POINT DEFECTS PRODUCED BY DEFORMATION IN Ti AND ITS INTERSTITIAL ALLOYS

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Introduction

Titanium and its alloys have been used in the aerospace, hydrospace and chemical engineering systems because of high strength/weight ratio and excellent resistance to corrosion. Oxygen, nitrogen and carbon are the major interstitial impurities existing in Ti and they are found to have strong interactions with dislocations. The mechanical properties of Ti-O, Ti-N and Ti-C alloys have been investigated by one of the present authors at low temperatures to furnish the detailed information on the interaction of dislocations and these interstitial atoms (for example. Ref. 1). At present, however, the knowledge is rather limited on point defects which are inevitably produced by plastic deformation and influence the mechanical and thermal properties of Ti through interactions with dislocations. The objectives of the present investigation are to study the deformation and annealing characteristics of Ti and its interstitial alloys and to obtain some basic properties of point defects produced by plastic deformation which may interact with interstitial impurity atoms.

Experimental Procedure

1.1 Materials and specimen preparation

Ti-O, Ti-C and Ti-N alloys were prepared with MARZ grade Ti, Ti O_2, C and TiN powders, respectively. Zone-refined MARZ Ti and 99.9% TiN were purchased from Material Research Corp., U.S.A., 99.96% Ti O_2 was from the Kantoh Chem. Co., Japan and spectroscopy grade C was from Kyoto University. They were melted in vacuum of less than 10^{-6} Torr with an electron beam. Zone-beam melted ingots were first swaged to 6mm diameter rods at room temperature and then homogenized in vacuum at 1073 K for 72 ks.

The interstitial contents of these alloys were analyzed by the Kjehdahl technique for N, vacuum fusion technique for O and combustion technique for C. The interstitial contents of these alloys and MARZ Ti are presented in Table 1.

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Table 1 Chemical Analyses of Ti and Alloys

Material	O	C	N	H	
MARZ Ti	63	78	6	4	Nom. ppm by wt
Ti-O	0.447				at.%
Ti-C		0.361			at.%
Ti-N			0.355		at.%

The increase in impurities except alloying element was within the same order of magnitude as as-received MARZ grade Ti.

Homogenized alloy rods and MARZ Ti of 6mm diam. rods were then swaged at room temperature to wires of 1.2mm diam. without any intermediate annealing. Commercial purity titanium rod supplied from Kobe Steel was swaged and then drawn to wires of 0.2 mm diameter, which were used as current and potential lead wires for electrical resistivity measurements.

MARZ Ti specimens were cut-off to 75 mm long and other alloy specimens to 50 mm long. These specimens were chemically polished to have 1 mm diam. in a solution of HNO_3 and HF to remove any surface contamination resulting from swaging and rinsed well under running water and dried. Two lead wires were spot-wleded at two ends of the specimen. The potential gauge length L and diameter D were measured with a Vernier caliper and a micrometer within accuracies of 0.01 and 0.005 mm respectively. The specimen size factor F is then calculated from

$$F = \pi(D/2)^2/L. \quad (1)$$

After determining the specimen size factor, the specimens were annealed in vacuum of less than 10^{-6} Torr at 1073 K for 3.6 ks and furnace-cooled at the expense of 36 ks. The resultant average grain sizes were about 40 μm.

1.2 Electrical resistivity measurement

A dummy specimen and a standard resistance of 0.1 Ω were connected in series with a specimen, the former being used for calibrating the temperature fluctuation of liquid nitrogen from time to time and the latter for measuring the current through the circuit. The usual reversing current procedure was followed to minimize the effect of thermal emf in the potentiometer and circuit. The combination of a Shimadzu PD-20 potentiometer with a Murayama GP-3 galvanometer and a Murayama GA-2 amplifier allowed to measure the resistivity within an accuracy of 2×10^{-10} Ωcm. The resistivities of the annealed specimens of MARZ Ti, Ti-C, Ti-O and Ti-N alloys measured at liquid nitrogen temperature were 5.9, 9.7, 9.4 and 9.6 μΩcm.

1.3 Plastic deformation

Plastic deformation of the specimens was carried out in an Instron-type tensile machine, Shinkoh TOM-200, which is illustrated schematically in Fig. 1 at the strain rate of 3×10^{-4} s^{-1} at 77 K. In the case of tensile tests to obtain the resistivity-strain relationship, a specimen was deformed in the tensile machine with potential and current leads attached to the terminals of the circuit for the resistivity measurements. First a specimen was strained to the pre-determined strain and then unloaded to measure the resistivity change, and further strained to another strain for the next measurement and so on. In other cases the deformed specimen in the chucks was taken off from the chuck holders and transferred to a box filled with liquid notrogen. Then the specimen was cut-off from the chucks in the box and transfered to the liquid nitrogen bath for electrical resistivity measurements.

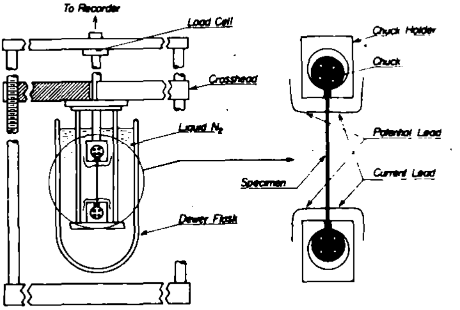


Fig. 1 Schematic of tensile test set-up

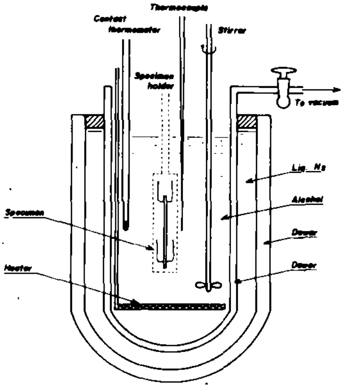


Fig. 2 Low temperature annealing bath

The resistivity change after deformation was computed in the following manner. The resistivity before deformation is given by

$$\rho_0 = R_0 \pi (D_0/2)^2 / L_0 \tag{2}$$

where R_0, D_0 and L_0 are the resistance, diameter and gauge length between two potential leads, respectively. After deformation the resistivity becomes

$$\rho = R\,\pi (D/2)^2 / L \tag{3}$$

where R, D and L are the resistance, diameter and the gauge length. Assuming no change in the density of the specimen during deformation one has

$$\Delta\rho = \rho - \rho_0 = \{(RL_0/R_0L) - 1\}\rho. \tag{4}$$

1.4 Annealing

Low temperature annealing, from 198 to 298 K, was carried out by immersing a specimen into a methyl-alcohol bath, which is schematically shown in Fig. 2. This bath was composed of two dewars whose inner dewar could be evacuated or opened to air. The coolant in the inner dewar could be cooled down to a desired temperature by liquid nitrogen stored between two dewars while the inner dewar was opened to air and then evacuated for keeping that temperature for at least 1 ks within $\pm$ 1 K. If necessary, the nichrome heater was used to raise the temperature of the coolant.

Higher temperature annealing was carried out using a water bath from 327 to 348 K, silicon oil bath from 373 to 548 K, fused sodium nitrate and potassium nitrate bath from 573 to 823 K and a vacuum furnace from 848 to 1073 K. Annealing temperature was measured with a Murayama potentiometer P-42 within an accuracy of 0.3 K. For annealing up to 348 K a specimen was transfered within 1 s exposure to air from the liquid nitrogen bath where the resistivity measurements were made to a certain annealing temperature bath. No serious additional annealing effect was observed during this transferring a specimen in air to the liquid nitrogen bath (thermal cyclings).

Experimental Results

2.1 Resistivity-strain relationship

The resistivity-strain relationship has been expressed by an emprical form of (2)

$$\Delta\rho = \alpha\varepsilon^n \tag{6}$$

where $\Delta\rho$ is the increase in resistivity, ε the plastic strain, α a constant and n the exponent which is 1 to 1.5 for the most fcc metal. The increase in resistivity due to plastic deformation at 77 K was measured for four materials as a function of strain, namely at 2, 4, 8, 10 and about 15%. These results are shown in Fig. 3, and can be described as

$$\Delta\rho = 7.5\varepsilon^{1} \quad \mu\Omega\text{cm for MARZ Ti,} \tag{7}$$

$$\Delta\rho = 11.3\varepsilon^{1} \quad \mu\Omega\text{cm for Ti-C,} \tag{8}$$

$$\Delta\rho = 14.4\varepsilon^{1} \quad \mu\Omega\text{cm for Ti-O} \tag{9}$$

and

$$\Delta\rho = 20.8\varepsilon^{1} \quad \mu\Omega\text{cm for Ti-N.} \tag{10}$$

Smith and Stagg (3) found that the resistivity was to recover even at the temperature of deformation (77 K). The amount of recovery was measured to be about 4% of the total increment for 24 ks and the half decay time was about 1.8 ks. Therefore, we determined the resistivity change after 1.8 ks annealing at 77 K. The pre-exponential factor α depends not only on the concentration of interstitial impurity but also its species. The present results indicate that the production of point defects increases according to the magnitude of the stress field of the interstitial atoms against dislocation motion (1). The detailed discussion will be given later.

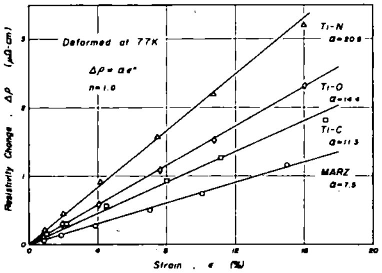


Fig. 3 Resistivity-strain relationship in Ti and its alloys

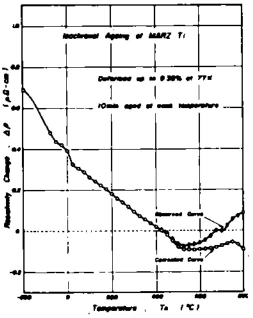


Fig. 4 Isochronal annealing curve for MARZ Ti deformed in tension up to about 9.4% at 77 K

2.2 Isochronal annealing

The recovery of electrical resistivity due to isochronal annealing for 0.6 ks period at every 25 K interval is shown in Fig. 4 for MARZ Ti which had been deformed in tension up to 9.38% at 77 K. In this isochronal annealing test a reference specimen which was fully annealed was measured its resistivity after annealed at each temperature similarly for 0.6 ks along with the deformed specimen. The purpose of having this reference specimen was to correct the resistivity change due to handling from the annealing bath to liquid nitrogen bath and to any oxidation during annealing especially at high temperatures, which has been claimed by Lucasson and Walker (4). The resistivities of the reference specimen increased with increasing annealing temperature. It is concluded from looking at the resistivity trend that this increase was due to oxidation of the specimen at high temperatures but not due to the thermal cycling between liquid nitrogen and annealing baths. Then the corrected curve was obtained by subtracting the resistivity of the reference specimen from that of the deformed specimen.

It is clearly shown that there are two remarkable recoveries in almost corresponding temperature ranges for the different interstitial impurities; one range is at about 270 K and the other range is between 270 and 310 K. The magnitude of recovery at 270 K is in the order of Ti-N, Ti-C, Ti-O and

MARZ Ti, while that at 270-310 K is five times larger in Ti-O than the recovery observed in the other alloys. Swanson (5) investigated the low temperature recovery of the resistivity produced by deformation of polycrystalline Zr at 4.2 K and found three recovery stages at 34, 190 and 310 K. Then it seems that the recovery peaks at 190 and 310 K correspond to those at 270 and 270-310 K in Ti and its interstitial alloys. Swanson also claimed that the peaks depend considerably on the interstitial impurity concentration.

At higher temperatures (310 to 773 K), there were no well-defined recovery stages. In order to clearly separate the recovery stages, the differential isochronal annealing curve is depicted in Fig. 5 for all of the materials. In the figure it is recognized that the gradual recovery from 310 to 773 K consists of four sub-stages, designated as stages c, d, e and f in the order of increasing temperature. The peak of stage f is not significant in Ti-O and Ti-N alloys. It seems also that the peak heights in stages c, d and e depend on the resistivity changes just after the deformation at 77 K. In the temperature range between 548 and 698 K the resistivities of four materials became smaller than before deformation and a minimum was exhibited at about 773 K. Then they increased gradually with increasing temperature. This phenomenon was also reported by Stanley et al. in V (6), by Williams et al. in Nb (7) and Hanada et al. in Ta (8). These investigators concluded that this resistivity increase was not due to the recovery of intrinsic defects but could be due to precipitation of interstitial impurity atoms onto dislocations and dissolution of interstitial impurity atoms from dislocations into the matrix upon heating.

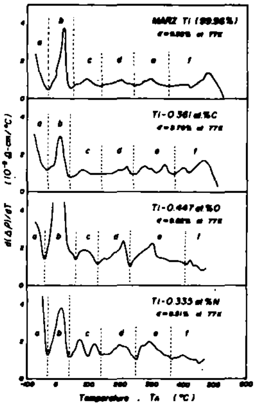


Fig. 5 Differential isochronal annealing curves for four materials deformed in tension at 77 K

2.3 Isothermal annealing

Isothermal annealings were carried out in order to determine the activation energies associated with stages a to f. If the migration of a certain species of defect is a thermally activated process with a single activation energy, E, the rate of annealing of this defect at temperature T (K) is generally assumed to be described by the equation of

$$dn/dt = -f(n)\ K_0 \exp(-E/kT) \qquad (11)$$

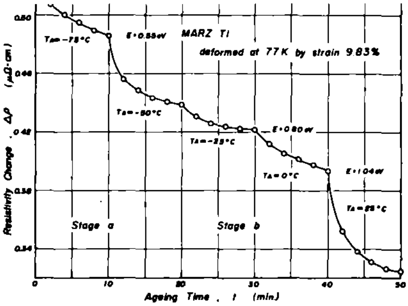
where n is the defect concentration, K_0 a constant and k the Boltzmann constant. If the resistivity change is a single-valued function of n, which is a reasonable assumption for sufficiently small n, then one has

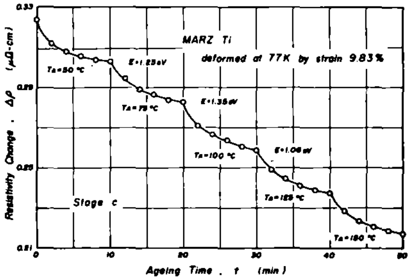
$$d\Delta\rho/dt = - f\ (\Delta\rho)\ K_0 \exp\ (-E/kT). \tag{12}$$

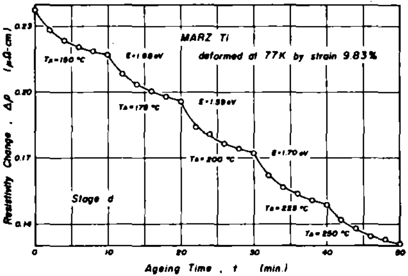
Using Eq. (12), the activation energies associated with each stage were determined by measuring the change in the slope of the isothermal resistivity-time curve with an interval of 25 K. The activation energy E was calculated from

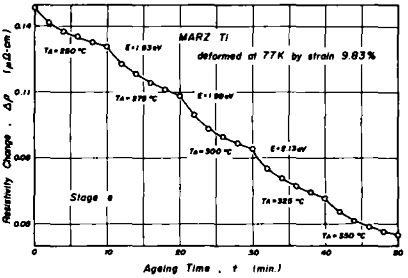
$$E = k(T_1T_2/\ (T_2 - T_1))\ \ln\{(d\Delta\rho/dt)_{T_2}/(d\Delta\rho/dt)_{T_1}\} \tag{13}$$

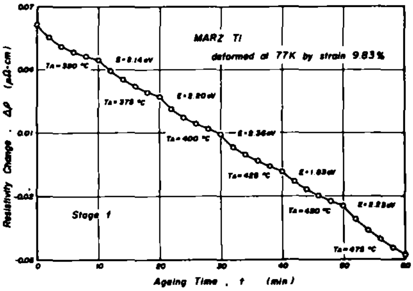
where $(d\Delta\rho/dt)_{T_1}$ is the final annealing rate at temperature T_1 and $(d\Delta\rho/dt)_{T_2}$ the initial annealing rate at temperature T_2. These results are shown in Figs. 6a to 6e for MARZ Ti as an example among others.











Figs. 6a to 6e Isothermal annealings for determining the activation energies at stages a to e in MARZ Ti deformed at 77 K in tension up to 9.83% strain

Activation analysis of the resistivity data gives the activation energies of the six stages of recovery for MARZ Ti, Ti-C, Ti-O and Ti-N alloys as given in Table 2.

Table 2 Activation energies of recovery in temperature range indicated of Ti and its alloys deformed to about 10% strain at 77K (eV)

Recovery Stage	MARZ Ti	Ti-C	Ti-O	Ti-N
a	238 K 0.55	243 K 0.59	233 K 0.56	243 K 0.56
b	238 to 313 K 0.80±0.15	247 to 313 K 0.76±0.15	233 to 333 K 0.77±0.15	243 to 363 K 0.72±0.15
c	313 to 411 K 1.22±0.15	313 to 413 K 1.22±0.15	333 to 403 K 1.28±0.16	313 to 411 K 1.21±0.15
d	413 to 513 K 1.66±0.15	413 to 513 K 1.60±0.10	403 to 503 K 1.63±0.15	413 to 513 K 1.48±0.15
e	513 to 618 K 2.02±0.11	513 to 638 K 2.11±0.13	503 to 618 K 2.05±0.12	512 to 618 K 1.93±0.15
f	618 to 773 K 2.36 to 1.83	638 to 773 K 2.44 to 1.31	No observation	No observation

Discussion

3.1 Production of point defects by plastic deformation

The factor α in Eq. (6) relates to the production rate of point defects per strain. As described in the previous section, it depends not only on the interstitial concentration but also on the species of interstitial impurity. Weyerer (9) showed that for Cu, Al and Fe there was a much higher rate of increase in resistivity for incompletely recrystallized wires that for those completely recrystallized. The rate of resistivity increase depends on the dislocation density of the specimen. In titanium and its alloys Conrad and Okazaki (10) found that dislocations are multipled by the double cross-slip mechanism and the interstitial impurities develop the stress centers in this mechanism. Larger stress fields about impurity atoms or higher densities of stress centers will result in greater dislocation densities. These higher dislocation densities result in the increased rate of production of point defects. The present results indicate that the magnitude of α increases in the order of the stress field strength (N, O and C).

3.2 Recovery stages

Although the recovery at 77K was not able to be measured in this investigation, we have observed a small increase in the flow stress due to strain ageing at 77 K. Smith and Stagg (3) have shown that the electrical resitivity of titanium stretched at 20 K was recovered about 20% up to 77 K. Swanson (5) noticed a recovery stage at 34 K for Zr deformed at 4.2 K and assigned that stage for the migration of point defects to oxygen atoms with the activation energies ranging 0.105 to 0125 eV. Then it appears that the resistivity recovery below 77 K in Ti and its interstitial alloys is due to the migration of intrinsic interstitial atoms produced by plastic deformation to annihilation sinks.

The amounts of recovery in stages a and b are directly proportional to strain, but when the interstitial impurity concentration is reduced to a half, the recovery amount is decreased only by 30% (see Fig. 7). This phenomenon is understood by the following argument; the amount of recovery in these stages is directly proportional to the resistivity change due to plastic deformation at 77 K. The amount of point defects produced by deformation depends on dislocation density. Conrad et al. (11) found the square root of dislocation increases linearly with the square root of strain. When the interstitial impurity concentration C is reduced to a half, the concentration of impurity on the slip plane of dislocations is then reduced to $(C/2)^{1/2} = 0.7C^{1/2}$. Therefore the probability that dislocations leave the original slip plane and multiply by the double cross-slip mechanism is reduced to 70%, and thus the amount of point defects produced by plastic deformation is reduced to 70%.

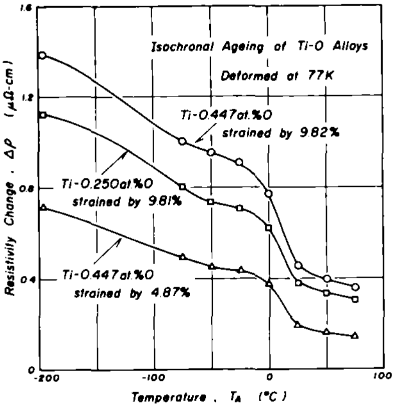


Fig. 7 Effects of strain and interstitial concentration on the recovery.

The stages a and b thus concern with intrinsic point defects produced by plastic deformation notwithstanding interstitial impurity concentration dependence. All the intrinsic point defects have been recovered up to the end of stage b, since the resistivity change Δρ happened to exhibit an identical value in all the materials. Therefore the stages a and b would be assigned to the recovery of intrinsic point defects but not to single intrinsic interstitial atoms.

The reported activation energies of self-diffusion in alpha-Ti are 2.6 eV estimated from stress-rupture by Dorn (12), 2.45 eV from creep by Conrad et al. (13) and 2.43 eV from grain growth kinetics by Okazaki et al. (14). There is only one reported value for the formation energy of a vacancy in Ti to be 1.55±0.15 eV from specific heat measurements by Shestopal (15). Then, the migration energy of a vacancy may be deduced from these values to be 0.8 to 1.05 eV. As shown in Table 2, the activation energy in stage b is approximately 0.9 eV which is in the range of 0.8 to 1.05 eV deduced above. Therefore the recovery in stage b is more likely due to the migration of single vacancies.

If the migration of a specific defect is a thermally activated process with an activation energy E, the jump number n required to reach to sinks is given by

$$n = t\nu Z \exp(-E/kT) \qquad (14)$$

where t is the time required to reach sinks, $\nu(\simeq 10^{13}/s)$ the vibrational frequrency of atoms and Z(=12) the coordination number. From the result of isothermal annealing of MARZ Ti at 270 K in stage b, the half decay time of 3.6 ks is adopted as the value for t. E is reasonably assumed to be 0.8 eV. Then the number of migrating jumps is calculated to be 500. This result shows that the sinks for single vacancies should be in the neighborhood of them, namely impurity atoms must be the sinks.

As the resitivity of the specimen annealed in the temperature range of 548 and 698 K becomes smaller than that of the original undeformed specimen, it is thought that interstitial impurities have migrated to dislocations below this temperature range. If each interstitial impurity migrates in Ti, the migration energy in the corresponding stage is equal to the diffusion energy of respective interstitial impurity atoms and the peak height in each stage depends upon the individual impurity concentration. The reported values of migration energy for O in Ti are 1.45 eV by Roe et al. (16) and 1.61 eV by Okazaki et al. (17), those for C are 1.89 eV by Wagner et al. (18) and 1.82 eV by Okazaki et al. (19) and those for N are 1.97 eV by Maykuth et al. (20) and 2.00 eV by Okazaki et al. (21). The activation energies obtained in stages d and e are rather are rather close to those for C and N respectively, however, the peak heights do not correspond to the interstitial impurity concentrations in these alloys. Therefore it is expected that three interstitial impurity atoms C, O and N recover in a complicated manner in stages c to e.

Okazaki et al. (14) found that MARZ Ti begins to recrystallize at 673 K, indicating that dislocations recover below this temperature. Therefore the stage f can be assigned to the dislocation recovery, if the activation energy for this stage is equal to the self-diffusion energy in Ti. In the present case, however, the recovery of dislocations in this stage involves the dissolution of interstitial impurity atoms which have migrated onto dislocations at lower temperatures into the matrix again, the apparent energy in this stage resulting in a smaller value than that expected from the self-diffusion energy.

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