September 1976

POSITRON LIFETIME MEASUREMENTS
AS A NON-DESTRUCTIVE TECHNIQUE
TO MONITOR FATIGUE DAMAGE

Technical Progress Report

Dr. J. G. Byrne

Principal Investigator

University of Utah

Salt Lake City, Utah 84112

MASTER

NOTICE
This report was prepared as a statement of work
sponsored by the United States Government. Neither
the United States nor the United States Energy
Research and Development Administration, nor any of
their employees, nor any of their contractors,
subcontractors, or their employees, make any
warranty, express or implied, or assumes any legal
liability or responsibility for the accuracy, completeness
or usefulness of any information, apparatus, product or
process disclosed, or represents that its use would not
infringe privately owned rights.

September 1976

Prepared for

THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

UNDER CONTRACT NO. E(11-1)-2128

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

ABSTRACT

1. TECHNICAL REPORT

1.1 Equipment

1.2 Fatigue

1.3 Hydrogen Embrittlement

1.4 Electron Microscopy

1.5 Electron Irradiation

1.6 Other Contract Activities

2. TIME INFORMATION ON PRINCIPAL INVESTIGATOR

FIGURE CAPTIONS

FIGURES

APPENDIX A

ABSTRACT

Two Ph.D. thesis were completed in 1976: that of F. Alex, "POSITRON LIFETIME STUDIES OF HYDROGEN EMBRITTLEMENT" and that of T.D. Hadnagy, "POSITRON LIFETIME STUDIES OF ELECTRON IRRADIATED COPPER".

In the thesis work of F. Alex, transmission electron microscopy was successfully applied for the first time in this contract and more importantly, for the first time, we think, in the hydrogen embrittlement field. In hardened steel, hydrogen charging produced damage at martensite plate and lath surfaces; the damage as revealed by TEM was in the form of small voids. No similar particle interface damage was found in charged steel of a pearlitic microstructure; however, dislocation density increases were noted in both pearlitic and martensitic materials as a result of hydrogen charging. It will be recalled that when charging samples already at a maximum positron lifetime due to tensile straining, the hydrogen charging caused a positron lifetime decrease. TEM has since shown that in such cases the dislocation density was higher than it was prior to charging proving that many of the hydrogen generated dislocations have been neutralized as positron traps by first trapping protons. Additional work of F. Alex and newer research of D. Boice, in this area, will be described.

The thesis study of T. Hadnagy was completed by additional irradiations and annealings which made it clear that stage III annealing of electron irradiated copper involves the motion and removal of both monovacancies and divacancies. A multivacancy unit exists as a stable entity even after annealing above the stage III region. These units are the probable nucleation sites for larger voids.

The fatigue studies of copper are developing a more full picture of dynamical hardening and softening at a number of intermediate conditions between the extremes of the fully annealed and cold worked conditions. A critical point has been discovered during early fatigue hardening, namely, the intensity of the primary lifetime starts dropping while that of the second lifetime increases. This is accompanied by a gradually decreasing mean second lifetime meaning that there is an increasing amount of positron trapping at defects with a longer lifetime than that ascribed to dislocations or vacancies and that this contribution is being averaged with the source lifetime of about 360 psec thus causing τ_2 to decrease. One such possibility is the small multivacancy (reported in the irradiation work) which can have a positron lifetime in copper of as much as 250 picoseconds.

1. TECHNICAL REPORT

1.1 Equipment

A high voltage power supply (Fluke #415B) was purchased to replace a similar unit which up to now had been on loan from Dr. G. R. Miller. New photomultiplier tubes are in the process of being selected for purchase. New detector crystals are on hand and will be installed in the late autumn. These should further increase the resolution of the system. (Our actual full width half maximum now, based on Na^{22} , is 280 picoseconds. This can probably be brought to 230 picoseconds by the changes described).

Our PDP8 has been re-programmed to automatically accumulate data at intervals as short as 2 hours, which now is all the time required for one run when operating with a strong source of 50 microcuries. The reproducibility of the system is currently ± 1 picosecond.

1.2 Fatigue

The plan⁽¹⁾ of measuring positron lifetime and x-ray "particle size" during each of fatigue softening and hardening of copper has been continued with interesting results. Fig. 1.2.1 shows data from cold worked copper cycled at a maximum stress of 75% of its yield stress. A fluctuation beginning at about 3.5×10^4 cycles is evident. This was earlier shown⁽¹⁾ to develop more fully if the copper was first annealed slightly* at 200°F (93°C). Fig. 7 of the previous technical progress report⁽¹⁾ showed about a 40 psec decrease prior to an ultimate increase in positron lifetime prior to fracture. The decrease was explained, on the basis of a concurrent increase in x-ray particle size, as being caused by dynamic softening^(1,2). Unexplained then was the final increase in positron lifetime. We have since found from scanning electron microscopy that subsidiary fatigue cracks and inclusion-matrix decohesion voids were present near the main fracture site (see Figs. 1.2.2a, b and c respectively) in the specimen pair which generated Figs. 7 and 8 of reference #1. Such voids and small cracks would account for an increase of positron lifetimes and a final decrease in the x-ray particle size. The latter type decrease was first seen long ago by Moll and Ogilvie⁽³⁾ and was then ascribed to the fragmentation produced by the formation of small crack branches. It is very interesting to notice in this connection that a typical spacing between the subsidiary cracks shown in Fig. 1.2.2a is about 0.1" which is $1067\text{\AA}$. This compares amazingly well with the value of the x-ray particle size of $1000\text{\AA} - 800\text{\AA}$ reached just prior to fracture for the above discussed copper (see Fig. 7 and 8 of reference (1).)

*This anneal evidently brought the defect density closer to the lower limit of saturation so that further cyclic softening could bring it out of the saturation range.

The former type increase in positron lifetime of course is attributable, as in the case of irradiation produced voids, to the longer trapping times associated with internal interfaces⁽⁴⁾. Finally one may note very similar shaped inclusion related voids and subsidiary (secondary) fatigue cracks in other f.c.c. materials from the work of Erhardt, Pelloux and Grant⁽⁵⁾.

To further develop the spectrum of events during fatigue hardening and softening of copper, specimen pairs have been annealed at temperatures of 650, 750 and 500°F. Fatigue tests on these conditions are in various stages of completion and will be described below. Finally, one temperature between 200°F and 500°F will be selected for fatigue testing when the results of all the aforementioned tests are known.

Fatigue of specimens annealed at 750°F has been studied in considerable detail. Fig. 1.2.3 shows fatigue hardening as an increase of some 50 psec but not to the high level attained by cold rolling (193 psec). Some softening then follows and an ultimate increase. All these changes are inversely reflected in the (200-400) x-ray particle size changes as before. The early stages of this cycling were restudied at much closer intervals. Fig. 1.2.4 suggests a change is occurring between 100,000 and 200,000 cycles. (X-ray runs on this are complete but in calculation at this writing). To understand better this early period of fatigue hardening, the data were reanalyzed in the computer in terms of a first and second lifetime. Fig. 1.2.5 shows that the intensity of the primary lifetime (τ_1) initially decreases and conversely for the intensity of τ_2 . We take the primary lifetime τ_1 to represent a combination of annihilations in the perfect lattice and at defects and the secondary lifetime τ_2 to include annihilations in the Na²² Cl source

and in any new defect with lifetime close to that of the source (360 psec) such as multivacancies generated during fatigue. One may say that since the intensity of τ_2 increased while the first lifetime τ_1 was increasing, there must have been generation of a new defect with a longer lifetime than that for either the vacancy or dislocation. Now if one examines the actual value of τ_2 one finds it first decreases during cycling as shown in Fig.

1.2.6. This probably means that multivacancies are being added to the source contribution and if the lifetime of di-vacancies (or higher) is ≈ 250 psec, the source lifetime is ≈ 360 psec and that of monovacancies is ≈ 170 psec, then multivacancy and or monovacancy production would decrease τ_2 as is observed in Fig. 1.2.6. The final rise in that curve could indicate that the early generated vacancies or multivacancies later go to sinks such as grain boundaries or dislocations. It must be kept in mind that over the total fatigue life of the 750°F material as depicted in Fig. 1.2.3 ($\sim 9.5 \times 10^6$ cycles) the x-ray particle size changes are uniquely indicating the way in which the dislocation arrangement is changing. Thus positron lifetime and intensity changes, in which the dislocation and monovacancy contributions are virtually indistinguishable, must be reconciled eventually with the facts revealed about dislocation arrangement via x-ray particle size data.

1.3 Hydrogen Embrittlement

1.3.1 Research on 4340 Steel and Nickel

The new information in this part of the research may be classified into three parts: transmission electron microscopy (T.E.M.) of pearlitic and martensitic 4340 steel in various states of tensile strain and/or hydrogen charging, studies of surface layer hardness related to positron lifetime values and T.E.M., and studies of hydrogen charging in nickel.

A unique thinning method⁽⁶⁾ was developed by F. Alex for producing 4340 steel transmission specimens. The structure of a Rockwell C 43 specimen is shown in Figs. 1.3.1a and 1.3.1b, which are positive and negative prints respectively for clarity. Fig. 1.3.1b will later be compared with a charged condition.

Appendix Fig. 3 of reference (1) showed how the positron lifetime varied with tensile strain for 4340 steel of four initial hardness levels. Thin foils were prepared from the annealed steel (R_B 91) after tensile strains of 6, 12 and 19% and their structures are shown in Figs. 1.3.2, 1.3.3 and 1.3.4 respectively. In Fig. 1.3.2 one finds dislocation cells approximately 750Å in diameter. In Fig. 1.3.3 one sees that straining to 12% actually lowered the dislocation density from its level at 6% strain. Finally, in Fig. 1.3.4 one sees that further straining to 19% again increased the dislocation density. Since these foils were carefully taken from surface⁽⁶⁾ regions of the tensile specimens, i.e. the region from which the positron data is obtained, we feel the shape of the curve in Fig. 3 of the appendix of the previous progress report now is explained. The reader may recall the shape of that curve of positron lifetime versus tensile strain showed a maximum at about 4% elongation and a minimum at about 12% elongation.

The dislocation density changes observed now make that behavior understandable. In order to further check the surface implications of both the T.E.M. and positron data, two types of hardness measurements were performed: superficial hardness change versus strain and microhardness versus strain; results are shown in Figs. 1.3.5 and 1.3.6 respectively. Fig. 1.3.5 shows that a slight dip in the difference between strained and annealed superficial hardness occurs in the vicinity of 12-13% strain. If one performs a similar study, but closer to the surface by utilizing microhardness, Fig. 1.3.6 shows a stronger indication of the change* at 12% strain than did the deeper measurement of Fig. 1.3.5. Finally, depth of positrons as a function of the density of the metal. Fig. 1.3.7 shows that most positrons entering iron (or steel) should annihilate within about 0.007". Thus the earlier mentioned τ vs E minimum can be explained by the direct observation of a lower dislocation density near the surface; this is confirmed by the larger response of the more surface sensitive of the two hardness measurements (microhardness) and the fact that the positrons are sampling material less than 0.007" in depth.

In earlier progress reports, the effect of embrittlement on the positron lifetime in 4340 steel was reported. In the current period we have found T.E.M. evidence of the embrittlement for the first time. In Fig. 1.3.8 a and b are shown positive and negative prints of the structure of hardened 4340 steel after hydrogen embrittlement. If this figure is compared with Fig. 1.3.1 one finds two significant differences:

- (1) networks of holes or cracks at the edges of the martensite plates and
- (2) the dislocations form clusters of higher density

* i.e. The minimum in reference (1) appendix Fig. 3 plot of positron lifetime versus strain.

Fig. 1.3.9 represents just cadmium plating and stripping. The structure is similar to that when electrolytic charging was included but the density of holes was lower.

The annealed and embrittled condition did not exhibit a "tight" cell structure such as in Fig. 1.3.2 but had the appearance seen in Fig. 1.3.10. No holes are present.

Last year we reported⁽¹⁾ data on the effects of charging steel microstructures of three initial hardnesses, each with two different tensile strains prior to charging. Table 1 is now more complete. The mechanism suggested then, and reinforced by Table 1, is that hydrogen atoms or protons trapped at dislocations and vacancies then screen these defects with respect to subsequent positron interactions. As this becomes more prevalent in a material with defects the mean positron lifetime should decrease to that more nearly associated with annihilation with electrons in the "perfect" lattice for that condition.

The condition represented in Table 1 described as: annealed, deformed 22% and charged for four 10 minute periods, was thinned for T.E.M. Its structure is seen in Fig. 1.3.11. The dislocation density seems higher than for the structure of Fig. 1.3.4 which was for a similar strain but no charging with hydrogen. Thus if the dislocation density is higher and the mean positron lifetime lower (152 psec versus 174 psec at zero charging time) then the suggestion of dislocation shielding by protons seems quite justified.

New data on the charging of nickel were obtained and the complete summary is given in Table 2. These data again show the clear tendency for the charging of protons into a worked structure to lower the mean positron lifetime. Conversely charging of soft nickel will increase the positron

TABLE 1

EFFECT OF HYDROGEN CHARGING ON STRAINED 4340 STEEL

Condition	Charging Times in "Poisoned" 1N H ₂ SO ₄					
	None	10 min	20 min	30 min	40 min	50 min
Annealed						
11% elongation	164	184	159	157		
22% elongation	174	177	153	148	152	
Rockwell C 37						
3.5% elongation	180	168	153	156		
7% elongation	185	168	154	146	158*	
Rockwell C 52						
3.5% elongation	178	183	177	167	154	153
7% elongation	182	184	157	159		

*This data point was obtained after repair of the fast-fast lifetime system and may have increased as a result of system calibration problems.

TABLE 2

EFFECT OF DEFORMATION, ANNEALING AND HYDROGEN CHARGING IN NICKEL

Condition	Lifetime (psec)
Cold Rolled (90% R.A.)	190
Cold Rolled (90% R.A.)	
Charged 10 min.	184
Charged 20 min.	170
Charged 30 min.	177
Cold Rolled and Annealed at 871°C for 1 hour	147
Cold Rolled, Annealed at 871°C for 1 hour and charged 10 min.	159
Cold Rolled, Annealed at 871°C for 1 hour and strained 3% (elongation)	156
Cold Rolled, Annealed at 871°C for 1 hour and strained 6% (elongation)	167
Cold Rolled and Annealed at 200°C for 24 hours	167

lifetime. For example, Table 2 shows that a 3% tensile strain gives about the same lifetime change as a 10 minute charge of hydrogen. In the proposal, experiments to quantify this type of comparison will be suggested.

1.3.2 New Study of Hydrogen Charging of Nickel

A new look is being taken at the kind of results in Table 2 by D. Boice in a master's thesis. To avoid potential problems with hydrides we have consulted with B. A. Wilcox (of Battelle and NSF) and J. A. Peterson (of Armco Steel Corp.) both of whom have had hydrogen embrittlement experience of great value. One approach being taken is to charge at a higher temperature ($\sim 90^\circ\text{C}$) as did Wilcox and Smith⁽⁹⁾. A charging arrangement with platinum electrodes and a hot-plate stirrer is now ready for this. The solution will not include a poison as in the case of the work of F. Alex⁽⁶⁾ because such was not present in the new reference work⁽⁹⁾ and because we may thus avoid surface oxide changes observed with charging time in 4340 steel⁽⁶⁾. Since surface changes are critical to positron trapping, we seek to minimize them.

Prior to this direction of work, D. Boice has acquired nickel data of the earlier type⁽⁶⁾ to complement same. These data will now be described.

Specimens of 304 stainless steel tubing involved in stress corrosion cracking were provided by Argonne Natl. Laboratory. Specimens were taken from the heat affected zone (HAZ) of a weld and from the base material. On the possibility that our ability to follow hydrogen effects with positron measurements might be useful on this problem, we examined these two specimen types. The results were positron lifetimes of 149 ± 4

psec for the HAZ and 156 ± 2 psec for the base material. The lower value in the HAZ could indicate hydrogen embrittlement, as in the case in Tables 1 and 2; however welded 304 stainless has many other metallurgical differences between itself and the base material than just dislocation density, hence a hydrogen diagnosis would be unwarranted as yet. One further check was made. If the HAZ behaved as did materials in Tables 1 and 2, additional hydrogen would further lower the positron lifetime. A 10 minute charging was given to each of the specimens with the following inconclusive results. The HAZ value became 150 ± 5 psec, i.e. no change, and the base material value became 160 ± 3 psec.

Some preliminary measurements were made on new nickel samples with the following results:

<u>Condition</u>	<u>Positron Lifetime (psec)</u>
Cold Rolled	187 ± 6
Cold Rolled + 10 min. charge	185 ± 6
Cold Rolled + 20 min. charge	196 ± 4
Cold Rolled + 30 min. charge	202 ± 4
Cold Rolled + 200°C anneal	174 ± 3
Cold Rolled + 300°C anneal	163 ± 3
Cold Rolled + 400°C anneal	155 ± 3
Cold Rolled + 500°C anneal	152 ± 3
Cold Rolled + 600°C anneal	147 ± 2
Cold Rolled + 700°C anneal	123 ± 2
Tension to fracture	188
Cold Rolled + 700°C anneal + sanded	140
Cold Rolled + 700°C anneal + 24 hrs. in H ₂ O	122 ± 2

Changes of interest are the high rise in lifetime with charging beyond 10 minutes contrary to the results of F. Alex. This will have to be checked further. The annealing sequence will be useful for later tension studies. The large increase due to gentle wet surface sanding is also interesting.

The tension studies mentioned on the previous page will be described in the accompanying renewal proposal.

1.4 Electron Microscopy

In addition to the TEM results discussed in section 1.3, considerable other efforts were made by R. LeHolm and D. Kramer in pursuing B.S. theses on the TEM of copper and nickel. After almost a year of effort on copper thinning with small success, one visit (by R. L.) was made to the TEM laboratories at U. C. Berkeley and Northwestern University. At the former about 60 copper specimens were thinned by the U. C. method and brought back for TEM examination. On deformed copper we are finally seeing real dislocation structures but results on annealed copper still need improvement. We have now ordered the jet apparatus recommended by Berkeley (manufactured by Fischone of Pennsylvania). This includes a photocell and lamp for quick detection of perforation. Our biggest problem has been polishing too long after first perforation. This new apparatus should solve that problem. LeHolm and Kramer will have this new apparatus operational before leaving the University of Utah this Fall.

1.5 Electron Irradiation

Please see Appendix A which will give a concise account of all the electron bombardment and annealing results. This account is in the form of a manuscript to be submitted for publication to Acta Metallurgica shortly.

1.6 Other Contract Activities

1.6.1 Two papers were delivered at the symposium on Positron Annihilation of the Annual Meeting of AIME in Las Vegas, February 22-26, 1976:

- A) Positron Studies of Fatigue Softening in Copper -
P. Alexopoulos and J. G. Byrne
- B) A Positron Lifetime Study of Electron Irradiated Single
Crystal Copper - T. D. Hadnagy, G. R. Miller and J. G.
Byrne

1.6.2 A contribution to the "Fourth International Conference on Positron Annihilation" August 23-26, 1976 in Helsingør, Denmark was presented. Its title is "Positron Studies of Fatigue, Hydrogen Embrittlement and Radiation Damage in Metals" by J. G. Byrne, P. Alexopoulos, P. Alex, T. D. Hadnagy, R. Waki, G. R. Miller and R. W. Ure.

1.6.3 J. G. Byrne was invited by AROD to review positron studies in connection with N.D.E. at the Sagamore Conference of August 1976 but the time conflict with item 1.6.2 above precluded acceptance.

1.6.4 J. G. Byrne was invited by Dr. Bill Hu of U.S. Steel on behalf of the Physical Metallurgy Committee of AIME to be a keynote speaker in the Fall 1977 AIME Symposium on Annealing. The subject is to be positron annihilation application to recovery, recrystallization and grain growth.

1.6.5 The paper "Positron Studies Made in Fatigue Damaged AISI 4340 Samples", by K. G. Lynn and J. G. Byrne was published in Metallurgical Transactions A, Vol. 7A, p. 604 (1976).

1.6.6 Written papers based on the oral presentations described under item 1.6.1 are in preparation.

1.6.7 The contribution to the 1975 Jackson Wyoming Hydrogen Conference has now been published in the proceedings of that meeting. The manuscript comprised Appendix A of last year's technical progress report ⁽¹⁾.

1.6.8 The remaining part of the Ph.D. Thesis of P. Alex is being prepared for publication in Metallurgical Transactions.

1.6.9 A patent application has been filed, with the consent of ERDA (Petition 87-6000 525-W), for "Positron Annihilation Measurements as a Nondestructive Technique to Monitor Hydrogen Embrittlement in Metals".

1.6.10 The College of Engineering in negotiating with the Terra Tek Company for a maintenance and instructional contract to better utilize our MTS fatigue tester. This could help our fatigue measurements.

1.6.11 A manuscript describing the earlier reported⁽¹⁾ work on porosity in Al_2O_3 has been submitted for publication in the Journal of The American Ceramic Society.

1.6.12 J. G. Byrne on just returning from the Denmark conference (item 1.6.2) is delighted to report that three plots from earlier work were included in the review talk of R. M. J. Cotterill on defects. These plots were the two from item 1.6.5 above on fatigue in 4340 steel and one from Acta Met. 22 (1974) 1075 on our grain size work. These citations were of a very complimentary nature and since they occurred in a general review before the entire group attending, they reflected very well on the ERDA research work here. The more current work presented at the meeting by this group also attracted considerable interest.

2. TIME INFORMATION ON PRINCIPAL INVESTIGATOR

Dr. J. G. Byrne, the principal investigator has spent one month full time during the summer of 1975 on this research. During the academic year 1975/1976 he has spent the equivalent of one month full time on this research (at no cost to ERDA).

Dr. R. W. Ure, Jr., Faculty Associate, spent one half of one month full time during the summer of 1976 and the equivalent of one half of one month full time during the academic year 1975/1976 on this research (the latter at no cost to ERDA).

REFERENCES

1. J. G. Byrne, COO E(11-1) 2128-12, Sept. 1975.
2. P. Alexopoulos and J. G. Byrne, AIME Annual Meeting, Las Vegas, (1976).
3. S. H. Moll and R. E. Ogilvie, INCO Seminar for the Steel Industry, Pittsburgh (1960).
4. R. M. J. Cotterill, I. K. MacKenzie, L. Smedskjaer, G. Trumpy and J. H. O. L. Traff, Nature, 239, 99, (1972).
5. K. Erhardt, R. M. N. Pelloux and N. J. Grant, AFML-TR-69-85 (1969).
6. F. Alex, Ph.D. Thesis, Univ. of Utah (1976).
7. W. Brandt, Proc. 3rd Intl. Conf. on Positron Annihilation, Springer, New York (1973).
8. T. D. Hadnagy, Ph.D. Thesis, Univ. of Utah (1976).
9. B. A. Wilcox and G. G. Smith, Acta Met. 13, 331 (1965).

FIGURE CAPTIONS

- 1.2.1 Fatigue cycling of cold-rolled copper at a maximum stress of 75% of its yield strength. Positron lifetime versus number of cycles.
- 1.2.2 Scanning electron micrographs from a region near the fracture location of a specimen of copper, cold-rolled, annealed at 200°F (93°C) one hour, and cycled at a maximum stress of 93% of its yield stress.
 - a. Subsidiary fatigue cracks at 24,000X
 - b. One subsidiary fatigue crack at 2500X
 - c. Void at 6200X
- 1.2.3 Fatigue of copper sample No. 6 initially at 750°F. Mean lifetime and X-ray particle size versus number of fatigue cycles.
- 1.2.4 Early stages of fatigue of copper sample No. 8 initially annealed at 750°F. Mean lifetime versus number of fatigue cycles.
- 1.2.5 Intensities of τ_1 and τ_2 versus number of fatigue cycles for sample No. 8.
- 1.2.6 Secondary lifetime, τ_2 , versus number of fatigue cycles for sample No. 8.
- 1.3.1 TEM of martensitic plates and laths, 4340 steel, heat treated to $R_c 43$, uncharged.
 - a. Positive print.
 - b. Negative print.
- 1.3.2 TEM of ferritic area of annealed 4340 steel, strained 6%.
- 1.3.3 TEM of cementite plates in a ferrite matrix of annealed 4340 steel, strained 12%.
- 1.3.4 TEM of cementite plates in a ferrite matrix of annealed 4340 steel, strained 19%.
- 1.3.5 Change in superficial hardness versus tensile strain for annealed 4340 steel.
- 1.3.6 Microhardness versus tensile strain for annealed 4340 steel.
- 1.3.7 Fraction of total annihilations of positrons versus penetration depth in iron.

- 1.3.8 TEM of martensite plates and laths of 4340 steel, heat treated to R_c 43, embrittled electrolytically with a "poisoned" H₂SO₄ solution, cadmium plated and stripped.
- a. Positive print.
 - b. Negative print.
- 1.3.9 TEM of 4340 steel heat treated to R_c 43, cadmium plated and stripped.
- 1.3.10 TEM of ferritic region of annealed and embrittled 4340 steel.
- 1.3.11 TEM of 22% strained and 40 minute embrittled ferrite region adjacent to cementite plate (upper center) in 4340 steel.

Figure 1.2.1

Figure 1.2.2a

Figure 1.2.2b

Figure 1.2.2c

Figure 1.2.3

Figure 1.2.4

Figure 1.2.5

Figure 1.2.6

Figure 1.3.1a

Figure 1.3.1b

Figure 1.3.2

Figure 1.3.3

Figure 1.3.4

Figure 1.3.5

Figure 1.3.6

Figure 1.3.7

Figure 1.3.8a

Figure 1.3.8b

Figure 1.3.9

Figure 1.3.10

Figure 1.3.11

APPENDIX A

Manuscript of paper to be submitted for publication in Acta Metall., based on the Ph.D. Thesis of T. D. Hadnagy.

POSITRON LIFETIME STUDIES OF ELECTRON IRRADIATED COPPER*

T. D. Hadnagy†, J. G. Byrne and G. R. Miller

University of Utah

Salt Lake City, Utah 84112

ABSTRACT

Single crystal copper has been irradiated at 80°K with 4.5 MeV electrons producing simple Frenkel defects as well as a significant concentration of divacancies. Mean positron lifetime characteristics, which are sensitive to the presence of vacancies and multivacancies in copper, have been monitored after isochronal anneals between 80°K and 800°K. A study of the dependence of the mean positron lifetime on the total electron fluence has been made and compared with existing theories relating these lifetimes to vacancy or multivacancy concentrations.

Numerical data from curve fitting procedures using a conventional trapping model for defect induced changes in positron lifetimes indicate that about 8% of the defects produced by the irradiation were divacancy units. Divacancy units appear to be several times more effective in trapping positrons than are monovacancies.

Further, the data suggest that stage III annealing processes in electron irradiated copper most probably involve the motion and removal

* Work supported by the United States Energy Research and Development Administration under contract E(11-1) 2128.

† Present address: Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

of both monovacancies and divacancies. A conglomerate (multivacancy) unit appears to exist as a stable entity even after annealing procedures are carried out at temperatures slightly above the stage III region. Such a stable unit could serve as a nucleation center for the appearance of voids.

INTRODUCTION

During the annealing of electron irradiated copper a defect is assumed to become mobile in a temperature regime designated as stage III (250°K - 325°K). The identity of the defect has long been the source of a great deal of discussion^{1,2}. Two models exist, the first one assumes that vacancy motion is responsible for stage III and the second assumes that the mobile defect is a di-interstitial. These models both assume that in stage I (below 80°K) interstitials migrate freely. The vacancy model assumes in stage I and III that interstitials are bound in stable clusters which are not free to migrate until well above stage III. The vacancy model further assumes that the mobile species for stage III is a monovacancy. The di-interstitial model assumes that the interstitials that cluster in stage I and II form a stable <100> dumb-bell which in turn migrates in stage III. Those vacancies remaining migrate at temperatures above the temperature range of stage III.

To differentiate between these two models on an experimental basis, a technique is required which is selectively sensitive to the presence and migration of vacancies or interstitials. Apparently positron annihilation experiments are quite insensitive to interstitial defects³ in metals but useful as a vacancy probe.

During the past few years, positron-annihilation experiments have been used to study vacancies produced from high temperature quenching,⁴ vacancies in thermal equilibrium, voids produced by neutron irradiation⁵, and

most recently Mantl and Trifthauser⁶ have used positron studies in electron irradiation and annealing studies. In the studies of Mantl and Trifthauser, Doppler broadening measurements of electron irradiated copper were carried out. In the work reported here, mean positron lifetimes have been studied as a function of fluence and isochronal annealing.

EXPERIMENTAL METHODS

A single crystal of 99.999 + pct copper was prepared in this laboratory by the Czochralski technique. From the boule a sample approximately 10 mm by 10 mm by 1 mm was cut using an acid saw. This procedure was used to minimize initial cutting damage since it is known that the presence of dislocations is detected by positrons⁷. The next step involved the electrochemical polishing of the surface. Finally, a small hole of 0.5 mm diameter was spark cut perpendicular to the short direction to a depth of about 6 mm with subsequent electrochemical polishing and sample annealing to 1000°K for 24 hours. Into the hole was placed a 50 μ Ci ²²Na source. The source was sealed into the hole by placing a small copper slab over the hole. With the sample sealed into a specially constructed dewar, all irradiations were done at 80°K with a 4.5 MeV electron beam from a Varian Model V7715 linear accelerator at the University of Utah. To monitor the damage for electrical resistivity, two Marz grade 0.08 mm copper wires measurements were placed near the sample, one in front and one behind the sample (with respect to the electron beam). These wires were used to assure that there was no damage gradient through the sample, and also to allow the monitoring of resistivity changes during irradiation

and isochronal anneals. (The size of the single crystal was too large to monitor its electrical resistivity directly and as a result, it was necessary to use these wires to gauge the change in the resistivity as a function of temperature.) Admittedly, the resistivity changes in the wire may not be the same as in the sample but it was hoped that the differences would be small.

All lifetime and resistivity measurements were made at 77°K and both were repeated at least twice to assure reproducibility. Lifetime measurements were performed on a system designed by Hall⁸. The system was constructed at the University of Utah with some modifications so as to allow measurement times of about 7-8 hours with a typical resolution of 295 picoseconds FWHM. The electronic system was temperature stabilized to $\pm 0.5^\circ\text{C}$ and runs which varied more than ± 5 psecs from a FWHM of 295 psecs were repeated.

Data analysis was done by a modified version of a program called PositronFit^{9,10}. Before irradiation the lifetime data was fitted to two exponentials. The sample yielded a primary mean lifetime 134 ± 8 picoseconds with a relative intensity of $96\% \pm 1\%$ and another lifetime of 575 ± 60 psecs with relative intensity of 3.3%. This second lifetime was attributed to the source, since, during annealing and all irradiations it was constant. Consequently it was subtracted out of all subsequent data. This procedure effectively yields a one lifetime fit to the remaining data from each anneal. At first this procedure was adequate but upon heavy irradiation or high temperature annealing it was found that a one lifetime fit did not adequately describe the effects observed. In these cases, a two lifetime fit was used with the source constrained at $575 \pm$ psec and relative intensity of 3.25 pct.

EXPERIMENTAL RESULTS

The first experiment was performed with two irradiation levels: one of 7.3×10^{18} el/cm² and after annealing the crystal to 770°K a second irradiation of 1×10^{18} el/cm² was performed. As can be seen in Figure 1, the behavior obtained from a two-lifetime fit, annealing after the first irradiation, showed less structure than annealing after the second irradiation. This was probably due to the first irradiation being well into the saturation region, a region in which the change in lifetime was very small for a large change in vacancy concentration. In both experiments one finds a decrease in the total relative intensity of the primary lifetime. This seems to indicate that there is now an additional lifetime for the positron in copper and that it manifests itself only after annealing. Figure 2 shows the second lifetime data for these two anneals. In this figure the large error bars in the beginning of the annealing experiment are due to the fact that only about 3% of the data was available to characterize the associated lifetime. As the intensity of this apparent second lifetime increases the scatter in the data decreases drastically. It should be noted that the two-lifetime fit procedure was motivated by the possibility of positrons annihilating in the ²²Na source. Upon annealing the sample, this second lifetime was seen to change in conjunction with the primary lifetime, changing both in intensity and value. This was strong evidence that these lifetimes were somehow related to one another. More importantly, it suggested that a new lifetime was growing and coupling with the first lifetime. The coupling was caused by the inability of the program to distinguish between the two lifetimes. At about 600°K the second lifetime

seems to reach a maximum in value. For emphasis, one should note that both of these lifetimes are mean lifetimes. The first is a mean of the lifetime associated with the free positron annihilating in the lattice and the positron annihilating in a bound state at a vacancy type defect. Another mean lifetime is associated with annihilation in the ^{22}Na source and whatever other possible annihilations are possible with longer lifetimes. Therefore in order to determine whether or not a two-lifetime fit would adequately characterize the data, the source lifetime was fixed and the data treated with a one-lifetime fit. This approach worked adequately in anneals after the first irradiation until about 450°K at which point the variance of fit became very large indicating that this model was inadequate. Subsequently, the data from the two experiments were processed with a two-lifetime fit with the source lifetime again held constant at 575 picoseconds. The first set of data revealed no new lifetime until 300°K at which point a lifetime of 250 picoseconds was seen to grow in intensity from 0% to 20% at 650°K. (See Fig. 3). Subsequent annealing caused this lifetime to decrease slightly.

Figures 4 and 5 show data for two irradiations of 7.3×10^{18} and 1×10^{18} el/cm² respectively. The second irradiation was performed after annealing out all apparent damage produced by the first irradiation as indicated by the first lifetime component, τ_1 . Figure 5 shows that upon the second irradiation, the 250 picosecond lifetime, τ_2 , appears throughout the annealing experiment but reaches its intensity maximum at 600°K rather than at 650°K was observed during annealing after the first dose.

At this time it was considered necessary to determine the mean primary lifetime as a function of fluence in order to produce a sample with greatest lifetime sensitivity to defects. The results of this series of experiments are shown in Figure 6. The lifetime data for a fluence around 1.0×10^{18} el/cm² seems to show an anomalously large increase in lifetime with a very small change in fluence, indicating that the primary lifetime itself is probably a conglomerate of more than two lifetimes. The effect of fluence on resistivity of the control wires is shown in Figure 7 indicating that the purity of the wire was not very high. The next irradiation was performed at a relatively high fluence (8.9×10^{18} el/cm²). The associated lifetime and resistivity curves are depicted as Figures 8 and 9. The coincidence of the increase in the primary mean lifetime and the decrease in resistivity at 250°K again bears out what the fluence curve indicated, i.e., the primary lifetime is a result of both monovacancy and multivacancy events. This behavior was seen again in a fourth irradiation. In this experiment, an attempt was made to irradiate to the inflection point of the mean primary lifetime - fluence curve. This was done to provide maximum sensitivity and structure in the annealing curves. Unfortunately, this series of measurements has also provided the greatest scatter in data. Data points were determined two or three times as the effect of annealing on the mean primary lifetime showed a great deal of erratic behavior. However, the characteristic growth of a second lifetime with the decrease of the primary lifetime was observed, the only difference being that the intensity maximum was reached at a lower temperature (Figure 10).

DISCUSSION

There are several models¹¹ in the literature which may be likened to the resistivity of the control wires as a function of fluence: unsaturable traps, nucleation traps and saturable traps. The latter model gave the best agreement. The relationship derived from the saturable trap model (the electron resistivity as a function of electron fluence) was introduced into the positron trapping models proposed by Bergeson, Stott,¹² Connors and West¹³. Such a procedure does not appear to satisfactorily predict the observed experimental behavior throughout the entire fluence region, however, it was possible to get excellent agreement in the region below 7×10^{17} el/cm², above 1.2×10^{18} el/cm² and in the central region. It was therefore felt that a single trap model did not adequately describe the data and that curve fitting should be attempted with a two-trap model. One plausible trap could be monovacancies and the second could be some type of multivacancy complex, most likely divacancies. Using Seeger's approach¹⁴ for two types of positron traps, one writes:

$$\bar{\tau} = \bar{\tau}_f \left(\frac{1 + \tau_{1v} \tau_{1v} C_{1v} + \tau_{2v} \sigma_{1v} C_{2v}}{1 + \tau_f (\sigma_{1v} C_{1v} + \sigma_{2v} C_{2v})} \right) \quad (1)$$

where: $\bar{\tau}_f$ is the mean positron lifetime in a perfect crystal

τ_{1v} is the mean lifetime in a monovacancy

σ_{1v} is the transition rate from a free state to a monovacancy trap

τ_{2v} is the mean lifetime in a divacancy

σ_{2v} is the transition rate from a free state to a divacancy trap

With a fitting program, it was possible to get rather good agreement with the data if, in this procedure, the following assumptions were made:

1. At the temperature of irradiation an unknown fraction, f , of the change in resistivity is due to divacancies and the remainder $(1-f)$ to monovacancies;
2. The trapping rate for a divacancy is much larger than for a monovacancy.
3. No detrapping of positrons from monovacancies or divacancies occurs once the positrons are trapped.

The fit to the data is seen in Figure 11. The parameters that gave the best fit were as follows:

$$\begin{aligned}\tau_{1v} &= 170 \text{ psec.} \\ \sigma_{1v} &= 2.5 \times 10^{14} \text{ sec}^{-1} \\ \sigma_{2v} &= 1.5 \times 10^{15} \text{ sec}^{-1} \\ \tau_{2v} &= 250 \text{ psec.,}\end{aligned}$$

The value for σ_{1v} and $f = 0.075$ is in excellent agreement with the work done by Corbett et.al.¹⁵ and McGervey and Trifthauser¹⁶. The value of τ_{1v} is the same as was observed by McKee and Kubica¹⁷ for thermally generated vacancies.

In order to get an adequate fit, the concentration, lifetime and trapping rate of divacancies were treated as floating parameters. It was assumed the defect responsible for τ_{2v} was present during all the anneals as well as during the irradiation. The only reason its characteristic lifetime was not observed immediately was either due to its low concentration or its "mixing with" τ_{1v} , and τ_f . Upon annealing, this lifetime was observed (became separable) and therefore some confidence may be had in the curve fitting which yielded it as one of the component lifetimes of $\bar{\tau}$.

The next step attempted was an analysis of the isochronal annealing data. The annealing spectrum that was observed had a great deal of structure and in order for one to gain a complete understanding of the behavior, isothermal anneals would be necessary, but were not carried out in this work. Nevertheless, it was possible to observe some very interesting behavior. If one studies the data from the first irradiation that was performed (total fluence of 7.3×10^{18} el/cm²) a new lifetime, designated τ_2 , appears in stage III (Figure 4). This lifetime is most likely associated with a new defect species. Even though it was only observable above room temperature it must have been present in low concentration before the annealing as indicated by the fluence measurements. The data acquisition system and the data analysis system did not allow for a unique extraction of this new lifetime. Since this new lifetime was so close to τ_f and τ_{1v} it must be coupled with them to give a mean lifetime, $\bar{\tau}$, that was a function of all three individual components, i.e., $\bar{\tau} = \bar{\tau}(\tau_f, \tau_{1v}, \tau_{2v})$ as in equation (1). This is supported by the fitting procedure carried out on the lifetime vs. fluence data. Once the concentration of vacancies was decreased to approximately 30 ppm by annealing there was very little contribution from τ_{1v} and the data decoupled into $\bar{\tau}_2 = [\tau(\tau_f, \tau_1) \text{ and } \tau_{2v}]$.

In fitting the fluence data it was necessary to introduce a viable for the concentration of divacancies in order to get good agreement with the data. Calculations done by Sosin and Brinkman¹⁸ indicate that at beam energies of 2.5 MeV, as much as 20% of the total damage might be in the form of divacancies. The value of 7.5% that came from the analysis therefore seems very reasonable. It is a well known fact that divacancies are more mobile than monovacancies and during the annealing process they

begin to migrate at lower temperatures. If one assumes that all remaining interstitials are trapped at imperfections, then a very inhomogeneous distribution of interstitials exists. Even though the interstitials are very localized, vacancies and divacancies are not. At the damage concentration for which most of the anneals were performed, (100 ppm), a divacancy would need only to migrate 50 lattice sites, on the average, to find a vacancy with which to combine. This resulting trivacancy (or higher vacancy multiple) is an energetically immobile species and would not anneal out until high temperatures are reached.

The only question that remains is that of the reasonableness of assuming that a divacancy and a trivacancy have experimentally unresolvable lifetimes. This would amount to saying that the electron density within a di- and trivacancy is the same and that what is really observed is a surface state in these multivacancies. Even though there have been some excellent calculations published recently on the effects of vacancies on the positron lifetimes in metals¹⁹, copper seems to behave in a manner different from most metals. For copper, the predicted bulk lifetime differs by 25 pct from experimental values, whereas for other metals the agreement with theory is excellent. It is quite possible that divacancies and trivacancies may prove to have the same lifetime. The calculations reported by Manninen et. al.¹⁹ are quantitative theoretical calculations done only on vacancies and there are presently no calculational results available for divacancies, trivacancies or other clusters.

Returning to the isochronal annealing data, let us further assume that those defects responsible for the lifetime component τ_{1v} have a higher migration energy than monovacancies. Assuming C_{mv} the concentration

of multivacancies is constant and C_{lv} has substantially decreased, one should observe a larger fraction of the positrons annihilating in multivacancy sites, with a lifetime characteristic of the multivacancy. With this behavior during annealing one would expect a net increase in $\bar{\tau}$ instead of a simple decrease until $\bar{\tau}_{mv}$ decouples from $\bar{\tau}$. Figure 8 shows exactly this behavior in stage III at about 250°K. If further we assume, with some justification from the fluence data, that $C_v \approx 8$ ppm and is stable and C_{lv} decreases to 40 ppm, a percentage decreases justified by the change in the resistivity, our expression for $\bar{\tau} = \bar{\tau}(\tau_f, \tau_{lv}, \tau_{mv})$ yields a mean lifetime of 192 which is within the errors of the experimental observations. One could continue this process and try to determine the behavior of the lifetime vs. isochronal temperature curve, but there are some problems with regard to trying to determine any numbers with confidence. The reasons for this have to do with the fact that the resistivity data was not taken on the same sample as the lifetime data. If this had been done it would allow one to make some very definite statements on the annealing behavior of vacancies and multivacancies.

It should be noted that the annealing of the second lifetime at about 500°K is in excellent agreement with measurements made by other researchers who have reported this temperature as that where void formation starts to decrease and voids begin to anneal out in copper²⁰.

SUMMARY

The irradiation of copper with electrons of 4.5 MeV yield a significant concentration of divacancies. These divacancies do not manifest themselves independently of monovacancies in resistivity data and are usually included in the total resistivity as simply more monovacancies. As a result of different local electron densities, divacancies and monovacancies have different characteristic lifetimes for positrons trapped in each defect. The models proposed by Seeger seem to adequately explain the observed change in lifetime. The values used to fit the data gave a trapping rate for divacancies that was about six times as large as monovacancies and a concentration of divacancies that was 7.5% of the monovacancy concentration for the irradiation conditions used here.

By controlling the concentration of defects, a change in the mean positron lifetime was observed. Thus one is able to study the behavior of vacancies and vacancy complexes via lifetime measurements.

By observing the change in lifetime during the latter part of stage III one may observe the nucleation stages of voids. We have observed the crucial temperature region that is the beginning stage of void formation. We can thus make some rather definite statements with regard to the state III dilemma. Stage III seems to be a region in which void formation is initiated and because there are a number of different species available for migration, a number of different activation energies are found in resistivity studies. With the available improvements in equipment and the addition of isothermal and isochronal annealing schemes, one should be able to determine the activation energies of multivacancies. In addition, one would be able to study the effects of impurities on void formation.

ACKNOWLEDGMENTS

The authors would like to acknowledge Professor A. Sosin for his encouragement and many helpful discussions during the course of this study. We also thank Professor F. Rosenberger of the University of Utah Physics Department for growing the copper single crystal.

REFERENCES

1. W. Schilling and K. Sonnenberg, J. Phys. F 3, 322 (1973).
2. W. Frank and A. Seeger, Radiation Effects 1, 117 (1969).
3. K. Petersen, Niels and R.M.S. Cotterill, Phil. Mag. 29, 9 (1974).
4. B.T.A. McKee, W. Trifthauser and A.T. Stewart, Phys. Rev. Lett. 28, 358 (1972).
5. O. Morgensen, K. Peterson and B. Hudson, Nature 239, 98 (1972).
6. S. Mantl and W. Trifthauser, Phys. Rev. Lett., 34, 1554 (1975).
7. K.G. Lynn, R.W. Ure, Jr. and J.G. Byrne, Acta. Met. 22 (9), 1075 (1974).
8. T.M. Hall, Nucl. Instrum. Methods, 117, 253 (1974).
9. K.G. Lynn, Ph.D. Thesis, University of Utah, Department of Materials Science and Engineering, (1973).
10. P. Kirkegaard and M. Eldrup, Computer Physics Comm. 3, 240 (1972).
11. R.M. Walker, Proceedings of the International School of Physics, Enrico Fermi Varenna, Academic Press, New York (1962) p. 594 ff.
12. B. Bergerson and M.J. Stott, Solid State Comm. 7, 1203 (1969).
13. D.C. Connors and R.N. West, Phys. Lett. 30A, 24 (1969).
14. A. Seeger, Phys. Lett. 40A, 135 (1972).
15. J.W. Corbett, R.B. Smith and R.M. Walker, Phys. Rev. 114, 1452 (1959).
16. D. McGervey and W. Trifthauser, Phys. Lett. 44A, 1 (1973).
17. Unpublished results, private communication.
18. A. Sosin and J.A. Brinkman in Properties of Reactor Materials and Effects of Radiation Damage, C.P. Haigh, ed., Butterworth Publishing, London (1962), p. 311.
19. M. Manninen, R. Niewinen, P. Gaatojarvi and T. Aropeneu, Phys. Rev. B12, 4012 (1975).
20. J.L. Brinshall, H.E. Kissinger and G.L. Kielcinski, Radiation Induced Voids in Metals, Proceedings of an International Conference, Albany, New York, 1971, J.W. Corbett and L.C. Zamiello, eds. (U.S. Atomic Energy Commission, Office of Information Services, Washington, D.C., (1972) pp. 338-375.

FIGURE CAPTIONS

- Figure 1 Primary lifetime and intensity for irradiation of 7.3×10^{18} el/cm² and 1×10^{18} el/cm² using a two-lifetime fit.
- Figure 2 Second lifetime for irradiation of 7.3×10^{18} el/cm² using two-lifetime fit.
- Figure 3 Intensity of second lifetime component for irradiation of 7.3×10^{18} and 1×10^{18} el/cm² using a two-lifetime fit.
- Figure 4 Primary lifetime and intensity of second lifetime component for irradiation to 7.3×10^{18} el/cm² using constraint $\tau_2 = 250$ picoseconds and source correction $\tau_s = 525$ picoseconds and $I_s = 3.25\%$.
- Figure 5 Primary lifetime and intensity of second lifetime component for irradiation of 1×10^{18} el/cm² using constraint $\tau_2 = 250$ picoseconds and source correction $\tau_s = 575$ picoseconds and $I_s = 3.25\%$.
- Figure 6 Primary lifetime as a function of fluence.
- Figure 7 Change of resistivity as a function of fluence.
- Figure 8 Primary lifetime and intensity of primary lifetime as a function of isochronal annealing temperature. Irradiation to 8.9×10^{18} el/cm².
- Figure 9 Change of resistivity as a function of isochronal annealing temperature.
- Figure 10 Primary lifetime and intensity of primary lifetime as a function of isochronal annealing temperature. Irradiation to 9×10^{17} el/cm².
- Figure 11 Best fit to fluence data using a two-trap model.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11