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STUDY OF POINT DEFECT CLUSTERING IN ELECTRON AND ION IRRADIATED ZIRCONIUM ALLOYS

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ABSTRACT

Dislocation loops created by 500 keV Zr^+ ions and 1 MeV electrons in zirconium have a/3 <1120> type Burgers vectors, and in ion irradiated samples, loops lie preferentially on planes close to (1010). From in-situ observations of loop growth under 1 MeV electron irradiation in zirconium and dilute Zr (Nb,O) alloys, a strong increase of the vacancy migration energy with oxygen concentration was observed, from 0.72 eV for pure zirconium to 1.7 eV for Zr and Zr-1% Nb doped with 1800 ppm weight oxygen, indicating large trapping of vacancies by O single interstitials or clusters.

INTRODUCTION

Irradiation growth in zirconium alloys is characterized by an anisotropic change in material dimensions without any applied stress [1] .
The purpose of this study is to analyse - the crystallography of the dislocation loops created by 1 MeV electrons and 500 KeV Zr^+ ions, and - the influence of alloying elements (oxygen, niobium) on the kinetics of clustering during electron irradiation. All the analysis have been made using transmission electron microscopy (T.E.M.).

MATERIALS

Zirconium and Zr/1% wt Nb have been studied, each of them with two different

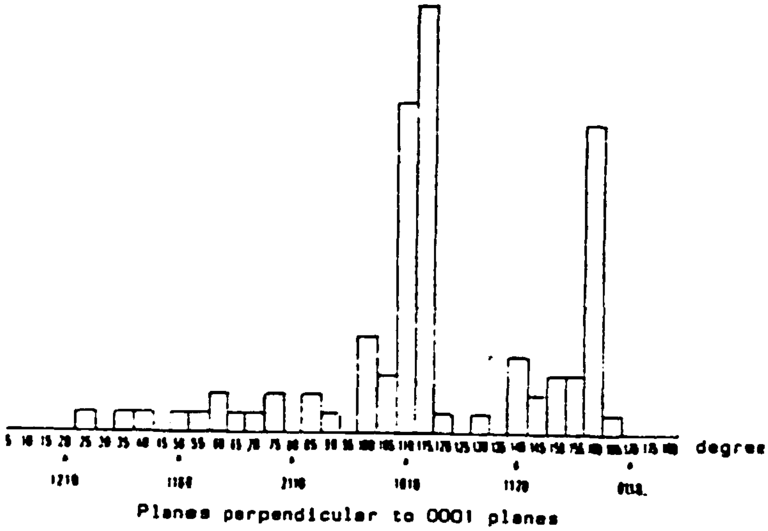
concentrations of oxygen : Zr (50 and 1760 ppm wt oxygen), Zr/1% wt Nb (430 and 1800 ppm wt oxygen).
Zirconium (50 ppm wt oxygen) has been prepared using Van Arkel proceeding, zirconium (1760 ppm wt oxygen) by melting a mixture of zirconium M.R.C. and ZrO_2, and the two Zr/1% wt Nb alloys have been taken from nuclear fuel sheaths.
All samples are polycrystals; the average grain size is 200 μm in zirconium (50 ppm wt oxygen) and 10 to 50 μm in the other materials. All samples have been annealed at 800°C during 2 hours under high vacuum (10^{-6} torr).

EXPERIMENTAL TECHNIQUES

Ion irradiations have been performed in an accelerator using 500 keV Zr^+ ions (SAMES accelerator, CEN Cadarache, 13108 Saint-Paul-lez-Durance, France) at 450°C and 500°C, in a very high vacuum (10^{-8} torr) and during 30 minutes. The ion flux was about 7.10^{14} ions. m^{-2}. s^{-1}. This type of irradiation has the following advantages : (i) the samples are quite thick (about 150 μm) because the thin foils used in T.E.M. are made after irradiation; (ii) by the way, oxidation is less important than in electron irradiated samples; (iii) moreover, ions induce defect cascades as for samples irradiated by neutrons in the pressurised water reactors.
Electron irradiation were made in a high voltage (1 MeV) electron transmission microscope (CNRS/ONERA, 92320 Chatillon, France), making possible the in-situ observation of point defect cluster growth during irradiation. The intensity of the electron beam was directly measured using a concealable Faraday cage located between the fluorescent screen and the projection lens. The flux at the sample level was $4.6.10^{22}$ e.m^{-2}. s^{-1}. Each irradiation took about 10 to 30 minutes. The range of irradiation temperatures was from 400 to 700°C.

CRYSTALLOGRAPHIC ANALYSIS OF DISLOCATION LOOPS

The dislocation loops created by 500 keV Zr^+ ions and 1 MeV electrons, in all samples have a circular shape; their density increases and size decreases as oxygen and niobium concentrations increase. For example : after 1 MeV electron irradiation at 600°C during 10 minutes under a flux of $4.6.10^{22}$ e.m^{-2}. s^{-1} in Zr/1% wt Nb (430 and 1800 ppm wt oxygen), the value of loop densities are respectively $1.5.10^{23}$ m^{-3} and $2.2.10^{23}$ m^{-3}, and the average loop diameters are respectively 100 nm and 70 nm.
All the examined loops have a/3 <1120> type Burgers vectors, in agreement with most of the previous work on electron irradiated [3] as well as on ion irradiated samples [4]. Loops with a/3 <1123> and a/6 <2023> Burgers vectors [5] were not observed. Loops preferentially lie on planes near the 1010 orientations of the hexagonal lattice, i.e. the loops are not totally edge dislocations. The distribution of loops (in terms of their orientation) leads to conclude that the sample orientation has an effect upon the planes of loop nucleation and growth.
Indeed on Figure 1, one observes fewer loops on planes (1100), which are closer to the sample orientation than the two other equivalent prismatic planes, i.e. (1010) and (0110). This can be explained by the presence of an external tensile stress, induced by a superficial oxide film [2].



(N.B. : all the samples which have been rolled have a crystallographic texture characterized by a preferential orientation : the (0001) direction is located at about 30° from the normal to the thin foil surface).

Fig. 1 Orientation distribution of loop planes

KINETICS OF CLUSTERING DURING ELECTRON IRRADIATION AND VACANCY MOBILITY

The growth of dislocation loops was observed during in-situ 1 MeV electron irradiation for the four samples (Figure 2). The density of loops remained constant during each irradiation. Histograms of loop sizes were established at several times during each 1 MeV electron irradiation (Figure 3), from which one can plot the change of average diameter with irradiation time. This variation is linear (Figure 4), then a constant value of growth speed for one irradiation temperature is obtained. Repeting the same experiment at several temperatures, one can plot the change of loop growth speed with temperature in an Arrhenius diagram, and obtain a value of apparent activation energy for each material (Figure 5).
We are in the same conditions than Kiritani has used in f.c.c. metals to determine values of vacancy migration energy [6] , i.e. the temperature is high enough to make possible vacancy migration, so dislocation loops are of interstitial-type and their growth is controlled by vacancies. One considers that a steady state of both kinds of point defects is reached. This steady level is represented by the equality of motion efficiency : $M = M_I C_I + M_V C_V$. (M_I and M_V are the mobilities of interstitials and vacancies). From the chemical kinetic model of interstitial and vacancy concentration variations, one supposes that the motion efficiency only depends on vacancy migration : $M_I C_I = M_V C_V \alpha M_V^{1/2}/Z_{IV}$ (Z_{IV} is the site number of spontaneous recombination of interstitials and vacancies). The variation of loop radii with irradiation time can be expressed by the difference between interstitial and vacancy flux which arrive on interstitial - type loops : $\dot{R} \alpha (Z_{IL}-Z_{VL}) M_V^{1/2}/Z_{IV}$ (Z_{IL} and Z_{VL} are the numbers of capture sites around one atomic site on the loop for respectively interstitials and vacancies). Consequently loop growth speed $\dot{R}$ is directly proportional to the square root of vacancy mobility.
According to this model the activation energy for vacncy migration is obtained as twice the apparent energy deduced from the slope of reciprocal temperature dependence of loop growth speed (Figure 5).
The average loop growth speed decreases as the oxygen concentration increases, moreover the vacancy motion energy increases with the concentration of oxygen.

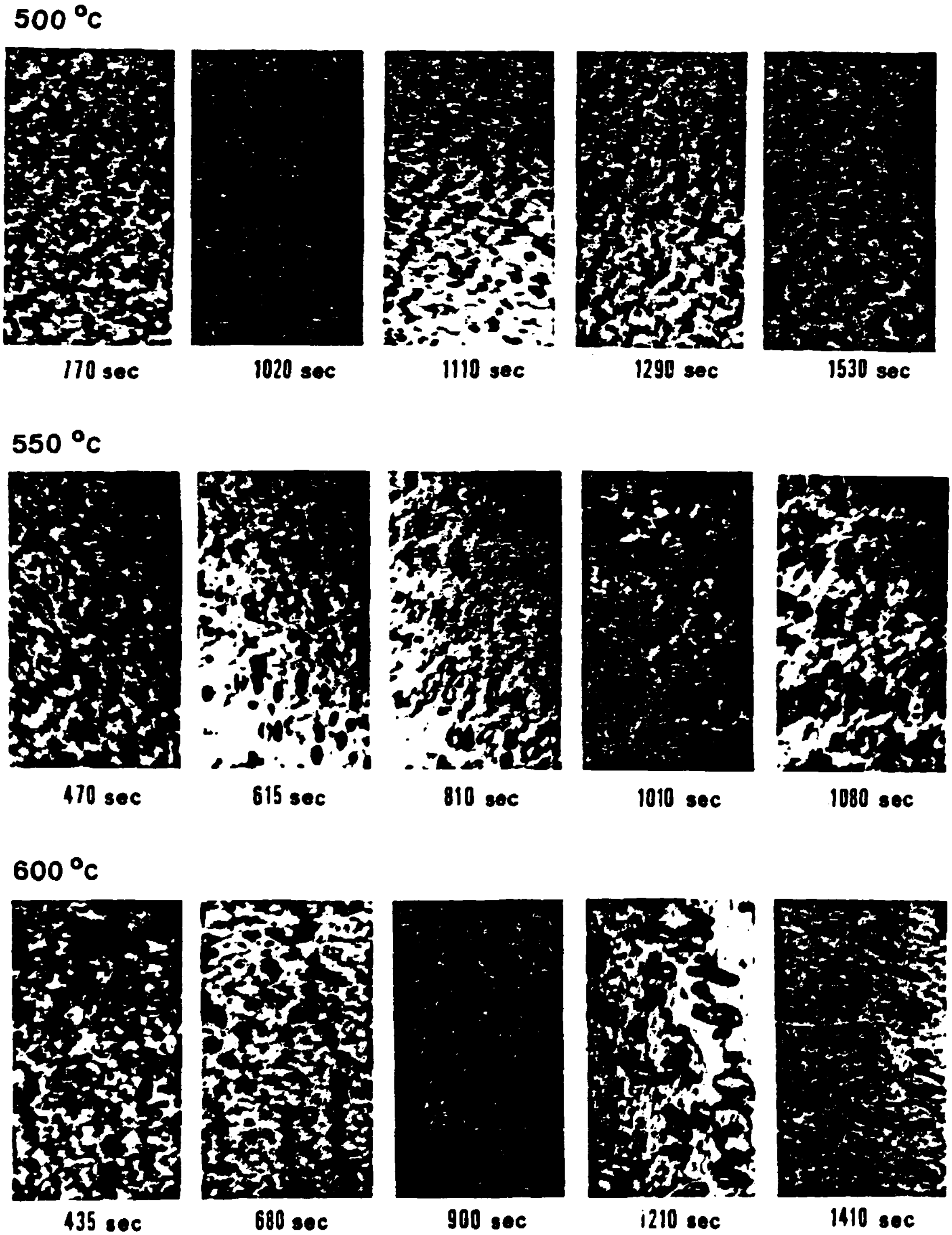


Fig. 2 Growth of dislocation loops in zirconium / 1760 ppm wt oxygen
$4{,}6 \times 10^{22}$ $e/m^2.s$

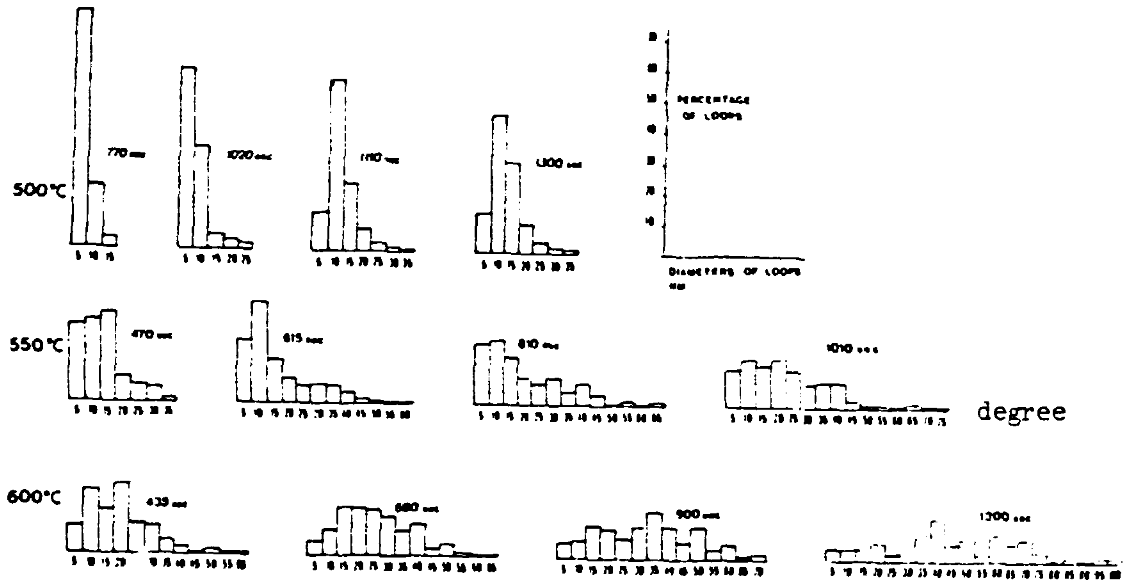


Fig.3 F'uence dependence of loop diameters in Zr/1760 ppm wt oxygen $4.6 x 10^{22}$ e/m^2.s.

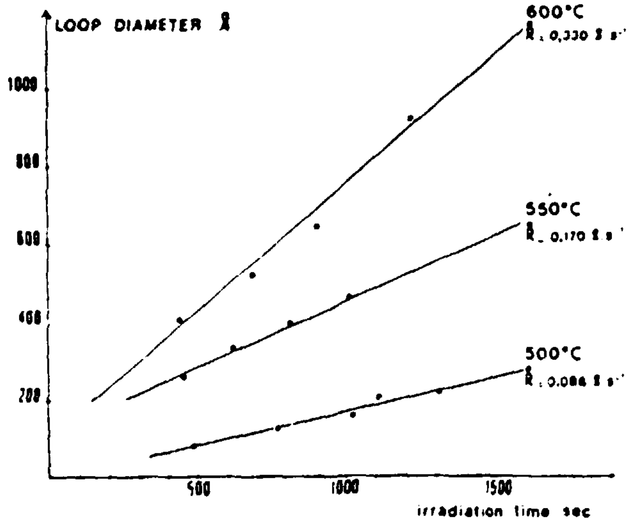


Fig. 4 Growth of dislocation loops under irradiation $4.6 x 10^{22}$ e/m^2.s, in Zr/1760 ppm wt oxygen

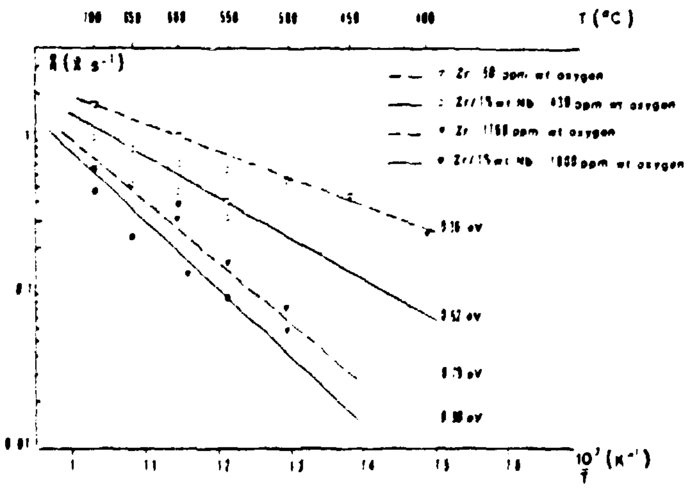


Fig. 5 Temperature dependence of the growth speed of loops, $4.6 x 10^{22}$ e/cm^2.s.

The influence of niobium on kinetic clustering is not appreciable. For pure zirconium (50ppm wt oxygen), zirconium (1760 ppm wt oxygen), Zr/1% wt Nb (430 ppm oxygen) and Zr/1% wt Nb (1800 ppm oxygen), the values of vacancy motion energy are respectively 0,72 ± 0,05 eV 1,58 ± 0,12 eV, 1,04 ± 0,15 eV, and 1,76 ± 0,15 eV. The value of the vacancy motion energy obtained for zirconium (50 ppm wt oxygen) is in agreement with the value obtained by G.M. Hood [7] from positron annihilation experiments.

CONCLUSIONS

The fact that the irradiations are performed at high temperatures where vacancies are mobile and that circular loops grow with a constant speed under irradiation strongly suggests an interstitial nature of loops. If this is the case, the fact that loops lie preferentially on planes (1010) is in agreement with the phenomenon of macroscopic growth in zirconium alloys under irradiation, along the prismatic directions 8 . The kinetics of clustering lead to conclude that there is a strong influence of oxygen on the vacancy motion energy; but it is quite difficult to define in which way does the oxygen act, because oxygen in hexagonal zirconium can be characterized by two different kinds of defects : single interstitials and interstitial clusters [9].

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