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NITROGEN VACANCY COMPLEXES IN NITROGEN IRRADIATED METALS

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ABSTRACT

Gas desorption and positron annihilation techniques have been employed to study the evolution of nitrogen associated defects in nitrogen irradiated metals: Fe, Ni, Mo and W. Nitrogen in these metals has a rather high affinity to vacancy type defects. The results obtained for low irradiation dose show that substitutional nitrogen (NV; with V=vacancy) is formed. The nitrogen vacancy complex dissociates at temperatures ranging from 350 K for Ni to 900K for Mo and 1100 K for W. At high doses defects are formed which can be characterized as nitrogen saturated vacancy clusters. These defects, as observed by helium probing, disappear during annealing for nickel at 800K, and for Mo at 1100 K. The direct observation of the desorbing nitrogen for nickel and molybdenum reveals a very fast desorption transient at the dissociation temperature of the clusters. This is the characteristic desorption transient of a small nitride cluster,e,g., by shrinkage with constant rate. For iron the nitrogen desorption is more complicated because of a general background that continuously rises with temperature. With the positron beam technique depth information was obtained for defects in iron and the defect character could be established with the help of the information provided on annihilation with conduction and core electrons of the defect trapped positrons.

INTRODUCTION

Nitrogen interaction with defects may occur on different occasions during processing of metals. A good example is nitrogen irradiation of metals to improve wear resistance and hardness [1,2]. The very early stages of the nucleation and agglomeration of nitrogen defects is not frequently studied [3]. In this article it will be shown that desorption techniques and positron beam techniques, here only used for iron, can be applied to monitor the defect evolution during implantation and thermal annealing. Helium and positrons are used to probe the formed defects. Both particles have a large affinity to defects, in particular when open volume is associated with the defect. Besides the use of helium desorption to learn about the binding of the helium probe particle also monitoring of the release of nitrogen directly is applied. The present study gives information on the type of defects formed, but even more important, it gives the thermal stability of the formed defects. The nitrogen defect complexes probably act as precursors to the different phase particles or precipitates that may occur. Therefore in a number of cases samples irradiated with high fluences are investigated.

MASTER

EXPERIMENTAL

The samples are single crystals Ni(110), Fe(100), Mo(100) and W(100). To ensure a low concentration of defects in the bulk of the samples they had been electropolished and subsequently vacuum annealed to about 0.8 of the melting temperature.

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The nitrogen implantations have been carried out by a mass analyzed ion beam from an ion source operating in the 0-3 keV range for the desorption experiments and a 30 keV ion implanter for the positron annihilation experiments. Helium for defect probing purposes was at low energy implanted by the former ion source. For a review on helium desorption studies see ref [4], and for the principles of the positron beam analysis see ref. [5].
For the positron annihilation experiments on iron a single crystal was prepared with a dose of with 10^{16} cm^{-2} N^+. Characterization of defects was done by monitoring two positron annihilation parameters which describe the Doppler broadening of the 511 keV gamma annihilation peak: the shape parameter *S* which is sensitive to the fraction of annihilations with low momentum conduction and valence electrons and the wing parameter *W* which is sensitive to annihilation with high momentum core electrons.

DESORPTION RESULTS

The irradiation and annealing experiments with helium as a probe were performed as follows: 1. Irradiation with N_2^+-ions, 2. Annealing to a specific temperature T_A , 3. Low energy helium implantation (50 eV for Ni , 300 eV for W) to decorate the defects with helium without creating aditional damage, and 4.The final helium desorption measurement. In addition nitrogen desorption measurements were done where the nitrogen was implanted and subsequently the sample was heated to observe the nitrogen release.
The results are summarized in table 1. and described in detail in the following.

Molybdenum The results earlier obtained by van Veen and Caspers [6], and Filius and van Veen [7] for nitrogen defects probed by helium indicated that all He_nV_mN complexes release helium first and thus show desorption spectra which are virtually indistinguishable from a sample with just multiple helium filled monovacancies He_nV. For high nitrogen doses nitrogen vacancy clusters are developing which contain more than one nitrogen atom. No nitrogen bubbles develop. The helium desorbs at a little higher temperature than from the monovacancy. This indicates that the free volume of the defect is rather limited. It might be concluded that the defects are small nitride nuclei with some mismatch with the surrounding lattice.
Nitrogen desorption spectra, not shown here, for nitrogen doses from 2×10^{14} to 10^{17} cm^{-2} reveal that at low dose desorption occurs from surface chemisorption sites β_1 at 1100 K and β_2 at 1350 K. When the implantation dose exceeds 10^{15} cm^{-2} N, i.e. , surface coverage >1 the β_1 peak grows fast. At 10^{16} cm^{-2} surface peaks are dominated by much narrower desorption peaks B_1 at 1100 K and B_2 at 1200 K (see table 1). We ascribe these peaks to nitride phases in the molybdenum. Eyre and Evans [8] observed Mo_2N precipitates to disappear at about 830 K whith a heating rate applied of 0.03 K/s. In our case the heating rate is about 1000 times higher. therfore, it is not unreaonble to expect nitrogen release from similar precipitates at temperatures some 300 K higher than Eyre and Evans found.

Nickel The helium desorption spectra shown in fig. 1 obtained for 2 keV N_2^+ ions at a dose of 10^{13} cm^{-2} show mainly the G and H peak. Like for molybdenum the vacancies and interstitial nitrogen will either recombine during the collision cascade or whenever one of the two defects becomes mobile. It is most likely that the room temperature decoration with helium will cause HeNV defects be formed. The appearance of E and H peaks is explained by the fact that nitrogen is dissociated earlier from the complex than the helium. The helium desorption in other peaks that appear at high nitrogen dose must partly be explained by helium release from otherwise stable nitrogen complexes or high nitrogen dose (5×10^{14} cm^{-2}) several of these new peaks

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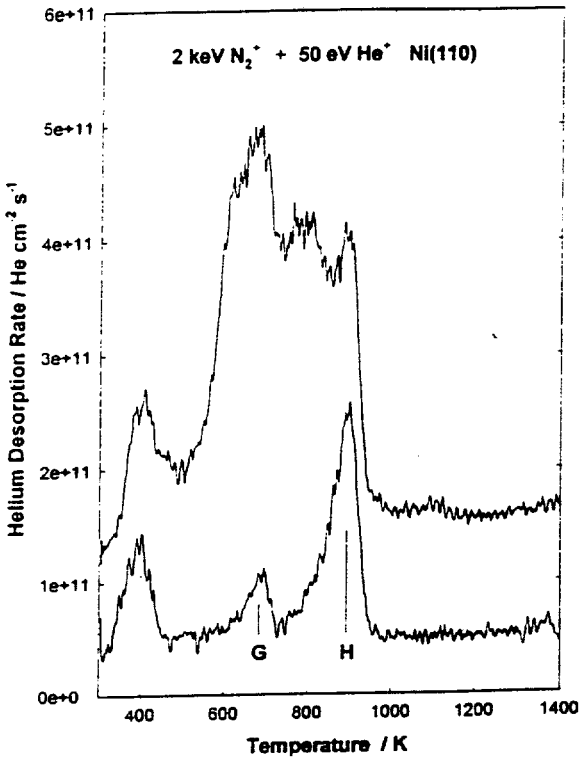
Table 1 *Desorption peaks and defect reactions; peak temperature in K, ΔT is relative width T/T_{FWHM} in %, energies in eV*

peaks	Nickel			Molybdenum			Tungsten			Iron	
	T	/ΔT	/ E^D	T	/ΔT	/ E^D	T	/ΔT	/ E^D	T	/ E^D
E:$He_{5-9}V$				790		2.1	860				
F:$He_{3,4}V$	660		1.9	900		2.5	902				
G:He_2V	660		1.9	970		2.9	1220				
H:HeV	855	7%		1170	7%		1545	7%			
$He_nV_mN_k$ => He	560		1.3								
$He_nV_mN_k$ => He	780 Ni_3N		2.1								
V => V_{mobile}	300		1.0	500		1.3	700		1.8		
NV ->N + V	360		1.0	950		2.55	1050		2.7		
V_mN_k =>N	350 Ni_4N		1.0	1000 Mo_2N	5%		900	7%		1000	
V_mN_k =>N	800/920 Ni_3N	3.5%	1.9								
N surface ads.β_1	870		1.9	1100			1250				
N => N_{mobile}	<300		0.5	450		1.2	500		1.24	350	0.85



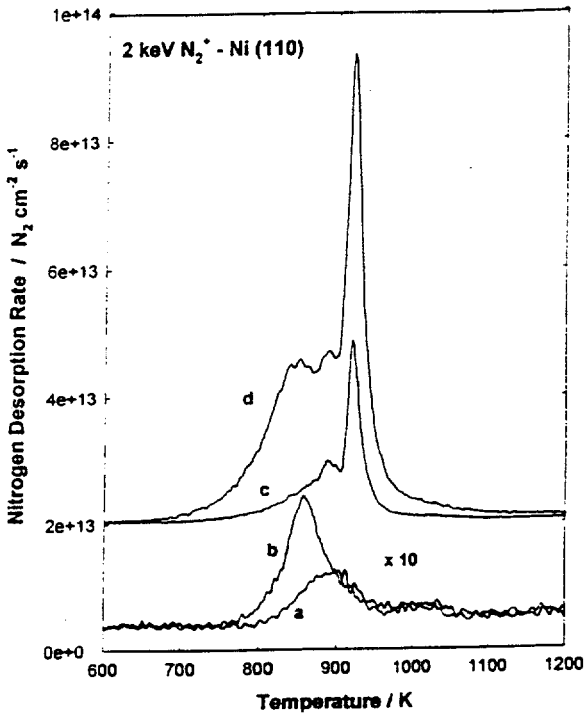


Figure 1. Helium desorption spectra obtained for 2 keV N_2^+ ion irradiated Ni(110) with doses (top) 5×10^{14} cm^{-2}, and (bottom) 10^{13} cm^{-2}. H and G peaks are indicated.
Figure 2 Nitrogen desorption spectra obtained for 2 keV N_2^+ ion irradiated Ni(110) with doses a. 10^{13} cm^{-2}, b. 2×10^{13} cm^{-2}, c. 2×10^{14} cm^{-2}, and d. 2×10^{14} cm^{-2}.

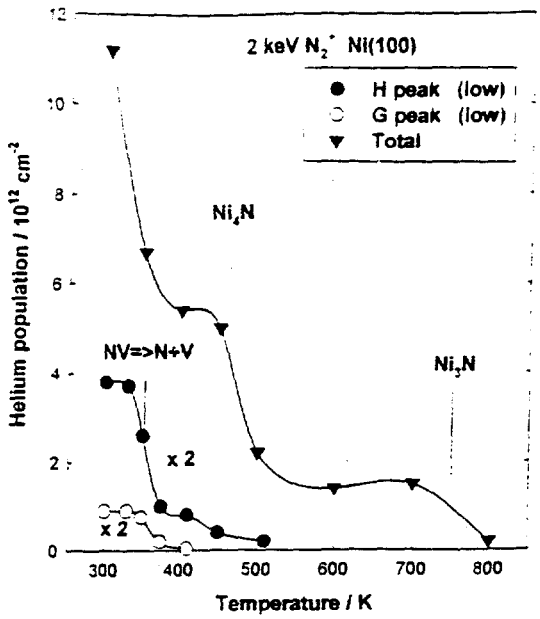


*Figure 3. Helium peak populations meaured during the annealing of 2 keV N_2^+ nitrogen irradiated nickel (low dose: 10^{13} cm^{-2}, and **high** dose: 5×10^{14} cm^{-2}). Dissociation reactions and precipitates are indicated.*

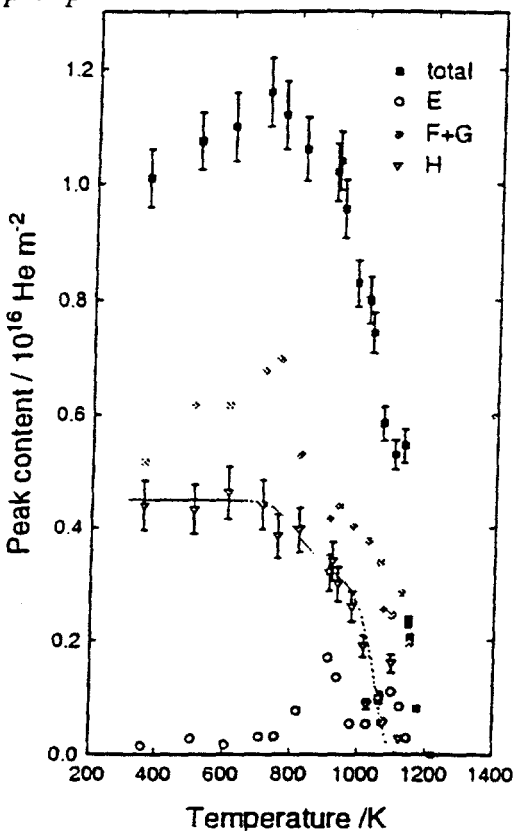


Figure 4. Helium peak populations vs anneal temperature for W(100) tungsten irradiated with 3 keV N_2^+ nitrogen ions (dose: 5×10^{13} cm^{-2}).

appear from 500K until 900 K. Rather pronounced is the increase of a 780 K peak and a rather sharp peak at about similar temperature as the H peak. In fig 1. these peaks are shown. Thermal annealing of the nitrogen implanted nickel causes changes in the helium trapping and helium peak populations as is shown in figure 3. In the low dose case all helium peak populations drop quickly at a temperature of 350 K. This is ascribed to the disociation of NV defects (see also the table). At high nitrogen dose extra recovery stages are observed at 450K and 750 K, respectively. Helium desorption spectra taken in the temperature interval from the last stage, e.g., at T_A=700 K, show a spectrum with a dominating peak at 780K. The nitrogen desorption spectrum undergoes a change from second order desorption at about 800 K for the low dose to a rather narrow desorption peak at about the same temperature for the highest dose in fig. 2. We ascribe the observed phenomena to the formation of cubic Ni_4N precipitates at intermediate nitrogen dose and the formation of hexagonal Ni_3N precipitates at high dose. Trapping of helium occurs at the interface between the precipitate and the matrix. The dissociation of the nitrogen precipitate is much faster than first or second order kinetics. Similar fast kinetics has been observed for regrowth of amorphous silicon, and the dissociation of helium vacancy clusters in molybdenum [4,5]. Analogously to the regrowth process the process might be ascribed by assuming a certain shrinkage velocity $dr/dt = \nu_0 \exp(-E^D/kT)$, with r the radius of the precipitate, and ν_0 a prefactor. This leads to a nitrogen release rate $dN/dt = -N^\alpha \nu \exp(-E^D/kT)$, with $\alpha = 0.5$ or 0.66 for flat and spherical precipitates, respectively, which is indeed faster than 1st and 2nd order processes. A similar explanation might apply to the nitrogen desorption from molybdenum. It should be remarked that the break up of the precipitate coincides with the release of all the helium. In this case the ratio of probe helium to nitrogen in a precipitate is much smaller than unity. Therefore the nitrogen dissociation governs also the helium dissociation.

Tungsten The helium desorption results for low dose nitrogen irradiation of tungsten with 5×10^{13} cm^{-2} N_2^+- ions and helium probe implantation of 300 eV 10^{13} cm^{-2} He^+-ions reveal helium desorption peaks which are indistinguishable from the desorption peaks obtained from samples with just multiply helium filled vacancies He_nV. The peaks E, F, G, H indicate the same dissociation reaction as in the case of molybdenum. Therfore also here must be concluded that whenever a single nitrogen occupies the He_nV-complex it will be released before the helium is released . Thus $He_nNV \rightarrow He_nV + N$. The results of thermal annealing (40 K/s) are shown in figure 4. It can be observed that the peak populations remain nearly constant until 750 K. Then a slow decrease is observed until T= 950K. Thereafter the defects disappear finally.
The behaviour is explained by assuming that the nitrogen irradiation produces vacancies which at T=550 K, when interstitial nitrogen becomes mobile, are filled with nitrogen. Then, at T= 750 K the monovacancies that are not filled with nitrogen become mobile and disappear, and finally at 1000 K they dissociate by $NV \Rightarrow N + V$. The increase of the E-peak at 950 K is ascribed to the effect that by reduction of the number of NV's the amount of helium per NV complex increases and therfore the population of the E-peak increases. It is of interest to note that by decoration of NV complexes with helium the nitrogen desorption temperature can be reduced. This also holds for nickel and molybdenum.

Iron It is more difficult to identify the contribution of nitrogen vacancy clusters in the desorption spectra from iron than it is for the previously investigated metals. In figure 5 the desorption spectra of nitrogen irradiated iron are shown. The spectra are dominated by a background of nitrogen release which starts at about 800 K and continues to rise up to T= 1200 K. At this temperature the phase transition from α- to γ- Fe takes place which causes a drastic reduction of the nitrogen release. The contribution of nitrogen from nitrogen vacancy complexes is found

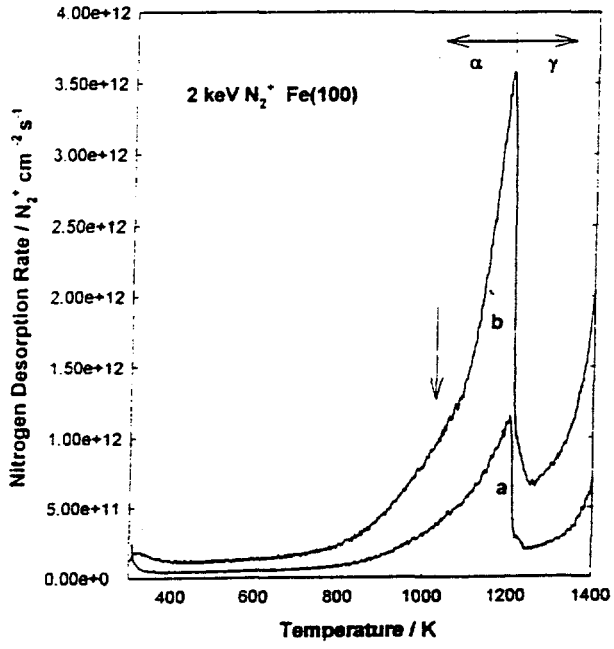


Figure 5. Nitrogen desorption spectra obtained for 2 keV N_2^+ ion irradiated Fe(100) with doses a. 10^{13} cm^{-2}, and b. 5×10^{13} cm^{-2}. At 1200K the α, γ phase transition is indicated.

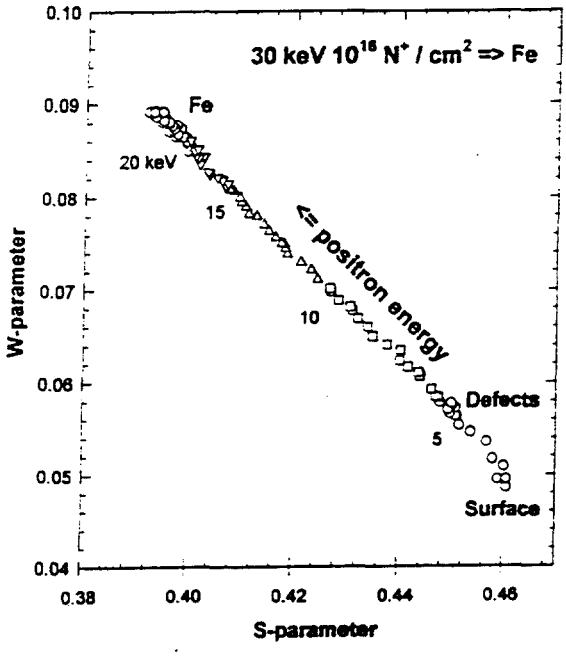


Figure 6. Positron beam analysis results for 30 keV N^+ ion irradiated Fe(100) with dose 10^{16} cm^{-2}. a. S- vs positron energy, b. W vs positron energy, and c. S-W plot

centered around 1000 K (indicated by an arrow). Apparently, considerable quantities of nitrogen are dissolved in the bulk of the material during the experiments. In particular, during annealing at T>1200 K nitrogen is easily dissolved because of the negative heat of solution in the γ-phase [9]. Positron annihilation results of nitrogen-irradiated iron are shown in the S-W map plotted in Figure 6. S- and W- parameters of the Doppler broadened annihilation peak have been measured as a function of the positron energy. From these results it is derived that defects are present in a zone centered around 170 nm deep below the surface. The defects have parameters relative to pure iron $S_{rel} = 1.13$ and $W_{rel} = 1.52$ which for metals indicate medium size vacancy clusters. It is likely that during the room temperature irradiation the vacancies and interstitial nitrogen atoms, which are both mobile at room temperature in iron, will agglomerate. Kumar et al [10] measured with a two detector coincidence set-up the core electron momentum distribution of positrons trapped in these defects and arrived at the same conclusion. In the future, positron measurements will be used to follow the evolution of the defect complexes. It will be of interest to see whether nitrides or nitrogen bubbles will be created.

CONCLUSIONS AND FINAL REMARKS

Helium desorption and nitrogen desorption measurements have proven to give useful information on the nucleation and intermediate phases of nitrogen agglomerates in metals. In the metals with low solubility for nitrogen the nitrogen atoms are able to immobilize the monovacancies and simple nitrogen vacancy complexes dissociate at temperatures of about 0.2-0.3 of the melting point. The formation of stabele nitrides was observed for molybdenum and nickel. In tungsten the nitrogen agglomerates turned to be less stable than in molybdenum. Nitrides appear to dissociate or shrink in rather narrow temperature intervals. The obtained data may be used to model the nucleation and growth of nitrides. Positrons are valuable to detect the open volume associated with the irradiation induced nitrides. The results are encouraging enough to apply the technique also to cases where fixed nuxleation centers, e.g. Al, Zr in Fe, are present.

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