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COMMENTS ON STAGE III AND STAGE IV ANNEALING MECHANISMS IN MOLYBDENUM

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Abstract

Recent work on molybdenum giving evidence for interstitial and vacancy migration in stages III and IV respectively has been critically examined. Although the suggested annealing scheme is attractive, it is demonstrated that the evidence does not quantitatively support such a model. Alternatively it is argued that other investigations including recent positron annihilation studies point strongly to vacancy migration in stage III. In addition it is proposed that stage IV after neutron irradiation is due to the migration of some small vacancy cluster, possibly the trivacancy or tetravacancy.

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1. Introduction

The resistivity recovery of molybdenum after neutron irradiation, cold-work or electron irradiation, is characterized by a prominent stage, stage III, occurring in the region of 200°C. The equivalent stage in the f.c.c. metals has long been the subject of discussion [1] as to whether it was caused by a vacancy or interstitial type defect, and in the b.c.c. metals, particularly molybdenum, the same controversy has existed [2]. In recent papers Stals and Co-workers [3,4] have presented resistivity recovery data on cold worked and neutron irradiated molybdenum and conclude from their results that stage III recovery in molybdenum is due to the migration of interstitials. In addition,a higher temperature stage, stage IV at~300°C, is deduced to be due to the migration of single vacancies. Since free migration of interstitials is known to occur at temperatures well below stage III [5,6], the migration of interstitials in stage III involves the two-interstitial model [7].

The purpose of this present paper is to demonstrate that the main arguments of Stals et. al. [3,4] are not supported by their data. It is concluded that there are no major arguments to support interstitial migration in stage III in molybdenum. On the other hand there appear to be experimental results, including some recent positron annihilation data on annealing in neutron irradiated molybdenum [8], which point strongly to vacancy migration. These points are discussed fully in the following sections while a further section covers discussion of the stage IV defect.

2. Discussion of Arguments for Stage III Interstitial Migration

From their extremely well documented and careful data on neutron irradiation and cold work recovery in molybdenum, Stals et.al. have

produced several arguments to support interstitial migration in stage III. Their main argument - and one that invokes vacancy migration in stage IV - rests on the experimental result that for low defect concentrations in cold worked material, stage IV becomes greater in magnitude than stage III. The suggested reason for this is that at low deformations the ratio of cold work dislocations to point defects rises rapidly: as this happens the probability of the migrating stage III interstitial finding a dislocation sink, rather than a vacancy, rises thus leaving more vacancies available to migrate in stage IV. The argument is supported by the change in apparent order of kinetics from 2 to 1 as the point defect concentration drops. On a qualitative basis there is no reason to question these arguments but unfortunately, when one comes to look at the situation more quantitatively there are two separate reasons for casting serious doubts on the suggested mechanism.

The first reason, (a), concerns the very rapid rise in $\Delta\rho^{IV}/\Delta\rho^{III}$ ratio with drop in $(\Delta\rho^{III}+\Delta\rho^{IV})$ (where the $\Delta\rho$'s refer to the magnitude of resistivity drop in stages III and IV), the data of Stals et. al. being shown in Fig. 1. It will be demonstrated that such a sharp rise is almost impossible on their mechanism, even assuming the most favourable behaviour of the dislocation content at low deformations. The second reason, (b), concerns this dislocation behaviour and seriously questions the assertion that the ratio of dislocations to point defects rises as the amount of cold-work drops.

(a) From figure 1 taken from reference [4] it can be seen that the value of $\Delta\rho^{IV}/\Delta\rho^{III}$ increases from ~ 0.25 to ~ 1.6 for a drop of a factor of 5 in $(\Delta\rho^{III}+\Delta\rho^{IV})$ from ~ 5 to 1 n.f.c.m. To see if such values were comparable with the mechanism suggested by Stals et. al. a small computer program [a] was set up to anneal interstitials in the presence of vacancies and dislocations using simple rate theory. The dislocation

[a] Program is shown in appendix.

density was kept constant and did not drop with lowering deformation as might be expected in practice: the ratio of dislocation concentration to point defect concentration therefore rose very rapidly with drop in point defect concentration thus giving the best possible conditions to simulate the suggested mechanism. Various starting ratios of vacancy to interstitial concentration were examined for different values of an important parameter, the ratio of vacancy and interstitial specific resistivities, ρ_v/ρ_i. The results closest to the experimental data were those for equal starting concentrations of vacancies and interstitials. These are plotted in figure 2 for various values of ρ_v/ρ_i. The experimental result of a drop in $\Delta\rho^{IV}/\Delta\rho^{III}$ from 1.6 to 0.25 over a five-fold increase in $(\Delta\rho^{III}+\Delta\rho^{IV})$ is hardly approached even with the unrealistically high value of $\rho_v/\rho_i = 5$, and certainly not with the generally accepted value of $\rho_v/\rho_i \sim 1$. It must be concluded that it is rather difficult to theoretically simulate the experimental results of Stals' et. al. using their suggested mechanism. However, it may not be possible on such a basis to completely rule out the mechanism and we will therefore also consider reason (b).

(b) This concerns the experimental behaviour of the dislocation density as a function of initial point defect concentration. It seems to be a reasonable assumption for both neutron irradiated and cold-worked specimens, that the resistivity remaining after the point defect stages (i.e. III and IV) is due to the dislocation component. Also it seems reasonable to assume that this resistivity (which we can call $\Delta\rho_\perp$) is directly proportional to dislocation content. On this basis if Stal et. al's proposed mechanism for stages III and IV is correct then the ratio $\Delta\rho_\perp / (\Delta\rho^{III} + \Delta\rho^{IV})$ should rise sharply in the cold-worked case as the total resistivity ($\Delta\rho_t$) drops, while in the neutron irradiation case

there should be a slow rise in ratio with increase in $\Delta\rho t$. To test this, data has been abstracted from reference [3] and is shown in table 1 and figure 3. Both $\Delta\rho_t/(\Delta\rho^{\overline{III}} + \Delta\rho^{\overline{IV}})$ and $\Delta\rho_t/\Delta\rho^{\overline{III}}$ are considered. It seems quite clear from figure 3 that neither of the predictions are met and in fact the tendency for the cold-worked ratios to drop as $\Delta\rho_t$ becomes smaller is exactly the opposite to the behaviour required by Stals et. al.'s mechanism.

In the face of these two arguments it would seem very difficult to accept the assertion that the behaviour of $\Delta\rho^{\overline{IV}}/\Delta\rho^{\overline{III}}$ at low defect concentrations after cold work is evidence for interstitial migration in stage III and vacancy migration in stage IV. The only positive argument given by Stals et. al. for this annealing scheme is thus removed. There is even doubt about the apparent change of stage III order of kinetics from 2 to 1: however this is not too important in the present context and will be discussed elsewhere [9]. In their other arguments Stals et. al. concern themselves with other stage III/stage IV schemes, namely vacancies/divacancies, vacancies/di-interstitials and divacancies/vacancies, rather than with the stage III defect itself. There is no doubt that the nature of this defect is elusive since, as pointed out by Stals et. al., most stage III phenomena are equally well explained by vacancies and interstitials. However, there seem to be some experimental results which favour vacancy migration: these will be discussed in the next section before returning to the stage IV defect.

3. Arguments for Stage III Vacancy Migration

There seem to be three sets of experimental results which appear to favour vacancy migration in stage III rather than interstitial migration. These are as follows:

(a) From the work of Afman [5] and Evans [6] it is generally accepted that the retention of defects in molybdenum during electron irradiation below stage III is due to the trapping of interstitials at impurities. Electron microscope studies [10] have confirmed that small interstitial loops are formed during high dose electron irradiation of molybdenum at 77°K. Since it is well known that interatitial loops are formed during neutron irradiation and are particularly stable on annealing [11], it seems curious that the interstitial clusters formed in the electron irradiation case can break up and be responsible for stage III annealing. However even if break up did occur following perhaps the conversion to a second type of interstitial within the cluster, it would be surprising if an appreciable fraction of the released interstitials were not recaptured to form a stable loop. In such a case the amount of annealing in stage III after electron irradiation would be appreciably less than the induced resistivity while in addition a higher temperature stage should exist due to the vacancies surviving the interstitial migration. In fact almost all the electron irradiation induced resistivity is found to anneal in stage III and from the above arguments this can only be consistent with vacancy migration and not with interstitial migration.

(b) Afman [5] has examined the isochronal annealing behaviour in electron irradiated molybdenum as a function of impurity content and dose, and demonstrated that increasing both these parameters decreases the temperature at which stage III takes place. Only on a vacancy model can these observations be easily explained; on an interstitial model it is rather more difficult. Afman conclusively eliminates the case where the binding energy of the interstitial to its cluster is rate determining while he shows that only if unusual parameters are chosen can the results be explained by the free migration of vacancies.

(c) The most recent work, and potentially the most conclusive, is the positron annihilation study of the annealing stages in room temperature neutron irradiated molybdenum by Petersen et. al. [8]. In an isochronal anneal they have shown that a continuous rise in vacancy cluster component takes place over the 50° to 350°C temperature range. Such a rise is clearly compatible with the formation of clusters within the neutron induced depleted zones as a result of vacancy and/or divacancy migration, but would be extremely difficult to explain on an interstitial type migration mechanism.

From the foregoing arguments it appears to the present author that the experimental results strongly support the case for vacancy migration in stage III in molybdenum.

4. The Stage IV Defect

If it is now accepted from the previous two sections that vacancy migration and not interstitial migration is responsible for stage III then we are left with the problem of the stage IV defect. In their considerations involving vacancy migration in stage III, Stals et. al. [3] proposed two possibilities for stage IV namely divacancies or di-interstitials. In agreement with Stals et. al. both these can be eliminated, the divacancy on possible theoretical grounds together with the absence of stage IV after electron irradiation while the di-interstitial can be ruled out by exactly the same arguments as used in section 2 against vacancy migration in stage IV. Stals et. al. did not consider any other possibilities for stage IV and excluded extrinsic impurities at an early stage of their arguments. For neutron irradiation the exclusion of extrinsic impurities is reasonable since the resistivity drop in stage IV can be quite substantial - up to 50 nΩ cm. However in cold work $\Delta\rho^{\overline{IV}}$ ranges only from 0.5 up to 1 nΩ cm so that it seems conceivable that in this case the

stage could at least be partially due to the migration of interstitial impurities. From work on nitrogen in molybdenum [12] only ~10 at. ppm would be required to give a 1 nΩ cm recovery stage. The rapid rise of $\Delta\rho^{\overline{IV}}/\Delta\rho^{III}$ with decreasing cold work could then be simply explained by an almost constant stage IV together with a dropping intrinsic stage III.

Nevertheless from the neutron irradiation work some intrinsic stage IV must exist. Simply from the process of elimination it is suggested that this is probably some small vacancy cluster, either a trivacancy or a tetravacancy, neither of which was considered by Stals et. al. It is reasonable that such complexes are formed either directly during neutron irradiation or during the annealing of the depleted zones. The migration of simple clusters to form larger clusters within the zone is again consistent with the positron annihilation evidence [8] which shows cluster growth up to 350°C. In comparison with the neutron irradiation situation, the probability of cluster formation after cold-work or electron irradiation must be slight though it is not impossible that inhomogeneous defect distributions in cold-work could give a measurable stage IV. However on the basis of the present evidence it is preferred to allocate stage IV after cold-work to an extrinsic defect and after neutron irradiation to a small vacancy cluster migration.

5. General Conclusions on the Recovery Stages in Molybdenum

1. The behaviour of $\Delta\rho^{\overline{IV}}/\Delta\rho^{III}$ after small cold-work deformation cannot be used as an argument for stage III interstitial and stage IV vacancy migration. The major argument of Stals et. al. [3,4] for such a scheme is therefore removed.
2. It is argued from evidence in the literature that at least three experiments exist whose results can only be explained by vacancy migration in stage III.

3. It is proposed that a small vacancy cluster, perhaps the trivacancy or tetravacancy, is responsible for stage IV in neutron irradiated molybdenum.

4. There are indications, particularly from the magnitude of $\Delta\rho^{\overline{IV}}$ and the $\Delta\rho^{\overline{IV}}/\Delta\rho^{III}$ behaviour, that stage IV in cold-worked molybdenum might be partly due to interstitial impurities.

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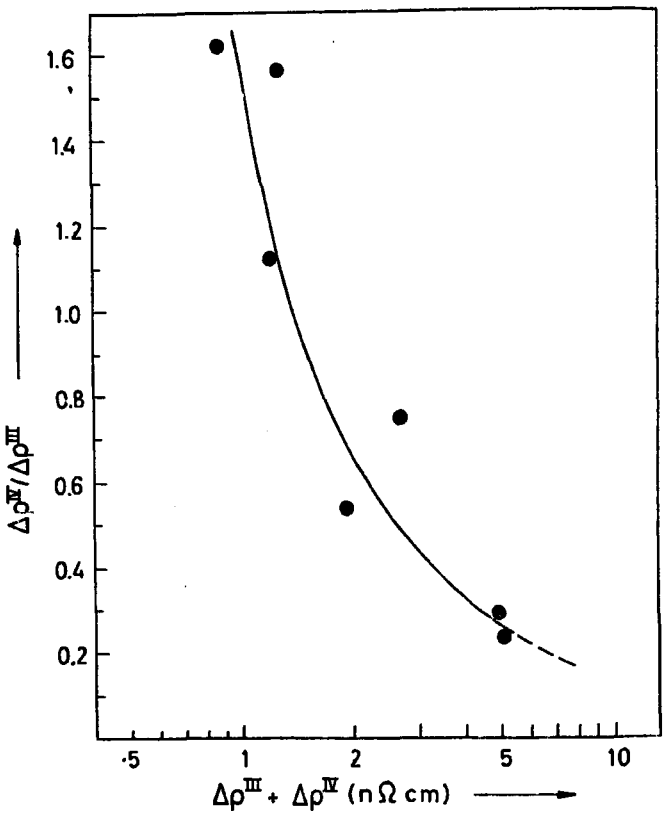

Figure 1. Experimental results taken from reference [4] showing the variation of $\Delta\rho^{IV}/\Delta\rho^{III}$ with $(\Delta\rho^{III} + \Delta\rho^{IV})$ for cold-worked molybdenum.

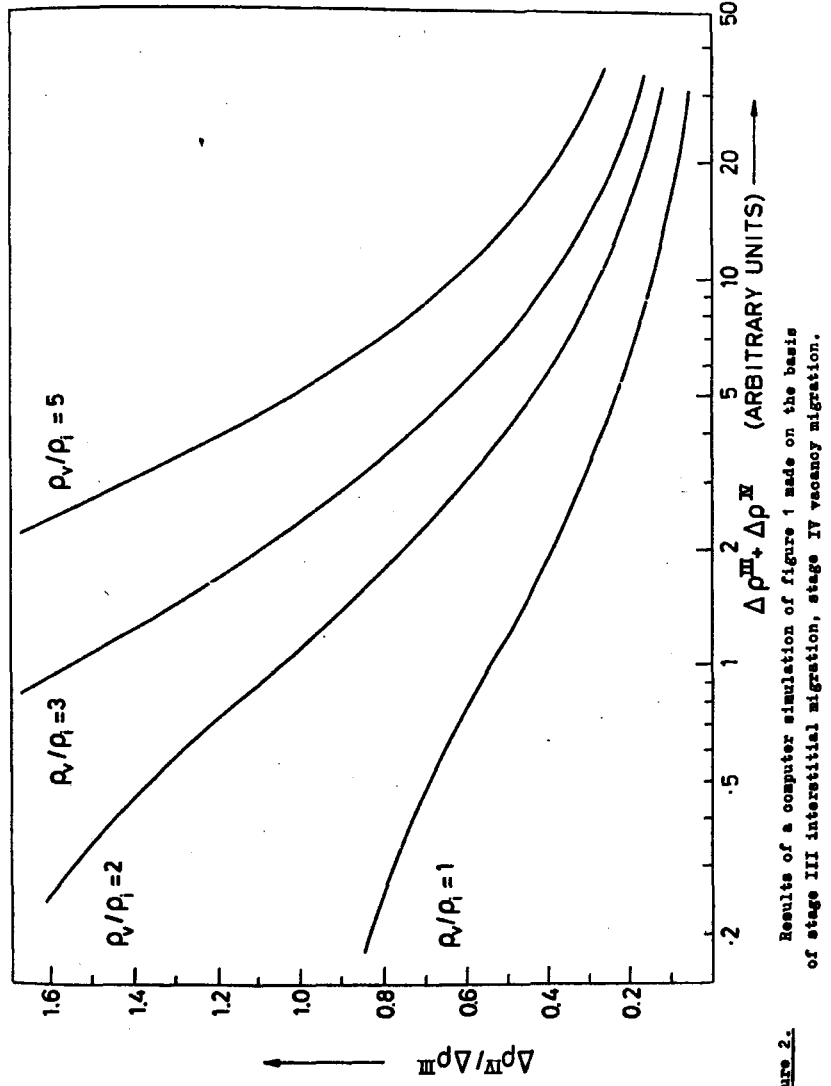

Figure 2. Results of a computer simulation of figure 1 made on the basis of stage III interstitial migration, stage IV vacancy migration.

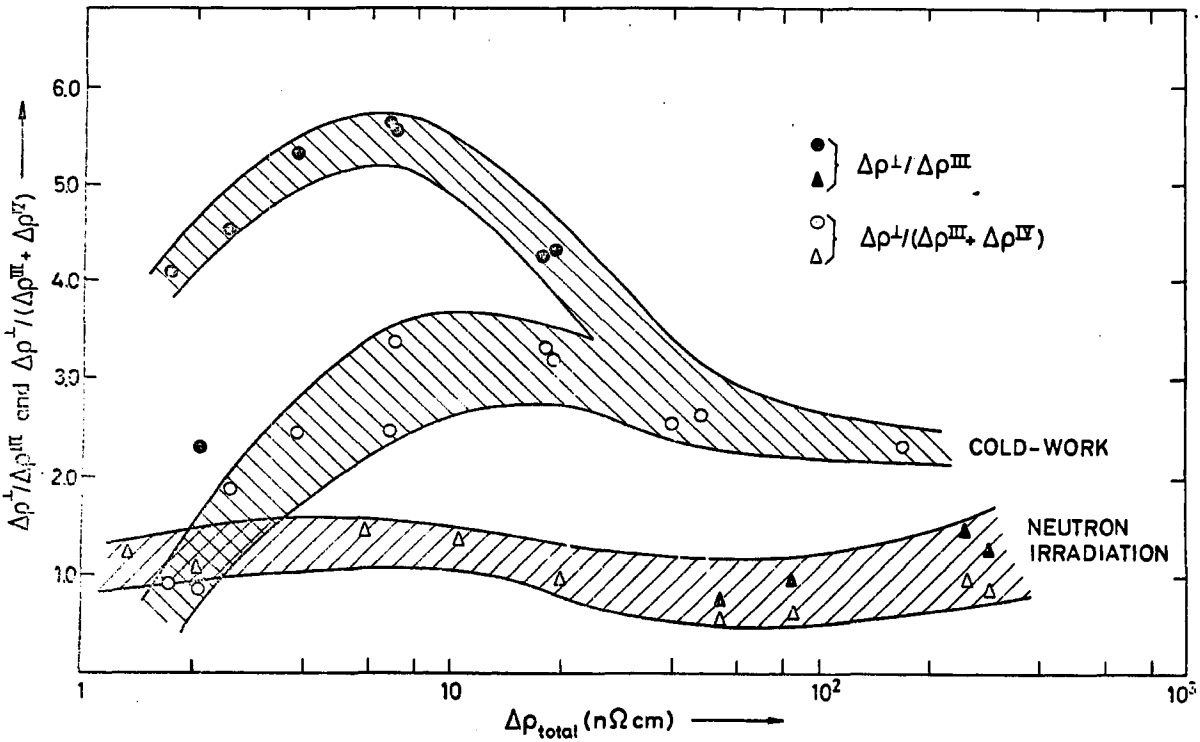

Figure 3. The variation in the ratio of dislocation to point defect resistivity with total induced resistivity. The data is taken from reference [3] and assumes $\Delta\rho_i^{III} = 2.\Delta\rho_i^{II}$ where (i) refers to the point of inflection.

Table 1 The table above values of parameters plotted in figure 3 based on data abstracted from reference [3]. (n = neutron irradiation, cw = cold-work)

Type of damage	$\Delta\rho$ total (n.Ω.cm)	$\Delta\rho^{III}$ (n.Ω.cm)	$\Delta\rho^{II}$ (n.Ω.cm)	$\Delta\rho^{II}+\Delta\rho$ (n.Ω.cm)	$\Delta\rho^{\perp}$ (n.Ω.cm)	$\frac{\Delta\rho^{\perp}}{\Delta\rho^{III}}$	$\frac{\Delta\rho^{\perp}}{\Delta\rho^{II}+\Delta\rho^{III}}$
n	294.16	108.0	51.8	159.8	134.36	1.24	0.84
n	252.73	84.0	45.6	129.6	123.13	1.46	0.95
n	86.95	37.0	14.8	51.8	35.15	0.95	0.60
n	84.36	35.0	11.1	46.1	40.26	1.15	0.87
n	64.70	25.0	8.6	33.6	31.1	1.24	0.92
n	54.06	25.0	10.0	35.0	19.06	0.76	0.54
n	31.86	12.0	4.1	16.1	15.76	1.31	0.98
n	19.85	10.6	--	10.6	9.25	0.87	0.87
n	10.49	4.4	--	4.4	6.09	1.38	1.38
n	5.86	2.4	--	2.4	3.46	1.44	1.44
n	2.05	1.0	--	1.0	1.05	1.05	1.05
n	1.33	0.6	--	0.6	0.73	1.22	1.22
cw	~170	52.2	--	52.2	~118	2.26	2.26
cw	47.89	13.2	--	13.2	34.69	2.63	2.63
cw	39.79	11.2	--	11.2	28.59	2.55	2.55
cw	19.07	3.4	1.1	4.5	14.57	4.28	3.24
cw	18.80	3.4	1.0	4.4	14.40	4.23	3.27
cw	7.07	0.98	0.64	1.62	5.45	5.56	3.36
cw	6.80	0.86	1.12	1.98	4.82	5.60	2.43
cw	3.76	0.50	0.60	1.10	2.66	5.32	2.42
cw	2.51	0.36	0.52	0.88	1.63	5.53	1.85
cw	2.05	0.40	0.72	1.12	0.93	2.32	0.83
cw	1.71	0.20	0.70	0.90	0.81	4.05	0.90

```
C     PROGRAM TO CHECK STALS ET AL'S STAGE 3/STAGE 4 ANNEALING MODEL

      IX=1
C     IX CONTROLS RATIO OF VACANCY TO INTERSTITIAL CONCENTRATIONS AT
C     START OF ANNEAL
      IY=2
C     CO = DISLOCATION SINK CONCENTRATION
      CO=1.0
      WRITE(6,2)

    2 FORMAT(1H ,29X,7HPV/PI=1,10X,7HPV/PI=2,10X,7HPV/PI=3,10X,7HPV/PI=5
     1/93H IX    I     CI     CVO     R3+R4    R4/R3     R3+R4    R4/R3
     2R3+R4    R4/R3     R3+R4    R4/R3 )
      DO 50 I=1,100
C     I CONTROLS STARTING INTERSTITIAL CONC RELATIVE TO DISLN CONCN
C     FOLLOWING LINES GIVE OUTPUT AT SUITABLE INTERVALS
      IF(I.GT.10)GO TO 10
      CI=0.1*FLOAT(I) *CO
      GO TO 20
   10 IP=I/10
      IF (IP.LT.IY) GO TO 50
      IY=IY+1
      CI=0.1*FLOAT(I) *CO
C     CV= CONCENTRATION OF VACANCIES.
   20 CV=CI+FLOAT(IX)
C     CVO = CONCENTRATION OF VACANCIES AT START
      CVO=CV
      DO 11 IA=1,100
C     ON EACH CYCLE 1/100TH OF THE INITIAL INTERSTITIAL CONCN ARE
C     PARTITIONED AMONG THE VACANCIES AND DISLOCATIONS ACCORDING
C     TO THEIR RESPECTIVE CONCENTRATIONS.
   11 CV=CV-(0.01*CI*CV/(CV+CO))
C     R3X = STAGE 3 RESISTIVITY DROP FOR SPECIFIC RESISTIVITY RATIO
C     RHO V / RHO I = X
      R31=CI*(1.0*(CVO-CV))
      R32=CI*(2.0*(CVO-CV))
      R33=CI*(3.0*(CVO-CV))
      R34=CI*(4.0*(CVO-CV))
      R35=CI*(5.0*(CVO-CV))
C     R4X = STAGE 4 RESISTIVITY DROP FOR EACH VALUE OF X
      R41=1.0*CV
      R42=2.0*CV
      R43=3.0*CV
      R44=4.0*CV
      R45=5.0*CV
C     R3PR4X = R3X + R4X
      R3PR41=R31+R41
      R3PR42=R32+R42
      R3PR43=R33+R43
      R3PR45=R35+R45
C     R4DR3X = R4X/R3X = RATIO OF STAGE 4/STAGE 3.
      R4DR31=R41/R31
      R4DR32=R42/R32
      R4DR33=R43/R33
      R4DR35=R45/R35
      WRITE (6,1) IX,I,CI,CVO,R3PR41,R4DR31,R3PR42,R4DR32,R3PR43,R4DR33,
     1R3PR45,R4DR35
    1 FORMAT(1H ,I2,I5,2F8.2,4(F9.2,F8.3))
   50 CONTINUE
      STOP
      END
```


IX	I	CI	CVO	PV/PI=1 R3+R4	PV/PI=1 R4/R3	PV/PI=2 R3+R4	PV/PI=2 R4/R3
1	1	0.10	0.10	0.20	0.839	0.30	1.554
1	2	0.20	0.20	0.40	0.731	0.60	1.288
1	3	0.30	0.30	0.60	0.652	0.90	1.110
1	4	0.40	0.40	0.80	0.591	1.20	0.981
1	5	0.50	0.50	1.00	0.542	1.50	0.882
1	6	0.60	0.60	1.20	0.503	1.80	0.805
1	7	0.70	0.70	1.40	0.469	2.10	0.742
1	8	0.80	0.80	1.60	0.441	2.40	0.689
1	9	0.90	0.90	1.80	0.417	2.70	0.645
1	10	1.00	1.00	2.00	0.395	3.00	0.607
1	20	2.00	2.00	4.00	0.270	6.00	0.396
1	30	3.00	3.00	6.00	0.211	9.00	0.303
1	40	4.00	4.00	8.00	0.176	12.00	0.249
1	50	5.00	5.00	10.00	0.152	15.00	0.214
1	60	6.00	6.00	12.00	0.135	18.00	0.188
1	70	7.00	7.00	14.00	0.121	21.00	0.169
1	80	8.00	8.00	16.00	0.111	24.00	0.153
1	90	9.00	9.00	18.00	0.102	27.00	0.141
1	100	10.00	10.00	20.00	0.095	30.00	0.131

PV/PI=3 R3+R4	PV/PI=3 R4/R3	PV/PI=5 R3+R4	PV/PI=5 R4/R3
0.40	2.170	0.60	3.177
0.80	1.727	1.20	2.375
1.20	1.450	1.80	1.920
1.60	1.257	2.40	1.624
2.00	1.116	3.00	1.415
2.40	1.007	3.60	1.259
2.80	0.920	4.20	1.138
3.20	0.849	4.80	1.041
3.60	0.789	5.40	0.961
4.00	0.739	6.00	0.894
8.00	0.469	12.00	0.549
12.00	0.355	18.00	0.410
16.00	0.290	24.00	0.333
20.00	0.247	30.00	0.282
24.00	0.217	36.00	0.247
28.00	0.194	42.00	0.220
32.00	0.176	48.00	0.200
36.00	0.162	54.00	0.183
40.00	0.150	60.00	0.169