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BORYS MIKUŁOWSKI *, VIKTOR GRÖGER **,
GERHARD KREXNER ***, MICHAEL HEWARTH **

ANNEALING CHARACTERISTICS OF SUPERSATURATED VACANCIES IN COPPER AND NICKEL

CHARAKTERYSTYKI WYŻARZANIA MIEDZI ORAZ NIKLU PRZESYCONYCH WAKANCJAMI

Defect processes during isothermal annealing of rapidly quenched Cu (from 1000°C) and isochronal annealing of quenched (from 1400°C) and deformed Ni (20% rolled at room temperature) have been investigated by residual resistivity and positron lifetime measurements. In Cu a transformation of vacancy loops of the Frank type into loops of split Shockley partials was concluded. In Ni the growth of ultrasmall stacking fault tetrahedra could be the dominating process in vacancy annealing.

Przeprowadzono badania przemian defektów punktowych podczas izotermicznego wyżarzania gwałtownie przechłodzonej Cu (z 1000°C) oraz izochronowego wyżarzania gwałtownie przechłodzonego Ni (z 1400°C) i odkształconego Ni (przewalcowanego 20% w temperaturze pokojowej). Badania wykonano metodą pomiaru oporności szczątkowej oraz metodą pomiaru długości życia pozytronów. W Cu stwierdzono, że następuje transformacja pętli wakancyjnych typy Franka w rozszczepione częściowe pętle typu Shockleya. W Ni w czasie wyżarzania dominuje proces wzrostu ultramałych tetraedrycznych błędów ułożenia.

1. Introduction

Deformation induced vacancies play an important role for the mobilization of dislocations or may alternatively cluster and thus act as obstacles for dislocation motion [1, 2]. For Cu and Zn it has been concluded from the comparison of

* KATEDRA STRUKTURY I MECHANIKI CIAŁA STAŁEGO, AKADEMIA GÓRNICZO-HUTNICZA, 30-059 KRAKÓW, AL. MICKIEWICZA 30

** INSTITUTE FOR PHYSICS OF MATERIALS, UNIVERSITY OF VIENNA, STRUDLHOFGASSE 4, A-1090 VIENNA, AUSTRIA

*** INSTITUTE FOR EXPERIMENTAL PHYSICS, UNIVERSITY OF VIENNA, STRUDLHOFGASSE 4, A-1090 VIENNA, AUSTRIA

high-resolution resistivity isochrones after quenching and after deformation (in tension by $\gamma = 0.1$) that a considerable fraction of the resistivity present after deformation must be due to very stable vacancy agglomerates which are annealed out in the same temperature range as the dislocations [3], in Cu even at the identical temperature. Thus a separation by means of resistivity measurements or calorimetric measurements is impossible.

In this paper it has been investigated whether the positron lifetime spectroscopy is able to monitor single vacancies and their transformation into planar loops with different Burgers vectors as well as into three-dimensional clusters also in the presence of dislocations. For quenched and deformed Cu and Ni in annealing experiments the electrical residual resistivities and positron lifetimes at room temperatures are measured. Whereas resistivity reacts on all changes in lattice periodicity, the positron lifetime is rather sensitive to the degree of reduction of electron density (compared with the undisturbed metal) at defects where the positron is trapped [4]. Vacancies and vacancy clusters are well known candidates for which a simple trapping model [5] is obeyed. Positron trapping at dislocations seems to be a two stage process [6] with the dislocation line acting as a shallow trap with low binding energy and deep traps at the dislocation-like jogs or vacancies where the Burgers vector determines the positron lifetime. Certain impurities and dislocation tangles could severely contribute to detrapping [7, 8]. A theoretical consideration [7] gives a minimum length of a straight edge dislocation segment for positron annihilation to occur as $1_{\mathrm{min}} = h/\sqrt{2}\,\mathrm{m}E_b$, where h is Planck's constant, m is the positron mass and E_b the binding energy. If E_b is estimated as 0.02 eV, one obtains for the minimum length $1_{\mathrm{min}} \approx 9$ nm. For high-purity fcc samples which contain mainly edge dislocations in simple geometries (low density of dislocation tangles) as the only defects it has been shown that the length of the Burgers vector can be deduced from two facts. The lifetime difference between trapped positrons and delocalized positrons in a defect-free sample is proportional to the length of the Burgers vector b [10, 8]. The lifetime for ordinary (unsplit) dislocations with $b = a/2<110>$ coincides with the lifetimes of positrons trapped at single vacancies [10]. The lifetime for Frank loops, Shockley partials and sessile Lomer-Cottrell dislocations can be deduced from a measured lifetime in annealed copper of $\tau_f = 121$ ps and from a lifetime increment for ordinary dislocations (or vacancies) with Burgers vector length $b_{\mathrm{or}} = a/\sqrt{2}$ ($b_{\mathrm{or}} = a/2<110>$) of $\Delta\tau = 80$ ps [10] which results in $\tau_{\mathrm{or}} = 201$ ps. Bearing in mind that the Burgers vector for Frank loops (with $b_{\mathrm{Fr}} = a/3<111>$) is by a factor $\sqrt{2/3}$ smaller, for Shockley partials (with $b_{\mathrm{Sh}} = a/6<112>$) by a factor $1/\sqrt{3}$ and for Lomer-Cottrell (LC) dislocations (with $b_{\mathrm{LC}} = a/6<110>$) by a factor 1/3, we obtain the calculated positron lifetimes of $\tau_{\mathrm{Fr}} = 186$ ps, $\tau_{\mathrm{Sh}} = 167$ ps and $\tau_{\mathrm{LC}} = 147$ ps. The numbers are in excellent agreement with measurements on Frank loops by Shirai [10] which gave $\Delta\tau_{\mathrm{Fr}} = 65$ ps (resulting here in $\tau_{\mathrm{Fr}} = 185$ ps) and with our own measurements on Cu single crystals deformed in a single slip which gave $\tau_{Sh} = 166$ ps. Making use of these data the lifetime measurements can be interpreted directly if one kind of defects is strongly dominating as shown earlier for misfit dislocations in solid two-phase alloys [11, 12]. Thus it is expected that vacancies and small vacancy clusters which are trapped strongly will dominate over dislocations and should therefore be easily detected by positron annihilation also in the presence of dislocations. For planar vacancy loops which are essentially closed lines of edge dislocations the situation is not so distinct. Therefore the quenched samples will be investigated first.

2. Experimental procedure

Copper single crystals of the size 30 mm × 3 mm × 1 mm were produced from 5N material by the Bridgman technique and were then thinned to 0.35 mm thickness. They were heated to 1000°C in a vertical furnace in high-purity argon atmosphere, kept there for 1 hour and rapidly water-quenched making use of a copper radiation shield. While one strip was used for resistivity measurements, a second strip was cut into four pieces suitable for positron lifetime measurement and treated identically as the first strip throughout the whole annealing and measuring procedure. The lifetime measurements were performed for sample-^{22}Na source-sample sandwiches in a fast-slow coincidence setup and have been analyzed by the *Resolution* and *Positronfit* programs [13, 14]. The width of the resolution function was 230 ps, the time for collecting the spectra (contaning at least 5×10^6 counts) was 33 hours. Thus the vacancy structure had to be stabilized after the quench by annealing at 100°C for 10 min in order to have constant conditions during the first lifetime measurement. Then resistivity and lifetime isotherms were measured at 250°C, where it is known that in single crystals Frank loops of about 20 nm diameter occur after quenching and annealing [15].

Nickel polycrystal pieces of 99.998% purity were prepared as samples measuring of 6 mm × 6 mm × 1 mm for the positron measurements and as strips 20 mm × × 3 mm × 1 mm for the electrical measurements. They were then water quenched from 1400°C from a horizontal furnace where no radiation shield could be used. Other single crystal samples were deformed by 20% by rolling. Again resistivity and positron lifetime isotherms were measured starting from 0°C in steps of 25°C and a holding time of 15 min.

3. Results and discussion

For copper crystals which were quenched (residual resistivity 7.1 nΩcm) and stabilized for 10 min at 100°C the annealing isotherms for 250°C annealing temperature are shown in Fig. 1a for the residual resistivity up to 62 min annealing time. Further annealing up to 4 h did not reduce the resistivity significantly.

Formation and growth of vacancy loops is known to occur at 250°C [15]. The defects could be removed by annealing at 700°C for 2 h and slowly cooling which reduced the residual resistivity to 3.79 nΩcm. During isothermal annealing the resistivity drops for annealing times below 2 min, then remains approximately constant and is gradually lowered again between 8 and 62 min. For an interpretation the positron lifetimes obtained at the companion samples were separated into a defect line and a line due to nonlocalized positrons. Fig. 1 b shows this defect lifetime versus the annealing time at 250°C. The lifetimes characteristic for different types of dislocations are also indicated. It can be concluded that fully collapsed Frank loops seem to be present after quenching and annealing at 100°C and the change into Shockley partial dislocation occurs between 3 and 10 min of the annealing time at 250°C. The resistivity does not change during this process. The resistivity drops seem to be caused by coarsening of the loops. As a mechanism for the transformation of the loops it was assumed [16] that at a critical diameter a single Shockley partial loop forms spontaneously, traverses the Frank loop and changes it into an ordinary dislocation loop which immediately splits into two Shockley partials. The driving force is the reduction of the total energy of the

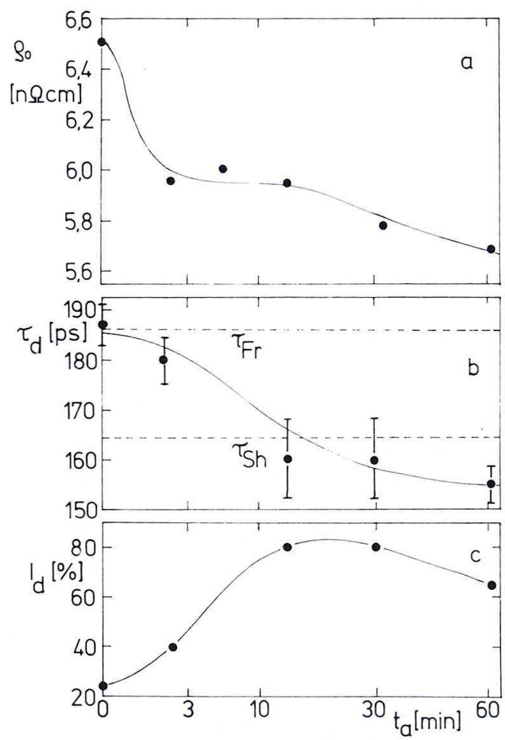

Fig. 1. Isotherms (annealing temperature 250°C) for quenched Cu single crystals: a) residual resistivity measured at 4.2 K; b) and c) positron lifetime and relative intensity of the defect line of a two line fit of a room temperature measurement (for the dashed lines see text)

stacking faults which are removed from the center of the F r a n k loop. The relative intensity of the defect line shown in Fig. 1c is rising until this transformation is over and the intensity is falling for annealing times exceeding 30 min. This behaviour can be understood if the critical loop diameter for positron trapping is reached for a gradually increasing number of loops. Thus the density of the positron trapping loops is at first increasing although the total loop density goes down by coarsening. After the central part of the distribution obeys the trapping condition the density of the positron trapping loops also goes down.

For deformed copper single crystals again deformation induced loops could be present and possibly could undergo a change, but the resistivity isochrone [3] is not conclusive in this respect. The presence of loops from S h o c k l e y partials would explain the annealing out at the absolutely identical temperature as that of the dislocations. The presence of clusters has been checked for copper and nickel by an independent determination of the true dislocation density as a function of deformation by X-ray B r a g g line profile analysis (XLPA) [17]. Small vacancy loops are expected to give no significant contribution to line broadening. The electrical dislocation resistivity can then be calculated by a well established theoretical model [18] which has been calibrated by TEM at very small deformations where hardly any vacancies are produced. By comparison with the measured resistivity increase due to deformation it was shown that for deformations of polycrystals exceeding $\varepsilon = 0.3$ a resistivity fraction (up to 40%) gradually increasing with deformation must be due to vacancy clusters [19].

For a clarification positron lifetimes (at room temperature) of copper single crystals deformed in tension at 77 K between $\varepsilon = 0.09$ and $\varepsilon = 0.2$ can be used [20]. Two lifetime regions seem to be present, one with $\tau > 180$ ps, a second one with $\tau < 150$ ps. This indicates again the presence of F r a n k loops, but in addition gives a hint for the presence of L o m e r C o t t r e l l dislocations. No lifetime component due to S h o c k l e y partials could be resolved in a free fit. Thus the arrangement of possible LC dislocations seems to trap considerably stronger than the dominating S h o c k l e y partials. L o m e r C o t t r e l l dislocations can be generated by a dislocation reaction between two partials of split dislocations gliding on intersecting gliding planes as it is the case after the secondary slip contributes to the deformation. Thus any LC segment is connected to two S h o c k l e y partials by two stacking fault ribbons in different gliding planes. Why positrons could be bound more stable to that arrangement than to a split dislocation and annihilate preferentially at the LC segment would have still to be explained. An additional possibility for the presence of strongly trapping LC dislocations would be the formation of stacking fault tetrahedra which consist of six LC dislocation segments interconnected with four stacking fault triangles. Small stacking fault tetrahedra (containing about 80 vacancies, typically 3 nm extended) of high density have been reported to be present in deformed copper [21] which are free from dislocation tangles where detrapping might occur and it could be the case that they will be able to trap due to the three-dimensional arrangement of the S h o c k l e y partials.

Nickel has a considerably higher stacking fault energy and a higher melting point than copper. Thus defects involving extended stacking faults are less likely. On the other hand, single vacancies are still immobile at room temperature where positron lifetime measurements are carried out. Fig. 2a shows the resistivity isochrones for the deformed (full circles) and water-quenched samples (open circles) up to temperatures where the lowest resistivity was reached. The first resistivity drop near 100°C is known to be due to the clustering or annealing out of single or double vacancies, the ultimate resistivity decrease above 500°C must be due to dislocation annealing [22]. The two small annealing stages for the quenched sample centered at about 220°C and 420°C could be due to annealing out of vacancy clusters. Again it is hoped to get additional information about the types of defects present from positron lifetimes of identically prepared samples where lifetime spectra were determined for selected temperatures. As reliable separations were not possible, Fig. 2b shows the mean lifetime τ_m.

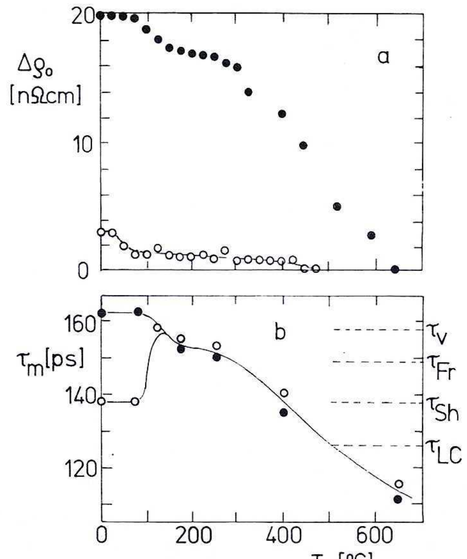

Fig. 2. Isochrones for deformed Ni polycrystals (20% in tension at room temperature: full circles) and quenched Ni polycrystals (water quenching from 1400°C, open circles); holding time 15 min, steps 25°C: a) residual resistivity increase measured at 4.2 K, b) positron mean lifetime measured at room temperature (for the dashed lines see text)

In nickel, no detailed positron measurements have been reported on single crystals deformed in a single slip. Thus no reliable lifetime is known for Shockley partials. For single vacancies the lifetime has been obtained from an equilibrium experiment [23] which gave $\Delta\tau_v = \tau_v - \tau_f = 48$ ps. If we use the interpolation scheme for the fcc metals as described for copper in the introduction, for our measured value $\tau_f = 110$ ps we obtain for dislocations and loops: $\tau_{or} \approx \tau_v = 158$ ps, $\tau_{Fr} = 149$ ps, $\tau_{Sh} = 138$, $\tau_{LC} = 126$ ps. These values are indicated for comparison in Fig. 2b.

We conclude that the quenching does not result mainly in single vacancies possibly because it was not quick enough. The smaller lifetime indicates the presence of planar loops of the Shockley type. It can be assumed that due to the higher stacking fault energy rather small Frank loops will turn spontaneously into ordinary dislocations which split up again.

The lifetime measured after deformation indicates the presence of vacancies and divacancies or alternatively a trivacancy at a Shockley partial being the smallest possible stacking fault tetraeder configuration [24] (see below). In ultra-pure polycrystalline nickel rolled by 5% Kuramoto et al. [25] have found $\tau = 200$ ps. The difference to our result is possibly due to the smaller deformation and the higher purity.

After isochronal annealing up to 175°C the lifetimes in the quenched samples show a marked increase at temperatures above 100°C which indicates the formation of three-dimensional vacancy clusters. The lifetimes for the deformed samples have fallen to very similar values and remain remarkably similar to those of the quenched samples during all the annealing out of defects. Thus we conclude that there is no strong influence from Shockley partials on the lifetime of a deformed sample which can be explained by a trapping probability being much smaller at the Shockley partial dislocations than at the vacancy clusters. Thus for both sample states mainly the annealing of the point defect clusters must be monitored. Despite the high stacking fault energy small (size about 3 nm, about 80 vacancies) stacking fault tetrahedra (SFT) have been found experimentally [21]. The positron lifetimes for even smaller SFT (hardly visible by TEM) nucleated at a Shockley partial have been calculated as a function of the number of vacancies [24]. The results are between 160 ps (3 vacancies) and 131 ps (for 28 vacancies), while the binding energy is decreasing. Our estimate for „large" SFT (Lomer-Cottrell dislocations) is $\tau = 126$ ps. Thus the main part of the lifetime isochrone for deformed nickel could be nicely explained by small SFT which are nucleated at Shockley partials, grow and possibly dissolve together with the dislocations themselves.

The lifetimes for the quenched samples are slightly higher but qualitatevely very similar. Thus it seems more likely that the planar loops have been formed as Frank loops near Shockley partials, have reacted with them and have transformed below 175°C into small SFT than that they would be present in the bulk, where in accordance with [24] 15-vacancies-SFT ($\tau = 159$ ps) could coarsen to 28-vacancy-SFT ($\tau = 130$ ps) and further.

4. Summary

Positron lifetimes and residual resistivities have been measured after:

- isothermal annealing of rapidly quenched (from 1000°C) monocrystalline copper,
- isochronally annealing od quenched polycrystalline nickel (from 1400°C),
- isochronally annealing of deformed polycrystalline nickel (20% rolling).

The results indicate than in fcc metals positron lifetimes seem to be helpful for the characterization of various deformation induced point defects and their annealing products. The background of the dislocations has turned out to be of minor influence presumably because point defect production is intimately connected with the presence of a dislocation network which seems to trap rather inefficiently due to the dislocation tangles. An interpolation scheme for untangled edge dislocations in fcc metals (connecting the defect lifetime with the length of the Burgers vector) has once more been shown to be a valuable tool in the interpretation of large vacancy loops or straight edge dislocations. In nickel the lifetime difference between the defect state and the delocalized state are considerably smaller than in copper.

For rapidly quenched monocrystalline copper the presence of Frank loops and their transformation into perfect dislocation loops which split into Shockley partials was clarified by positron lifetime measurement. In quenched nickel the presence of perfect dislocation loops split into Shockley partials has been concluded. During the annealing they seem to transform into very small stacking fault tetrahedra which are possibly also connected to a Shockley partial as it seems to be the case after deformation and annealing. Directly after the deformation by rolling to 20% at room temperature mono- and divacancies (or trivacancies at a Shockley partial in stacking fault tetrahedra configuration) seem to be present. This is in contrast to monocrystalline copper deformed in stage II where possibly due to the lower stacking fault energy Frank loops and Lomer Cottrell dislocations have been reported. For a total clarification more experiments in other sample and deformation states and in other fcc metals are intended.

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