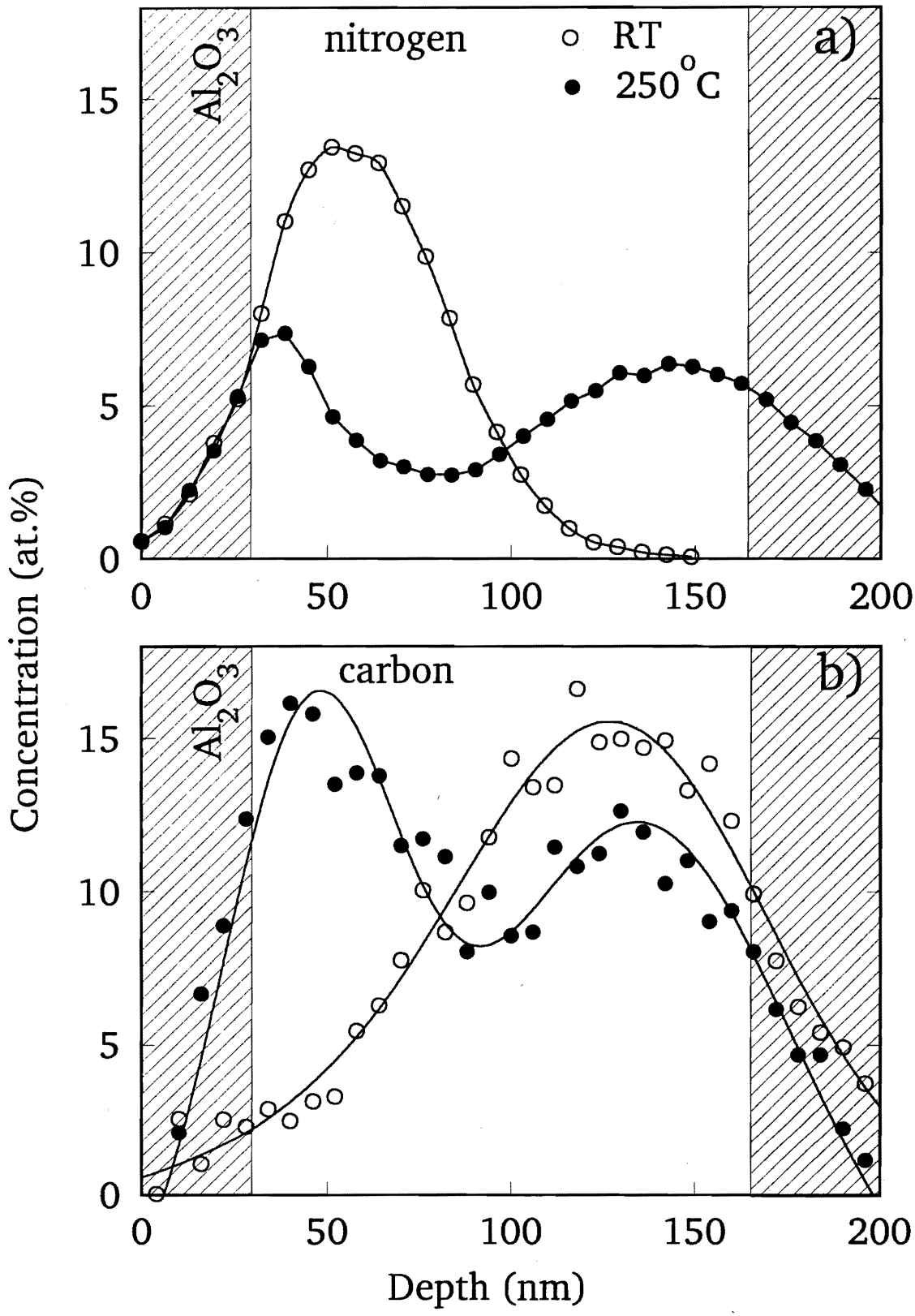
nitrogen
RT
250°C
a)
Al_2O_3
carbon
b)
Al_2O_3
Concentration (at.%)
Depth (nm)
0
5
10
15
0
50
100
150
200

FIG. 2

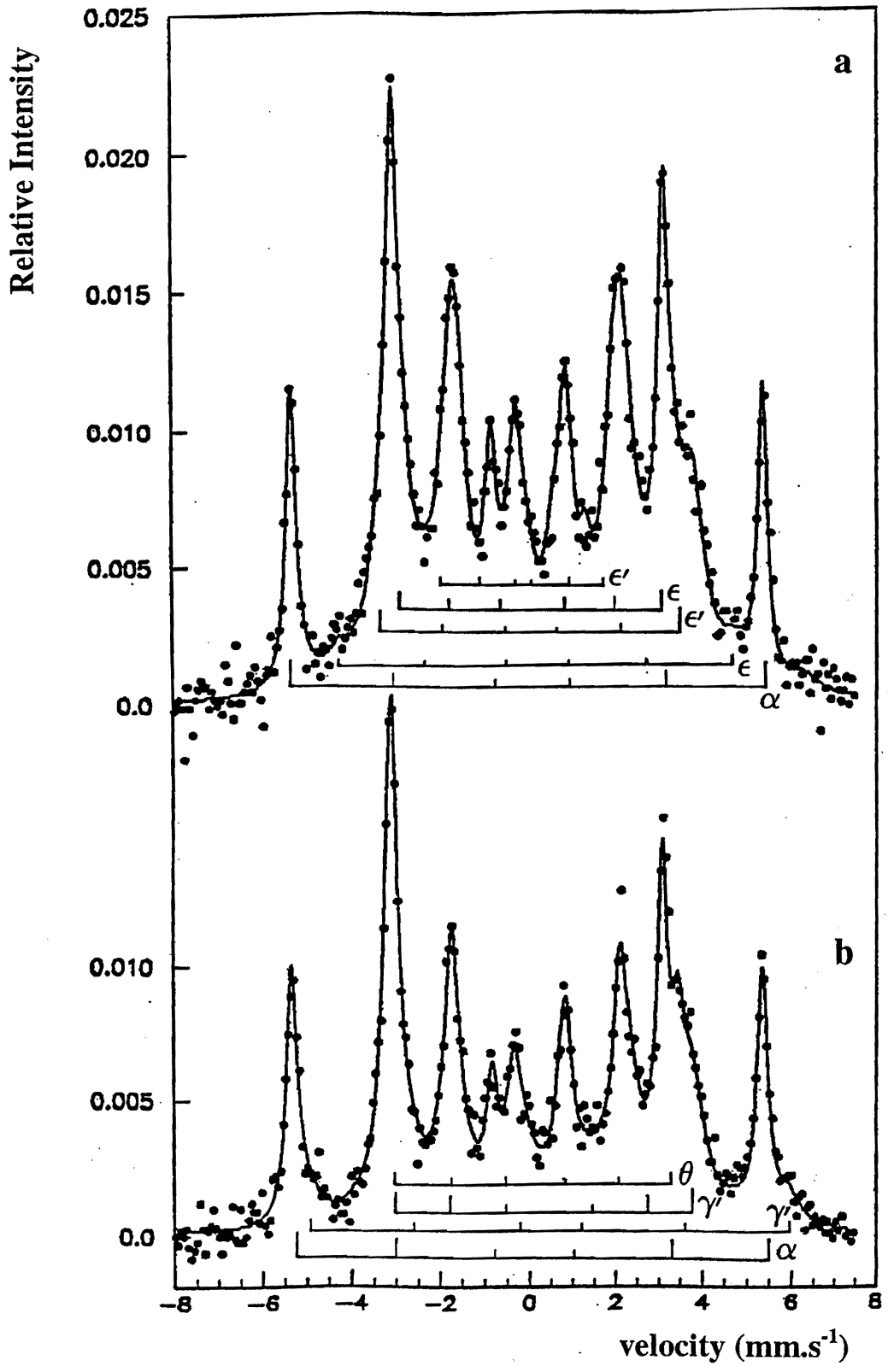
Relative Intensity
0.025
0.020
0.015
0.010
0.005
0.0
a
ε'
ε
ε'
ε
α
0.010
0.005
0.0
b
θ
γ''
γ''
α
−8
−6
−4
−2
0
2
4
6
8
velocity (mm.s-1)

FIG. 3

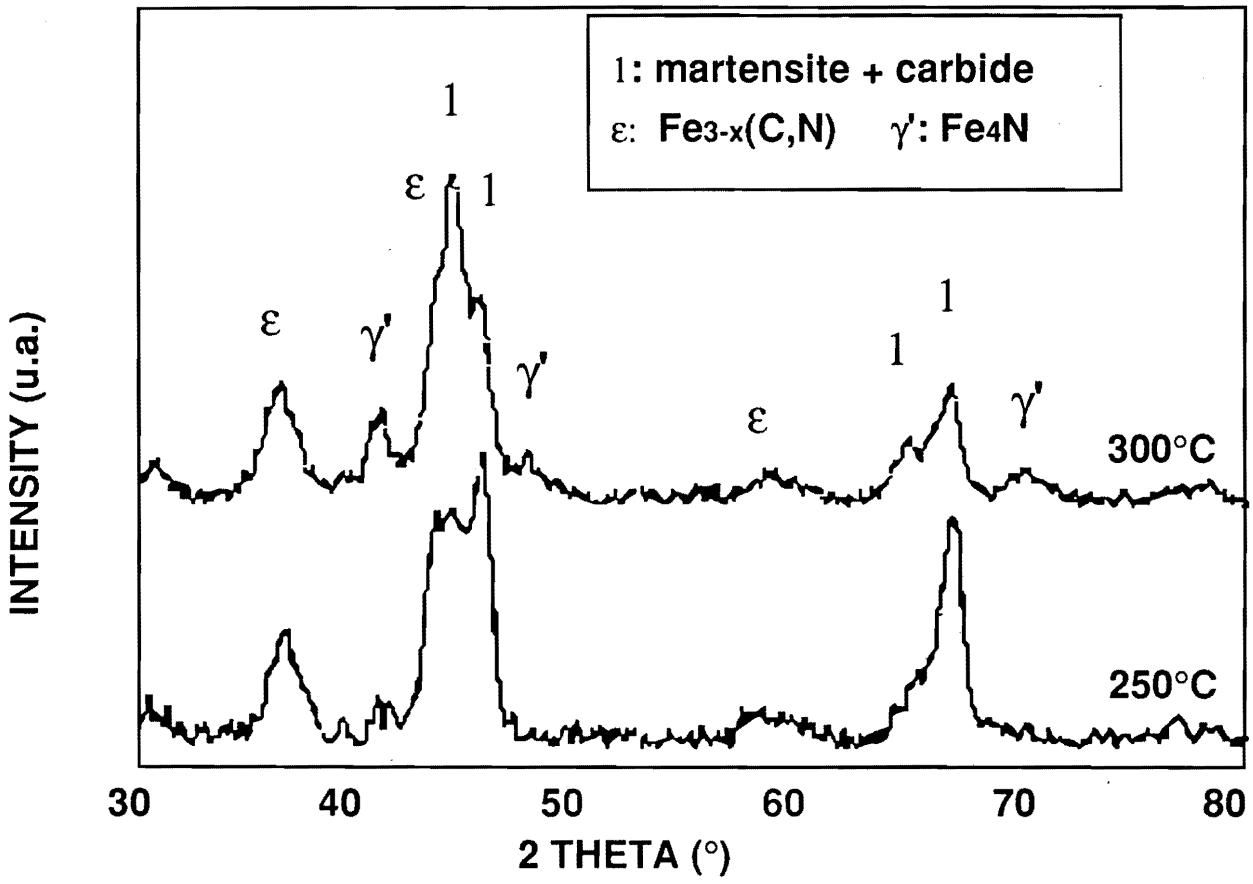

FIG. 4

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