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The influence of constitution and microstructure on the temperature coefficient of resistivity in Ti-base alloys

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The electrical resistivity of beta titanium alloys has been examined to determine the influence of the constitution and microstructure on the temperature coefficient of resistivity ($d\rho/dT$). The reports of previous investigations have attributed the negative value of $d\rho/dT$ in the metastable beta phase to the formation of a reversible athermal omega phase. The present investigation shows that the negative value of $d\rho/dT$ in beta stabilized Ti alloys is a singular property of the beta phase and is independent of the reversible athermal omega transformation. Variations in the value of $d\rho/dT$ due to solute concentration, modifications in constitution and microstructure, and plastic deformation have also been examined.

1. Introduction

There is considerable evidence in the literature establishing the fact that many titanium- and zirconium-based alloys have negative values of $d\rho/dT$. For convenience these are summarized in Table I.

Table I shows that there is a wealth of information documenting the negative value of $d\rho/dT$ in some titanium and zirconium base alloys. There is no consistent explanation to account for this anomalous behaviour since it has been attributed to changes in both the microstructure and the electronic structure of these alloys. Very meagre data [2, 3, 5, 6] are available to relate electronic factors with the negative value of $d\rho/dT$ in Ti- and Zr-base alloys. On the other hand, the occurrence of a negative value of $d\rho/dT$ correlates directly with the microstructure in these alloys. The value of $d\rho/dT$ is found to be negative for alloys in the quenched condition when these exhibit (i) $\beta + \omega$ and (ii) 100% retained beta phase. In addition, the negative value of $d\rho/dT$ in Zr-Nb alloys has been identified with the occurrence of a reversible athermal omega reaction during cooling to a sub-zero temperature [13, 14]. This poses the question as to whether or not the beta phase is solely responsible for the negative value of $d\rho/dT$ and the extent to which the presence of the omega phase influences this anomalous behaviour.

2. Experimental procedure

Binary titanium alloys with the compositions shown in Table II were prepared by a standard levitation melting technique in combination with a purified and dried He atmosphere that was maintained at a positive pressure during the melting and casting process.

The cast alloys were homogenized for 36 h at 1050°C in a vacuum of 5×10^{-6} Torr, following which they were swaged into rods of 0.1 in. diameter. Lengths 2 in. long were cut from the swaged stock for shaping into tensile specimens to be used for resistivity measurements. A JEM-7 electron microscope and a Philips EM-200 electron microscope equipped with a uniaxial-tilt cold stage were used to monitor changes in the constitution at low temperatures. Selected-area diffraction patterns were taken at a series of temperatures ranging from 25 to −180°C. Thin foils for electron microscopy were prepared by employing a technique described by Blackburn and Williams [15]. Solution heat-treatments were performed at 1050°C for 30 min after encapsulating the specimens in evacuated vycor tubes, using tantalum foil as a getter around the specimens.

TABLE I Literature survey

Authors	Ref.	Alloy system	Comments
Ames *et al*	1	Ti-Nb	20 to 25% Nb negative $d\rho/dT$. 26 to 34% Nb positive $d\rho/dT$. Their extrapolation indicates that β-Ti should have a negative $d\rho/dT$ below 473 K.
Wasilewski	2	Ti-O, Ti-N, Zr-O	Oxygen accentuated rather than caused the negative $d\rho/dT$. A model was proposed based on relative shift of the "s" and "d" bands.
Brotzen *et al*	3	Ti-V	The negative $d\rho/dT$ in 15 to 20% V was attributed to an energy overlap across the {200} planes of the second Brillouin zone for bcc structures.
Yoshida *et al*	4	Ti-Mo	12 to 17% Mo have negative $d\rho/dT$ below 150°C. This behaviour was attributed to a characteristic electronic structure of the beta phase or to some kind of intermediate structure formed during quenching.
Hake *et al*	5	Ti-Mo	7 to 12% Mo exhibit negative $d\rho/dT$. It was suggested that the anomaly is due to spin-disorder scattering and not due to atomic ordering or structural transformations.
Gardner *et al*	6	Ti-Mn	The resistance minimum in dilute Ti-Mn alloys has been partly accounted for in terms of a negative $d\rho/dT$ associated with a transformation to omega at low temperatures of any beta phase present in the alloys.
Gusev *et al*	7	Ti-Cr	A 100% beta alloy exhibited a negative $d\rho/dT$ on heating as well as cooling. Formation of aged omega phase caused a reduction in electrical resistivity and the $d\rho/dT$ became positive.
Raub *et al*	8	Ti-Cr	Negative $d\rho/dT$ in beta Ti-Cr alloys. $d\rho/dT$ became positive with appearance of alpha and the compound Ti_1Cr_2 upon ageing.
Luhman *et al*	9	Ti-Cr	Negative $d\rho/dT$ in Ti-12% Cr attributed to beta phase.
	10	Ti-Cr	Calculations based on shift in energy between the "s" and "d" bands in titanium alloys to account for negative $d\rho/dT$.
Narayanan	11	Ti-13V-11Cr-3Al (B120VCA)	Negative $d\rho/dT$ associated with beta phase. No omega formation in this alloy due to extensive beta stabilization.
Tanner	12	Ti-15%V-2.5%Al	Negative $d\rho/dT$ in the beta condition.
Cometto *et al*	13	Zr-Nb	Negative $d\rho/dT$ in the composition range 12-17.5% Nb attributed to thermally reversible formation of omega.
Perkins *et al*	14	Zr-Nb	

Standard potentiometric techniques were used to measure the electrical resistance of the alloy specimens at temperatures ranging from 0 to −196°C. Short potential and current leads were spot welded to the specimen which was connected in series with a 1 Ω standard resistor. The current through the specimen and the standard resistor was maintained at 0.2 A. The voltage drops across the specimen and the standard resistor were measured by employing a Leeds and Northrup K5 potentiometer and a Keithly Nano-voltmeter as a null detector. By reversing the current through the specimen and averaging the voltage drop for both current directions, the effects of thermal emf could be eliminated during the measurement of the electrical resistance.

3. Results and discussion

3.1. Effects of omega phase on $d\rho/dT$

An investigation of the Ti-Cr system by Luhman *et al* [9] showed that a Ti-12% Cr alloy having

TABLE II Titanium base alloys used in the present investigation

Element	At. %	Source of alloying element
Chromium	10	Iochrome chromium
	13	(99.9%)
	15	
	20	
Molybdenum	9	VP grade (99.95%)
Titanium	10	Iodide titanium (99.97%)

an all beta microstructure in the as-quenched condition at room temperature exhibits a negative value of $d\rho/dT$ over the temperature range −196 to 200°C. This alloy composition represents a case of marginal beta stability and could be expected to experience a reversible-athermal omega reaction at sub-zero temperatures. Fig. 1a is a selected-area diffraction pattern, from a quenched Ti-13% Cr alloy, at −180°C showing intensity maxima at positions corresponding to the omega reflections. This observation indicates that the negative value of $d\rho/dT$ reported in the Ti-12% Cr and Ti-13% Cr alloys in the temperature range between 0 and −196°C cannot be identified unambiguously with the beta phase.

In order to avoid any contribution attributable to the reversible athermal omega reaction, beta stabilized Ti-Cr alloys containing 15 and 20% Cr were examined since these compositions are well above the minimum value for beta stability.

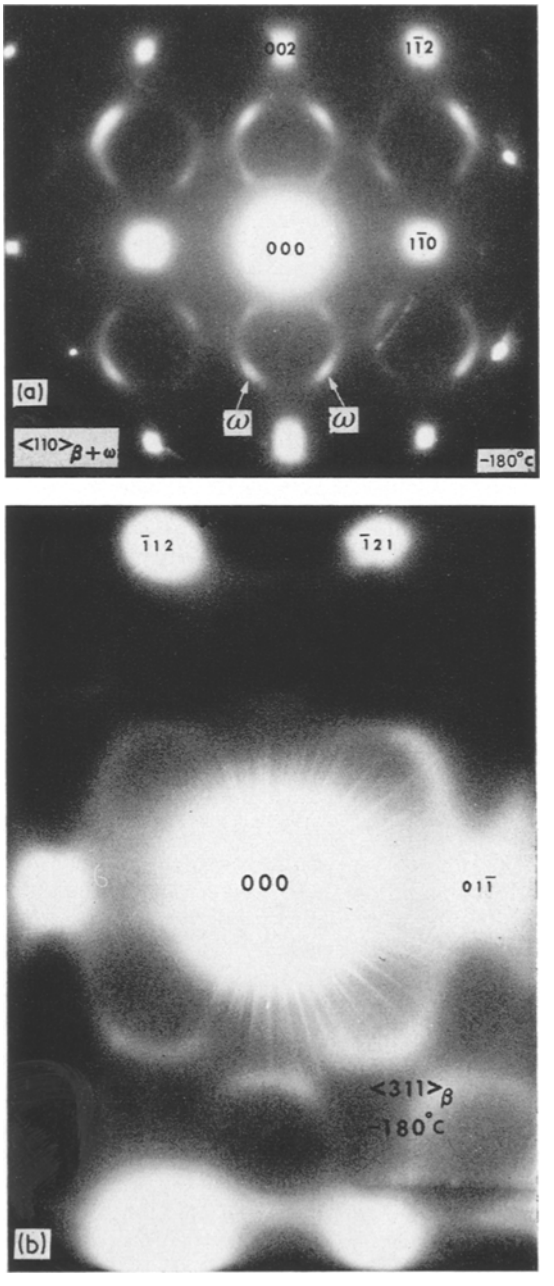

Figure 1 Selected-area diffraction patterns from quenched Ti-Cr alloys at −180°C. (a) Ti-13 at. % Cr. Note the formation of intensity maxima at positions corresponding to the omega reflections. $\langle 110 \rangle_\beta$ zone normal. (b) Ti-20 at. % Cr. Note the absence of intensity maxima characteristic of omega formation.

Both of these compositions were examined in the electron microscope at sub-zero temperatures and the selected-area diffraction patterns for the

as-quenched condition did not exhibit the intensity maxima that would be expected if omega forms in the temperature range down to −180°C. This observation is confirmed in Fig. 1b which shows a selected-area diffraction pattern taken from a solution treated and quenched Ti-20% Cr alloy at −180°C. Omega phase reflections are absent, indicating that the metastable beta phase is retained without any apparent athermal transformation down to −180°C. This observation is strong evidence that the negative value of $d\rho/dT$ in Ti-Cr alloys is independent of any reversible athermal omega transformation and is, in fact, an inherent characteristic of the metastable beta phase.

TABLE III Resistance-temperature data for an as-quenched Ti-20 wt % Mo alloy

Temperature (°C)	Resistance ($\times 10^4\ \Omega$)
0	395.35
− 67	399.84
−196	403.83

In the current investigation, a Ti-20 wt % Mo alloy was found to have a negative value of $d\rho/dT$, as is evident from the values presented in Table III. Hake *et al* [5] reported that a Ti-28.7% V alloy has a negative value of $d\rho/dT$, while de Fontaine *et al* [16] have reported that Ti-V alloys containing 25 to 50% V and Ti-Mo alloys containing more than 18.5% Mo do not contain any reversible athermal omega phase after cooling to −171°C in the electron microscope. Hake *et al* [5] have also reported negative values of $d\rho/dT$ for higher compositions. The resistivity data for the Ti-V and Ti-Mo alloys together with the low-temperature electron microscopy results of de Fontaine *et al* [16] therefore establish that the negative values of $d\rho/dT$ in all these alloys are associated with the metastable beta phase and not with the reversible-athermal omega reaction.

A negative value of $d\rho/dT$ has also been observed in a commercial beta titanium alloy B120 VCA(11) in which it has been established that the omega phase cannot be produced, either athermally or by isothermal ageing, because of the high degree of beta stabilization. This observation augments the indications that for binary alloys the negative value of $d\rho/dT$ is associated with the metastable beta phase.

The evidence associating the negative value of $d\rho/dT$ with the beta phase in titanium base binary alloys is not in agreement with the results reported for the Zr-Nb system. An examination of the data for Zr-Nb alloys [13] makes it evident that the value of $d\rho/dT$ is negative over a very small range of composition from 15 to 21 wt % Nb. The selected-area diffraction patterns for the as-quenched Zr-Nb alloys [14], at room temperature, reveal the presence of intensity maxima at positions corresponding to the omega reflections and these could be expected to sharpen and intensify with progressive cooling to lower temperatures. The conclusion by Cometto *et al* [13] that the negative value of $d\rho/dT$ in Zr-Nb alloys results from the thermally-reversible formation of omega phase is valid, if it is argued that Zr-Nb alloys are unique in this respect. Otherwise the presence of the athermal omega phase in these alloys must tend to obscure the true behaviour of the beta phase if the metastable omega phase forms over the beta composition range corresponding to negative values of $d\rho/dT$.

Gusev *et al* [7] and Luhman *et al* [9] have shown that the value of $d\rho/dT$ in a 100% beta Ti-Cr alloy is negative not only during cooling but also during heating. No reversible-athermal reaction would be expected to occur during heating since the ω_s temperature in these alloys is below room temperature. These observations lend added strength to the argument that the negative value of $d\rho/dT$ in beta titanium alloys is a singular characteristic of the metastable beta phase.

3.2. The effect of ageing on $d\rho/dT$

The discussion so far has been confined to an explanation for the relationship that exists between the negative value of $d\rho/dT$ and the constitution of the as-quenched Ti and Zr alloys. Fig. 2 shows the change in the values of $d\rho/dT$ with composition for Ti-Cr alloys. The value of $d\rho/dT$ is a minimum around 15% Cr and is expected to have a zero value at approximately 25% Cr. Fig. 3 shows the change in the value of $d\rho/dT$ with ageing time for Ti-Cr alloys of different solute contents ranging from 10 to 20 at. % Cr. The Ti-10% Cr alloy has a beta plus omega microstructure in the as-quenched condition. The 13% Cr alloy represents a case of marginal beta stability and the 15 and 20% Cr alloys represent the highly stabilized beta condition. The existence of an incubation time prior to omega phase nucleation in the 15 and 20% Cr alloys is evident from the shift in the curves along the time axis, as the solute content

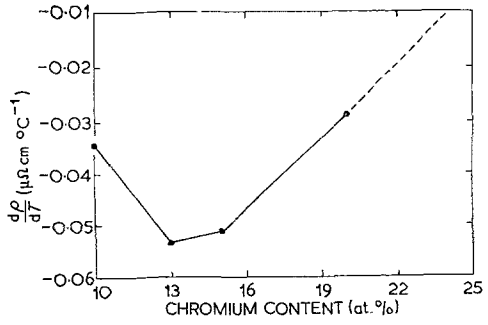

Figure 2 Change in $d\rho/dT$ as a function of Cr content in as-quenched Ti-Cr alloys.

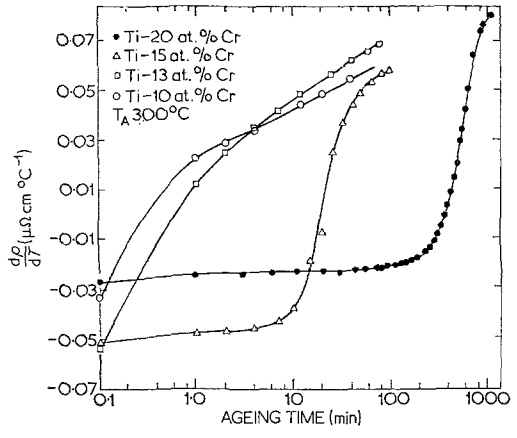

Figure 3 Change in $d\rho/dT$ as a function of ageing time for Ti-Cr alloys containing 10 to 20% Cr. Ageing temperature 300°C.

is increased. All the alloys have a negative value of $d\rho/dT$ at zero time and upon ageing at 300°C the value of $d\rho/dT$ becomes positive and tends to stabilize at a limiting value. The positive value of $d\rho/dT$ during ageing in all cases is associated with the precipitation of the aged omega phase. This observation is in agreement with earlier investigations [3, 6, 10, 13]. The sigmoidal shape of the curves reflects the nucleation and growth character of the reaction and the analysis of such kinetic data for omega precipitation will be discussed in a subsequent paper. The pronounced changes in the value of $d\rho/dT$ accompanying omega precipitation make it possible to use the value of $d\rho/dT$ as a parameter to monitor the omega reaction from start to completion. Electron microscopy studies in this investigation have revealed that the start of the omega phase nucleation is associated with the upturn in the

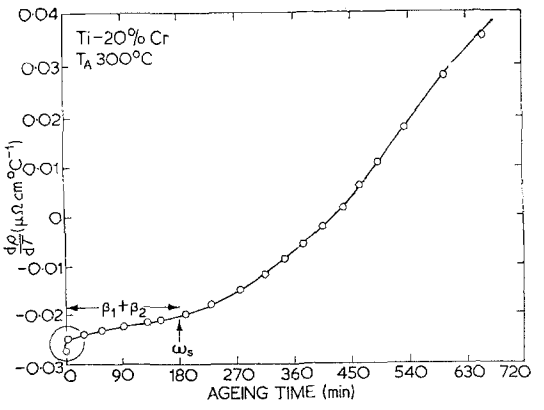

Figure 4 An exploded view of the initial part of the isothermal ageing curve for a Ti-20% Cr alloy showing the initial increase in $d\rho/dT$ within the first 5 min of ageing. Also the start of omega precipitation is indicated by ω_s.

curve indicated by ω_s in Fig. 4. Beyond this point the volume fraction of the omega phase increases with ageing time and tends to a limiting value. This observation is in agreement with Hickman [17], who has shown that the volume fraction of omega phase increases with ageing time and reaches a maximum.

The omega phase formed by ageing the metastable beta phase can be reverted by upquenching the alloy to temperatures above the level of omega stability, which is 400°C for this alloy. The effect of such ageing and reversion treatments on the values of the electrical resistance, and $d\rho/dT$ is shown in Table IV. Composition gradients exist within the beta phase after the omega reversion treatment because of the very short reversion time that was employed. The results presented in Table IV indicate that the values of R and $d\rho/dT$ resulting from the reversion treatment are not significantly different from the values corresponding to the as-quenched condition. The sensitivity of the values of R and $d\rho/dT$ to the structural change brought about by the reversion of the omega phase is evident from Table IV. In particular, it should be noted that the value of $d\rho/dT$ is once again negative for the beta phase as it was for the as-quenched condition.

The very initial stages of omega phase precipitation, following the incubation period, could be accompanied by a reversible-athermal omega reaction upon cooling to sub-zero temperatures. It should be pointed out that such an athermal reaction occurs at a stage when the

TABLE IV Values of R and $d\rho/dT$ for a Ti-20% Cr alloy for different heat-treatment conditions

Heat-treatment	Resistance, R, ($\times 10^4\ \Omega$)		$d\rho/dT$ ($\times 10^3\ \Omega\ cm\ °C^{-1}$)
	0°C	−196°C	
As-quenched	251.56	262.00	−27.55
Aged 300°C/1140 min	256.84	225.19	83.47
Rev. 435°C/4 min	252.84	262.98	−26.74

value of $d\rho/dT$ is becoming increasingly positive. When the omega phase initially appears during ageing in a Ti-15% Cr and Ti-20% Cr alloy, the line drawn through the omega phase reflections, as shown in Fig. 5a, does not correspond to the $\langle 1\,1\,2\rangle$ direction through the bcc spots. According to Sass [18], such a displacement of the omega reflections is indicative of a non-ideal omega structure. The selected area diffraction patterns shown in Fig. 5a and b represent the initial and later stages respectively, in the development of the aged omega phase; there is a transition from a non-ideal to an ideal omega structure, as indicated by the shift in the omega phase reflections. This transition in the structural perfection is accompanied by a progressive change in $d\rho/dT$ from a negative to a limiting positive value. Further, the commencement of the omega phase nucleation and its initially non-ideal structure render the value of $d\rho/dT$ increasingly positive rather than increasingly negative. Hence, the lattice displacements associated with the omega phase nucleation make a positive contribution to the value of $d\rho/dT$.

3.3. The influence of phase separation on $d\rho/dT$

The occurrence of a phase separation reaction in the Ti-15% Cr alloy has been established [19] and, in a recent study of Ti-Cr alloys [20], it has been found that the incubation times prior to the detection of the omega phase increase with increasing Cr content. The incubation time can be partly accounted for by the initial decomposition of the beta phase into solute lean and solute rich regions. The effect of such a decomposition reaction on the value of $d\rho/dT$ is shown in Fig. 4, for a Ti-20% Cr alloy aged at 300°C. The initially negative value of $d\rho/dT$ increases sharply to a less negative value during the first 3 min of ageing. Thereafter, the change in the value of $d\rho/dT$ is gradual until the omega phase begins to precipitate. It is evident from these data that the change in $d\rho/dT$ associated with the phase separation process is far less than the change

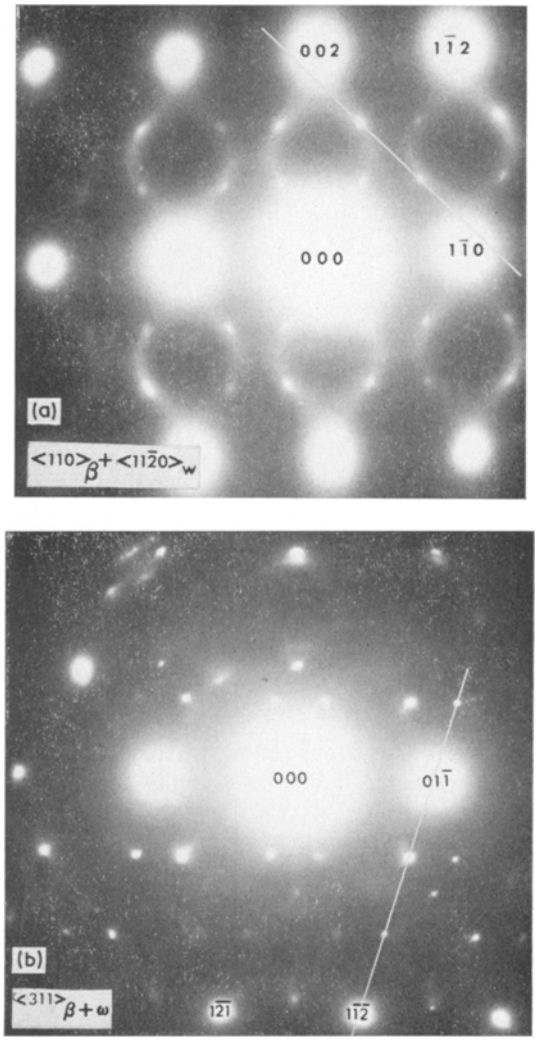

Figure 5 Selected-area diffraction patterns from a Ti-15% Cr alloy aged at 300°C for (a) 15 min and (b) 180 min, indicating the shift in the omega phase reflections as the degree of perfection of the structure improves.

accompanying the precipitation of the omega phase. An earlier investigation of the Ti-V alloys by Brotzen *et al* [3] and a more recent study by Gragg [21] of the same alloy system have shown

TABLE V Effect of strain on the $d\rho/dT$ of a Ti-20% Cr alloy

Heat-treatment	Microstructure	$d\rho/dT$ ($\times 10^3\ \Omega\ cm\ °C^{-1}$)
Solution heat-treated and quenched to room temperature	All beta	−27.55
As-quenched and deformed 1% in tension	All beta	−26.84
Aged 300°C/6 min	All beta	−24.13
Aged 300°C/6 min and deformed 1% in tension	All beta	−23.41
Aged 300°C/320 min	$\beta + \omega$	− 1.68
Aged 300°C/320 min and subjected to a small plastic strain	$\beta + \omega$	− 3.32

that the value of $d\rho/dT$ becomes increasingly negative during the early stages of ageing. Gragg [21] has attributed this behaviour in the Ti-V alloys to the phase separation process. The causes for these apparent anomalies between the Ti-Cr and Ti-V system have not been identified.

3.4. The effect of deformation on $d\rho/dT$

The influence of deformation on the value of $d\rho/dT$ for beta stabilized alloys has been studied in a Ti-20% Cr alloy in order to avoid any complications that might result from the formation of strain-induced martensite and strain-induced omega. The effect of plastic strain on the value of $d\rho/dT$ for a Ti-20% Cr subjected to different treatments is shown in Table V. When the Ti-20% Cr alloy containing the aged omega phase, is subjected to plastic strain the value of $d\rho/dT$ is found to become more negative, as evident from the values in Table V. Some of the omega phase in this alloy may be destroyed by plastic deformation in a manner similar to that described by Blackburn *et al* [22] for Ti-Mo alloys. A decrease in the volume fraction of the omega phase could account for the increasing negativity of the $d\rho/dT$ due to deformation in the specimen aged to produce the omega phase.

4. Conclusions

Correlations between data reported by previous workers and the results of the current investigation establish that the negative value of $d\rho/dT$ in titanium alloys is associated with the metastable beta phase. The phenomenon is not governed by the occurrence of a reversible-athermal omega phase even though such a reaction can occur at sub-zero temperatures in alloys of composition below a critical limit.

During the initial stages of ageing the value of $d\rho/dT$ continues to remain negative when a phase separation reaction occurs in the beta phase. The value of $d\rho/dT$ undergoes a progressive change from negative to positive when the omega phase precipitates. Also the magnitude of the change in the value of $d\rho/dT$ during omega precipitation is greater by a factor of 9 than the change in value of $d\rho/dT$ associated with phase separation. Hence the sensitivity of the value of $d\rho/dT$ to omega precipitation provides a possible way to monitor the kinetics of omega formation during the ageing of beta stabilized alloys.

The value of $d\rho/dT$ in Ti-Cr alloys is not constant with Cr additions. There appears to be a minimum in the value of $d\rho/dT$ at approximately 13% Cr and, as the Cr content is increased, the value becomes less negative. An alloy containing 25% Cr is expected by extrapolation to have a zero value of $d\rho/dT$; the ease of formability in the beta condition combined with the stability of the beta phase at low temperatures suggest that such a material may be useful for precision resistors that are relatively insensitive to temperature.

The value of $d\rho/dT$ becomes less negative after the deformation of a Ti-20% Cr alloys in the as-quenched condition and after ageing at 300°C for 6 min. Such an effect could result from the destruction of zones representing localized solute lean regions. Deformation of a Ti-20% Cr alloy containing $\beta + \omega_{aged}$ causes the value of $d\rho/dT$ to become more negative, which would be expected if deformation destroys some of the omega phase.

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