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Influence of beta phase decomposition on the temperature coefficient of resistivity of titanium alloys

MARY ANN HILL, D. H. POLONIS
Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195, USA

The temperature coefficient of resistivity (TCR) of beta stabilized titanium alloys is sensitive to minor constitutional changes produced by quenching, ageing and precipitate reversion. The influence of omega and alpha phase precipitation on TCR is demonstrated for binary and ternary alloys of composition $Ti_{80}(Nb + V)_{20}$. It is concluded that TCR measurements provide a sensitive method for detecting the early stages of beta phase decomposition in these alloys.

1. Introduction

Negative values of the temperature coefficient of electrical resistivity (TCR) have been reported for beta stabilized titanium alloys, including both binary and complex compositions [1–5]. Although several explanations of this anomaly have been proposed [1, 6–8], experimental work has clearly established that the phenomenon in titanium alloys is characteristic of the beta phase over limited composition ranges and is sensitive to minor modifications of constitution and microstructure [3–5, 9]. Consequently, the TCR is potentially useful for monitoring minor microstructural changes during the initial stages of beta phase decomposition. In some cases TCR values are reported to become increasingly negative during initial ageing, an effect attributed to a phase separation reaction in the parent beta phase [1, 2, 10]. The precipitation of the omega phase during ageing leads to a transition from an initially negative or low positive value of TCR in the 100% retained beta condition to increasing positive values as the reaction proceeds.

The present work examines the sensitivity of TCR values to minor modifications of microstructure due to ageing in three titanium base alloys. It is shown clearly that the processes of ageing and reversion can be monitored with considerable sensitivity by employing the TCR as a kinetic parameter.

2. Experimental procedures

Alloys having the compositions $Ti_{80}V_{20}$, $Ti_{80}Nb_{20}$ and $Ti_{80}V_{10}Nb_{10}$ were prepared by arc melting. Specimens were arc cast in the form of rods, from which resistivity specimens approximately 25–40 × 5 × 1.75 mm were prepared. A special vertical drop-quench furnace was employed for vacuum solution treatment at 975° C for 1 h, followed by quenching. Ageing and reversion treatments were performed over the temperature range 300–475° C; neutral salt baths were used without significant specimen contamination for periods up to 10 000 min. A standard four lead potentiometric technique was employed for the electrical resistance measurements which were made at four temperatures, −196° C, −78° C, 0° C and 20° C. Resistivity values were calculated and the TCR is represented as follows:

$$\text{TCR} = \frac{\Delta\varrho/\varrho_{\text{LN}}}{\Delta T}$$

where $\Delta\varrho$ is the resistivity difference over the interval ΔT and ϱ_{LN} is the value of ϱ at −196° C. The electrical resistance was measured at the four temperatures as a function of ageing time for determining TCR values. The reaction progress was also monitored by microhardness, X-ray diffraction analysis and microscopy.

3. Results

Microhardness measurements were conducted on the three alloys in the as-quenched condition and after ageing at 300° C, 350° C and 400° C. Fig. 1 shows the increasing hardness with ageing time at 350° C for each of the alloys; such changes are expected during the precipitation of omega phase and/or fine alpha phase particles. X-ray diffraction results confirmed the formation of the omega and alpha phases during the period of hardness increase up to 10 000 min. The time corresponding to the initial detection of both phases is indicated on the curves of Fig. 1.

The sensitivity of the TCR to beta phase decomposition is illustrated by the set of curves in Fig. 2 which show the TCR dependency on ageing time at 300, 350 and 400° C for the $Ti_{80}V_{20}$ alloy. Similar curves were generated for each of the three alloys. Fig. 3 is a combined plot showing TCR as a function of ageing time at 350° C for all three alloys.

In the quenched condition the $Ti_{80}V_{20}$ alloy exhibited a negative value of TCR, whereas the alloys containing niobium exhibited either slightly positive or negative values due to their sensitivity to the quenching conditions. All three alloys exhibited slight increases in TCR values during the initial few minutes of ageing, as shown in Fig. 3 for ageing at 350° C. The crossover from negative to positive values occurred after approximately 10 min at each of the ageing

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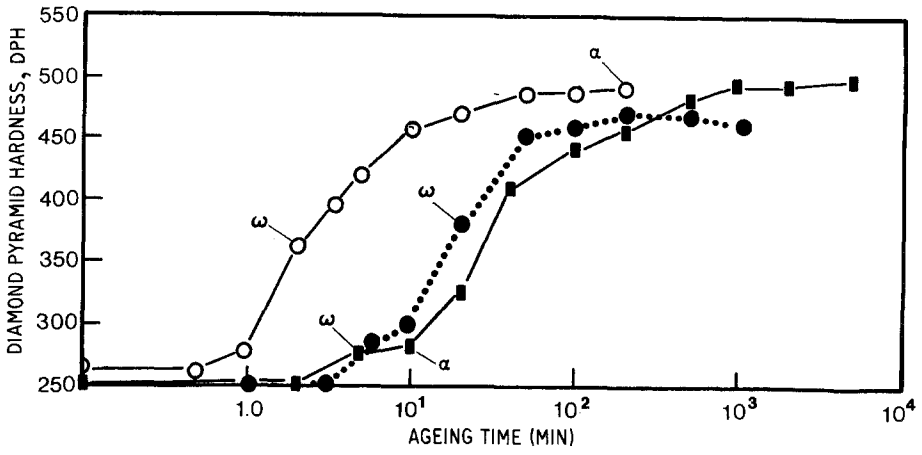

Figure 1 Influence of ageing at 350° C on the microhardness of ○, $Ti_{80}V_{20}$; ■, $Ti_{80}Nb_{20}$ and ●, $Ti_{80}V_{10}Nb_{10}$ alloys.

temperatures in the two alloys containing niobium. The crossover occurs in the $Ti_{80}V_{20}$ alloy within about 1 min at each ageing temperature. The maximum resistivity values increased with increasing ageing temperature. Fig. 3 shows that the $Ti_{80}V_{20}$ alloy experiences a significant increase in TCR after 4 min ageing at 350° C, whereas the $Ti_{80}Nb_{20}$ alloy requires 10 min for a similar increase. The TCR of the ternary alloy shows a sharp increase beginning after 6 min, but exhibits the largest increase in TCR after a period of 100 min, reaching a value of +0.24457 after 10 000 min at 350° C. Resistance measurements were also performed following reversion treatments at 475° C on the three alloys previously aged to the intermediate and late stages of ageing at 300 and 350° C. Table I gives a list of the results which indicate a significant decrease in the TCR value as a result of up-quenching to 475° C for periods up to 60 sec; however, none of the alloys achieved the original as-quenched TCR value, thereby suggesting the continued presence of irreversible remnants of the ageing reaction.

4. Discussion

Negative TCR values were determined for each of the three alloys in the as-quenched condition. However, some as-quenched $Ti_{80}V_{10}Nb_{10}$ specimens displayed slightly positive TCR values; X-ray results revealed such positive values to be associated with several vol % of the alpha double prime phase formed during the quench. The $Ti_{80}Nb_{20}$ and $Ti_{80}V_{10}Nb_{10}$ alloys possessing negative TCR values also contained traces (< 5%) of the alpha double prime phase. The negative TCR values in the solution treated and quenched $Ti_{80}V_{20}$ alloy were associated in all cases with 100% retained beta phase; this result is consistent with earlier findings [1] for this alloy and with negative TCR values reported in other titanium alloys containing 100% beta phase [2–5].

The TCR value of $Ti_{80}V_{20}$ more than doubles following one minute of ageing at temperatures above 300° C. This increase is consistent with the dramatic increase in hardness accompanying the initiation of the omega reaction, as shown in Fig. 1. The initiation of beta decomposition in the two niobium-containing alloys is more sluggish than for the binary $Ti_{80}V_{20}$, as shown by Figs. 1 and 3. In the $Ti_{80}Nb_{20}$ alloy a slight increase in TCR was evident after 10 min at 300° C; the increases were more dramatic after 10 min at 350° C (×1.4) and 400° C (×2.5). The TCR curves indicate that beta decomposition in the ternary alloy is initiated more rapidly at 300 and 350° C than at 400° C. X-ray diffraction analysis confirmed that omega precipitation predominates during the initial 10 min period at each of these temperatures, thereby pointing to the sensitivity of the TCR parameter for detecting the early stages of the omega reaction.

The TCR values of the $Ti_{80}V_{20}$ alloy exhibited sharp increases, as shown in Fig. 2, following 50 min of ageing at 300° C, 5 min at 350° C and 3.5 min at 400° C. X-ray diffraction analysis revealed evidence of alpha precipitation when ageing was continued

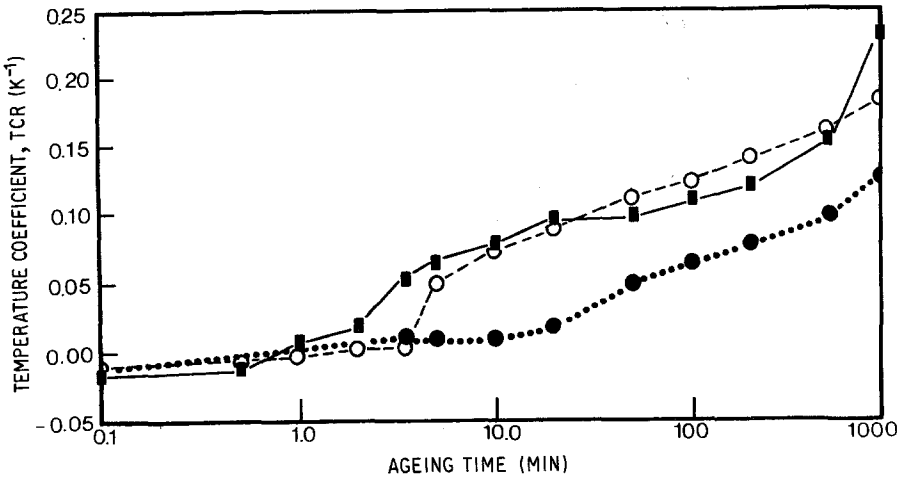

Figure 2 Temperature coefficient of resistivity (TCR) against ageing time for the $Ti_{80}V_{20}$ alloy at ●, 300° C; ○, 350° C; ■, 400° C.

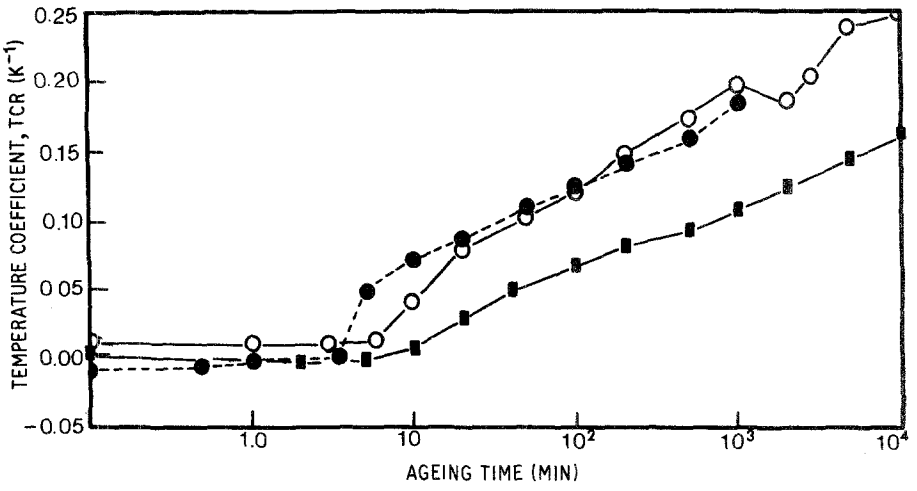

Figure 3 Temperature coefficient of resistivity (TCR) against ageing time for the ●, $Ti_{80}V_{20}$; ○, $Ti_{80}V_{10}Nb_{10}$ and ■, $Ti_{80}Nb_{20}$ alloys at 350° C.

beyond these times at the respective temperatures. The use of TCR measurements therefore permitted the detection of the precipitation reaction prior to confirmation by X-ray analysis. Similar results were obtained for the $Ti_{80}Nb_{20}$ and $Ti_{80}V_{10}Nb_{10}$ alloys, except that the initiation times for alpha precipitation were increased substantially in the alloys containing niobium; for example, in the $Ti_{80}Nb$ alloy, alpha precipitation was detected by TCR measurements after 20 min at 350° C, whereas more than 50 min were required at 350° C in the ternary alloy. X-ray results confirmed that the large increases in TCR after longer ageing intervals were associated with alpha phase precipitation. In each of the alloys the magnitude of TCR increased with increasing ageing temperature, which is consistent with the fact that the kinetics of alpha precipitation are favoured as the ageing temperature is increased.

The decrease in TCR after up-quenching to 475° C is interpreted as direct evidence of the reversion of the omega phase [11–13]. The $Ti_{80}V_{20}$ alloy aged 4 min at 350° C to produce omega phase exhibited a higher value of TCR after reversion than in the original quenched condition. Possible explanations include (i) incomplete reversion of omega; (ii) the presence of unreverted alpha phase; (iii) remnant solute lean zones in the beta phase following omega reversion. The presence of solute lean zones after reversion has been confirmed by TEM work on several titanium systems [11–14]. X-ray analysis in the present work also points to solute lean regions as the likely explanation for the incomplete reversion of TCR. The omega phase reflections associated with *hkl* indices of 1 1 0, 2 0 0, 2 0 1 and 1 1 2 disappeared as a result of the reversion process while the peaks due to the beta phase exhibited broadening in the absence of the omega, suggesting non-uniform solute distribution in the beta phase following the up-quenching treatment.

The reversion processes conducted after prolonged ageing periods are less likely to achieve the quenched values of TCR due to the formation of the non-revertible alpha phase.

5. Summary

The microstructural sensitivity of the TCR makes it an excellent parameter for monitoring beta phase stability in titanium alloys. The negative TCR is a characteristic of the beta phase over a limited composition range and is extremely sensitive to the presence of small amounts of omega phase formed either athermally or isothermally; an increase in TCR also accompanies alpha precipitation. TCR values are therefore useful for monitoring omega phase reversion; while omega reversion may appear to be complete on the basis of microhardness or X-ray techniques, the failure of TCR measurements to undergo complete reversion is evidence of residual ageing effects such as solute lean zones in the matrix. It is therefore concluded that TCR measurements provide a way of detecting minor perturbations within the beta phase that may not be

TABLE I Temperature coefficient of resistivity alloys reverted at 475° C after ageing

Alloy	Ageing temperature (° C)	Ageing time (min)	Reversion time (sec)	Aged TCR	Reversion TCR
$Ti_{80}V_{20}$	300	30	10	+0.028 231	+0.004 643 7
(As-quenched TCR = −0.009 73)	300	1000	10	+0.120 66	+0.011 200
	350	4	8	+0.001 123 6	−0.002 138 3
	350	200	14	+0.158 84	+0.086 045
$Ti_{80}Nb_{20}$	300	500	30	+0.066 132	+0.028 799
(As-quenched TCR = −0.002 71)	300	10 000	35	+0.116 44	+0.088 915
	350	100	30	+0.049 139	+0.024 239
	350	5000	60	+0.132 29	+0.118 15
$Ti_{80}V_{10}Nb_{10}$	300	100	15	+0.065 836	+0.034 363
(As-quenched TCR = +0.008 01)	300	10 000	40	+0.197 41	+0.080 154
	350	20	25	+0.059 106	+0.026 202
	350	1000	40	+0.172 08	+0.087 811

detected by conventional techniques in this particular class of alloys. It is also apparent that the complexity of the reactions accompanying beta phase decomposition require the TCR parameter to be used in conjunction with other techniques, including X-ray analysis and electron microscopy for the purposes of monitoring phase stability.

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