THERMALLY ACTIVATED DEFORMATION IN Ti 1% Si AND Ti 5%Zr 1%Si

H.M. Flower, P.R. Swann and D.R.F. West
Department of Metallurgy
Imperial College
London, S.W.7

Synopsis

An investigation has been made of the deformation characteristics of Ti-1wt%Si and Ti-5wt%Zr-1Wt%Si alloys in the range 77°-973°K; martensite structures and aged structures containing silicide particles were studied. Silicon and zirconium were found to produce substantial strengthening of martensite structures up to 850°K and the martensitic ternary alloy can be strengthened significantly by silicide precipitation. The binary alloy shows strain ageing at 750°K to an extent depending on the concentration of silicon in solution. From activation analysis the rate-controlling mechanism of thermally activated deformation in both alloys up to 400°K was found to be the overcoming of interstitial barriers.

Introduction

Deformation mechanisms in α-titanium have been studied by various workers, e.g. (1,2) and it has been reported that below ~0.4 Tm the step which controls the rate of deformation is the thermal activation of dislocations moving on $\{10\bar{1}0\}$ planes over interstital atom barriers. There appears however to have been little study of the operative mechanism of thermally activated deformation of martensitic α'titanium alloys.

The present results concerning Ti-Si and Ti-Zr-Si alloys form part of a wider study of alloys in the Ti-Al-Zr-Mo-Si system: in

alloys of this complex system small amounts of silicon (typically 0.5% or less) contribute significantly to the mechanical properties at elevated temperatures. In previously reported work (3) it was shown that precipitation of $(TiZr)_5Si_3$ occurs on ageing martensitic titanium-silicon and titanium-zirconium-silicon alloys containing 1% silicon at 823°K(550°C). In the binary alloy the age hardening effect is very small because of the unfavourable precipitate dispersion and the loss of solid solution strength by depletion of the matrix in silicon. In the ternary Ti5%Zr1%Si alloy ageing at 823°K gives a greater hardening, associated with the matrix nucleation of G.P. zones and their transformation to the equilibrium precipitate. The work reported here is aimed to correlate structure with strength over a wide temperature range and to determine the rate-controlling deformation mechanisms by using activation analysis.

Experimental methods

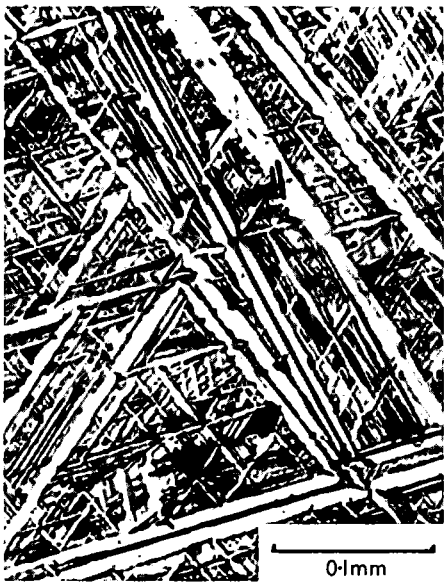
The alloys were prepared by arc melting using high purity sponge titanium and zirconium and semiconductor grade silicon. The oxygen and nitrogen content of the sponge titanium is typically <~500 ppm. The specimens, in the form of rod approximately 1 cm in diameter, were wrapped in molybdenum foil, sealed under argon in silica capsules and given a solution/homogenisation treatment of 24 hours at 1473°K(1200°C). The specimens were then water quenched to produce α'martensite, the capsules being broken on contact with the water. Compression specimens 2.5 mm square and 6 mm in length were cut from the rods using an oil cooled carborundum slitting wheel. The surfaces were lightly polished and some specimens were aged to peak hardness at 823°K in argon filled pyrex capsules (3000 minutes for Ti1%Si, 4000 minutes for Ti5%Zr1%Si).

Compression testing was carried out over a range of temperatures between 77°K and 973°K(-196°C and 700°C) using an Instron testing machine with specimen rigs which are described elsewhere (4). Specimens tested above 800°K were protected from oxidation by passing a slow, continuous stream of high purity argon through the specimen chamber. The initial crosshead speed was $\sim 8 \times 10^{-7}$ m/sec giving a strain rate of approximately 10^{-4} sec^{-1}. In the immediate post yield region the strain rate sensitivity was measured by increasing the strain rate by a factor of ten. At room temperature stress relaxation tests were also carried out. The activation volume and activation enthalpy were calculated employing the methods used by Conrad(1).

Results

The microstructures illustrated in Figure 1 are described in detail elsewhere (3,5). Essentially, the martensitic structures

a) Light micrograph of Ti1%Si after water quenching from 1200°C.



b) Light micrograph of Ti5%Zr1%Si after water quenching from 1200°C.

c) The precipitate dispersion in Ti1%Si aged to peak hardness at 550°C.

d) The precipitate dispersion in Ti5%Zr1%Si aged to peak hardness at 550°C.

Fig. 1.

consist of highly dislocated plates which exhibit a partly massive morphology in binary alloy; the aged binary alloy contains heterogeneously nucleated Ti_5Si_3 rods lying in the <11$\bar{2}$0> directions, whereas the aged ternary alloy contains a high density of matrix nucleated G.P. zones together with a small proportion of $(TiZr)_5Si_3$ precipitates.

The variation of the 0.1% proof stress (0.1%p.s.) with temperature is shown in figure 2(a) and 2(b) for the unaged and aged alloys respectively. Data obtained by Winstone (6) from quenched unalloyed titanium of similar purity as that used in making the alloys are also included. The specimens tested at the highest temperatures necessarily undergo some ageing during the test since approximately twenty minutes were required to achieve temperature stability and to carry out the test. In both of the unaged alloys (Figure 2(a)) the proof stress is a sensitive function of temperature below 500°K and above 850°K. Over almost the entire temperature range the 0.1%p.s. of the ternary alloy is ~150 MN m^{-2} greater than that of the binary alloy which itself is ~ 200 MN m^{-2} greater than that of the unalloyed martensitic titanium. The binary alloy has essentially the same form of 0.1%p.s./temperature relationship in both the aged and unaged states (cf figure 2(a) and 2(b). However the aged ternary alloy exhibits a significant increase in 0.1%p.s.(20%) over the as quenched material in the temperature range 150-700°K. Above 700°K the strength of the aged alloy drops rapidly and approaches that of the as quenched material at 850°K. Since testing at these temperatures inevitably involves some additional ageing, two specimens, aged to peak hardness, were further aged for 30 minutes at 870°K and were then tested at room temperature. The results are included in figure 2(b). The additional ageing produces a slight increase in 0.1%p.s. thus indicating that the loss in strength at 870°K is not due to overageing.

The stress-strain curves from unaged Ti 1%Si tested at 750°K exhibited a series of small (2-4 MN m^{-2}) intermittent serrations in the post yield region. Much larger serrations (10 MN m^{-2}) could be produced upon restraining after stopping the crosshead for some minutes during the test: these serrations died away to the smaller and intermittent serrations previously observed. Aged specimens of the binary alloy produced small serrations only after stopping the crosshead for prolonged periods (10 minutes). The ternary alloy did not exhibit serrated flow at any temperature.

Values of the activation for deformation (V*), calculated from the strain rate sensitivity, are presented in Figure 3; V* is given in dimensionless units obtained by dividing by b^3 where b is the Burgers vector of the 1/3<11$\bar{2}$0> dislocations. At 950°K and below 600°K identical results were obtained (within the limits of experimental accuracy) for both alloys, aged and unaged. In the intervening temperature range the activation volume of all except the aged ternary alloy rose to extremely high values indicating that

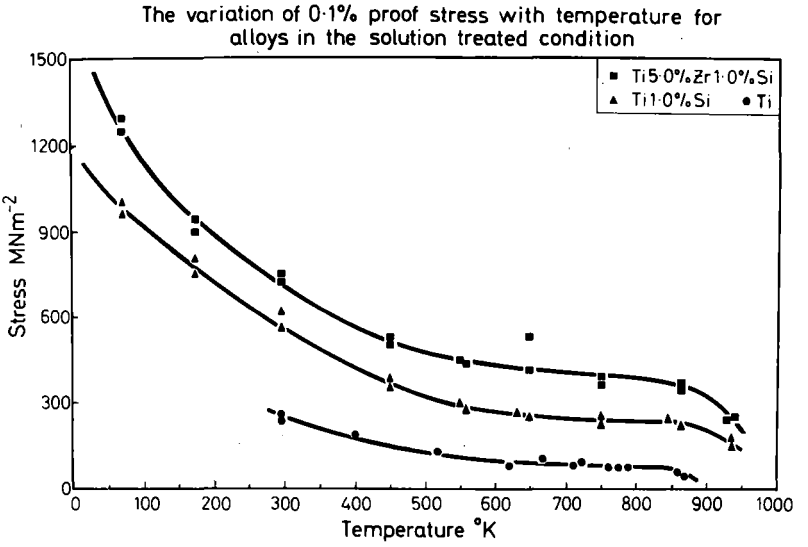


Fig. 2a. The variation of 0.1% proof stress with temperature for alloys in the solution treated condition.

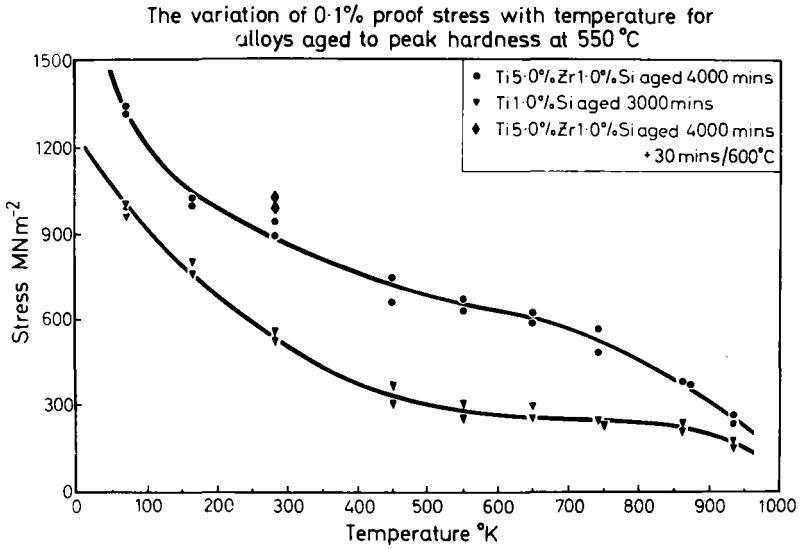


Fig. 2b. The variation of 0.1% proof stress with temperature for alloys aged to peak hardness at 550°C.

the deformation is not thermally activated. As a check, the activation volume was also calculated at room temperature from stress relaxation tests using the method described by Evans and Rawlings (7). These results, together with those obtained by the change of strain tests are presented in Table I and show excellent agreement.

Table I

Values of Activation Volume, V^*/b^3 at Room Temperature

	Stress relaxation	Strain rate sensitivity
Ti 1% Si		
Unaged Specimen A	21	27
" " B	19	21
Aged Specimen A	21	21
" " B	21	23
Ti5%Zr1%Si		
Unaged Specimen A	23	25
" " B	23	24
Aged Specimen A	26	24
" " B	25	24

The thermal component of the 0.1%p.s. (σ^*) was determined for both the aged and unaged alloys by extrapolation of the linear part of the stress/temperature curve (corresponding to the "athermal" deformation range) and subtracting the "athermal" component so obtained from the 0.1%p.s. In the temperature range 77 to 350-400°K the thermal component of the flow stress was found to be linearly related to the square root of the absolute temperature. The linear portion of the $\sigma^*/T^{\frac{1}{2}}$ graph extrapolates to $\sigma^* = 0$ at 425-450°K: this is approximately 100°K less than the temperature at which σ^* extrapolates to zero in Figure 2. However the latter value is of limited accuracy only as a result of the limited number of 0.1%p.s. measurements made in the temperature range over which σ^* approaches zero.

The graph of V^* as a function of $\tau^*(\frac{1}{2}\sigma^*)$ (figure 4) shows the same relationship for both alloys and heat treatments. Extrapolation of the linear portion of the plot at high stresses back to $\tau^* = 0$ gives a value of 30 for V^*/b^3 which agrees closely with values reported for titanium containing only interstitial solutes (1,2,8).

Values of activation enthalpy and total activation enthalpy are presented in figure 5. The scatter above 400°K is due to the

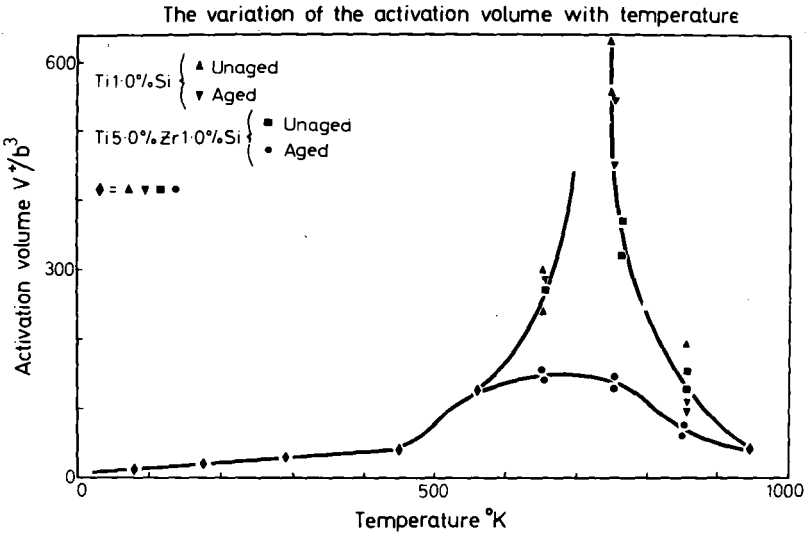


Fig. 3. The variation of the activation volume with temperature.

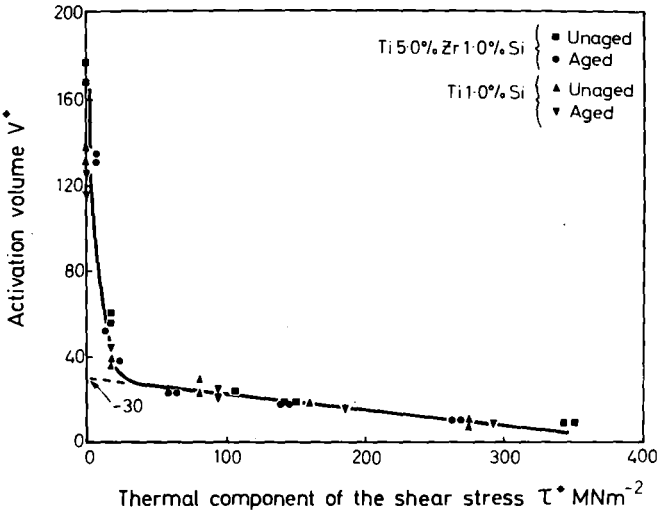


Fig. 4. The variation of activation volume with thermal component of the shear stress.

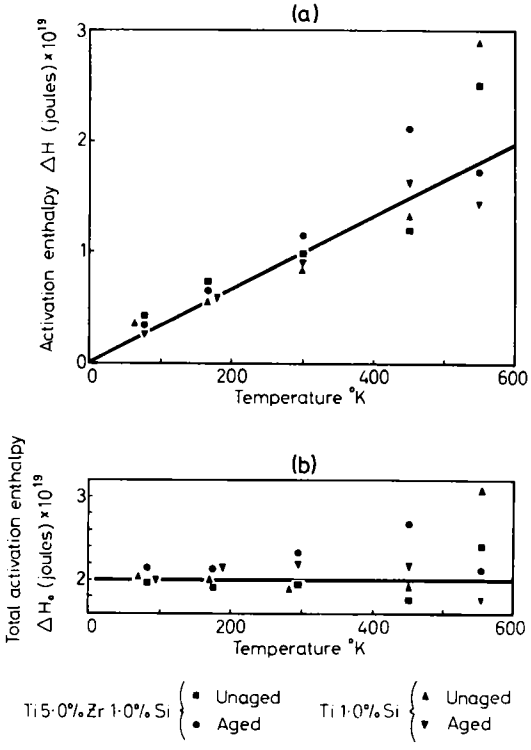


Fig. 5. a) The variation of activation enthalpy with temperature; b) The variation of the total activation enthalpy with temperature.

difficulty of evaluating accurately the gradient of the τ^*/temperature curve above this temperature where σ^* is very small. The total activation enthalpy is similar for both alloys and heat treatments and is equal to 2.10^{-19} joules $atom^{-1}$ or 1.25 eV, which is identical to that reported previously for titanium containing interstitial solutes (2).

Discussion

The serrated yielding observed in the binary alloy is a manifestation of strain ageing. Since the aged binary alloy, whose matrix is solute depleted by precipitation, exhibited a much smaller tendency to serrated yielding than did the unaged alloy it appears that the amplitude of the strain ageing is a function of the concentration of silicon in solution at 750°K. Recent work by Winstone et al (9) on samples with oxygen and nitrogen levels in the range ~1000-1500 ppm has shown that the oxygen content also affects the strain ageing, so that some silicon-oxygen interaction may be involved. The absence of strain ageing in the ternary alloy may indicate that the silicon atoms are less mobile, possibly being trapped in zirconium silicon clusters: such clusters may act as the nuclei of the G.P. zones observed to form in this alloy, although there is insufficient evidence to substantiate this suggestion.

The insensitivity of the 0.1%p.s. to changes in strain rate (with consequent large values of V^*) in the temperature range 550°K to 800°K indicates that the deformation is athermal at these temperatures; a possible exception is the aged ternary alloy for which the activation volume rises only to 150 b^3: if in this case the deformation is still thermally activated above 550°K a possible deformation mechanism would be the interaction of dislocations with the G.P. zones present in the aged alloy. In all cases the deformation is thermally activated above 800°K.

The observation that the activation volume and enthalpy results are similar for both alloys and heat treatments indicates that the same thermally activated deformation mechanism is rate controlling in all cases in the temperature range 77-400°K. In the range 400-550°K the deformation is still thermally activated but the limited number of results in this temperature range do not permit the identification of the mechanism although the breakdown of the linear relationship between σ^* and $\tau^{\frac{1}{2}}$ implies that the mechanism is different from the operating below 400°K.

The present results, including the linear $(\sigma^*)^{\frac{1}{2}}$/temperature relationship, are almost identical to those obtained by Conrad and co-workers (1,2,8) who employed similar methods to study titanium containing interstitial elements only. This suggests that the same rate controlling mechanism for deformation is operative for the range

of microstructures shown by the alloys studied in this work (with the possible exception of the aged ternary alloy which exhibited a relatively small activation volume in the "athermal" deformation temperature range): according to Conrad the mechanism is one of the overcoming of interstitial atoms by mobile dislocations on the $\{10\bar{1}0\}$ planes.

It should however be noted that the methods of activation analysis used in this work and the quoted references of Conrad and his co-workers assume (i) that the temperature region of negligible strain rate sensitivity is a region of athermal deformation and (ii) that the athermal component of the flow stress varies linearly with temperature as a result of the temperature dependence of the shear modulus. Both these assumptions have been questioned recently (10,11).

Conclusions

1. Silicon and zirconium both produce substantial strengthening in martensitic titanium up to 850°K. The binary Ti1%Si alloy has a negligible ageing response. However the Ti5%Zr1%Si alloy shows a strength increase of 20% on ageing at 823°K and a substantial contribution from the precipitation is maintained throughout the range of testing temperatures from 77°-850°K.

2. Strain ageing has been shown to occur in the binary alloy at 750°K the strength of the effect being a function of the concentration of silicon in solution.

3. The rate controlling mechanism of thermally activated deformation in the temperature range up to 400°K is the same for both alloys, aged and unaged, and is the same as that previously determined for titanium containing only interstitial solutes, namely, the overcoming of interstitial barriers.

Acknowledgements

The authors wish to thank Imperial Metal Industries (Kynoch) Ltd. for the provision of the titanium used in this work. Thanks are also due to Professor J.G. Ball for the provision of laboratory facilities and to Dr. R.D. Rawlings for useful discussions concerning activation analysis.

References

1. Conrad, H. "Thermally Activated Deformation of α Titanium Below 0.4Tm", Canad.J.Physics, vol. 45, pp. 581-590.

2. Conrad, H. and Jones, R., "Effects of Interstitial Content and Grain Size on the Mechanical Behaviour of α Titanium Below 0.4Tm", The Science, Technology and Application of Titanium, 1970, Pergamon Press, pp. 489-501.

3. Flower, H.M., Swann, P.R. and West, D.R.F., "Silicide Precipitation in Ti-Zr-Al-Si Alloys", Metallurgical Transactions, vol. 2, 1971, pp. 3289-3297.

4. Pascoe, R.T., Radford, K.C., Rawlings, R.D. and Newey, C.W.A., "Instrumental Modifications for Compressive Testing at Temperatures up to 1800°C", Journal of Scientific Instruments, vol. 44, 1967, pp. 366-370.

5. Flower, H.M., Swann, P.R. and West, D.R.F., "The Effect of Si, Zr, Al and Mo on the Structure and Strength of Ti Martensite", Journal of Materials Science, To be published.

6. Winstone, M.R. Private Communication.

7. Evans, A.G. and Rawlings, R.D., "The Thermally Activated Deformation of Crystalline Materials", Phys.Stat.Solidi, vol. 34, 1969, pp. 11-31.

8. Sargent, G. and Conrad, H., "Stress Relaxation and Thermally Activated Deformation in Titanium", Scripta Met., vol. 3, 1969, pp. 43-50.

9. Winstone, M.R., Rawlings, R.D. and West, D.R.F., Unpublished work.

10. Monteiro, S.N., Santhanan, A.T. and Reed-Hill, R.E., "A thermal Plastic Deformation in Commerical Purity Titanium", The Science, Technology and Application of Titanium, 1970, Pergamon Press, pp. 503-516.

11. Tung, P.R. and Sommer, A.W., "Dislocation Energetics in α Titanium", Metallurgical Transactions, vol. 1, 1970, pp. 947-953.