Saturation and pressure effects on the resistivity of titanium and two Ti-Al alloys

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ABSTRACT

The electrical resistivities of α phase titanium and two Ti-Al alloys have been measured as functions of temperature, T, between 4 and 700 K and, in the range 175–700 K, as a function of pressure up to 1.2 GPa. All materials showed resistivity saturation effects at the highest temperatures. A "parallel resistivity" saturation model could be fitted to all data with excellent results if Mott-Fermi smearing, expected for a transition metal, was included by adding a term in T^3 to the phonon-induced resistivity. However, in the standard saturation model the fitted resistivity parameters were not always realistic. A modified saturation model which partially retained Matthiessen's rule could be fitted equally well and gave numerically acceptable results for both residual, electron-phonon and saturation resistivities. This new model also fitted the T dependence of the pressure coefficients with a single set of coefficients, each valid for all three materials. Although simple free-electron and Debye models could apparently explain the observed pressure dependence of the impurity and electron-phonon resistivities, a model taking band structure changes with pressure into account showed that the electron-phonon interaction factor of titanium is practically independent of pressure while the plasma frequency has a strong pressure dependence. This model gave reasonable numerical results for the pressure dependence of both the residual, electron-phonon and saturation resistivities and also agreed with experimental data for the superconducting critical temperature T_c under pressure for α titanium.

1. Introduction

Titanium and its alloys are light, strong, biocompatible and corrosion resistant, but in spite of their immense technological importance there are still many gaps in our knowledge and understanding of these materials. We address here three questions related to electrical transport in Ti and its alloys in an attempt to provide not only new, accurate data for these materials but also an improved understanding of highly resistive materials in general.

First, to our knowledge, only two groups have studied the electrical resistivity, ρ, of Ti under high pressure [1,2]. Bridgman [1] studied an impure specimen under hydrostatic conditions up to 3 GPa at room temperature. (Data for another sample, published in 1920, and later results to 10 GPa are less accurate.) More recently, highly pure Ti was studied [2] over wide ranges of pressure, p, and temperature, T, using solid hexagonal BN as pressure transmitting medium. Titanium and its dilute alloys crystallize in a hexagonal close-packed (hcp) α phase at ambient conditions but above 1155 K Ti transforms into a body-centered cubic β phase [3]. Both phases transform into a hexagonal ω

phase when a high pressure is applied [3,4]. Unfortunately, most data for ρ from earlier studies [1,2] have been fitted to polynomials over ranges in p that include both the α and ω phases. It is thus uncertain whether published data are characteristic for the α phase, the ω phase, or mixtures of both. To obtain accurate data for ρ under pressure we have thus measured the resistance of several specimens of α Ti and two of its alloys under hydrostatic conditions from 175 K to 700 K in the range where only the α phase is stable.

Second, at high T the resistivities of Ti and its alloys are very high and the T dependence deviates strongly from linearity. Mooij [5] showed that when ρ exceeds about 150 $\mu\Omega$cm in metals and alloys it tends to become constant, sometimes even showing a negative $d\rho/dT$ (the "Mooij correlation"). This effect, given the descriptive name "resistivity saturation" by Fisk and Webb [6], is usually observed when the semi-classical electron mean free path, Λ, approaches its minimum value, the nearest-neighbour atomic distance a (the Ioffe-Regel criterion [7]). In many materials the resulting $\rho(T)$ can be described by a simple "parallel resistivity" model [8],

$$1/\rho = 1/\rho_{ideal} + 1/\rho_{sat}. \tag{1}$$

Here ρ is the experimental value, ρ_{ideal} the sum of the residual (ρ_0) and phonon-induced (ρ_{ep}) resistivities and ρ_{sat} the high-T limit. Surprisingly, several studies [9–11] claim that Eq, (1) is not valid for Ti and its alloys; fitted functions do not describe correctly the T dependence and fitted values for ρ_{sat} vary strongly with alloying, from very high for pure Ti to much lower for alloys. We find that this is due to a neglect of band-structure effects. Basic theory [12,13] predicts ρ_{ep} to be linear in T at constant volume, V, for $T > \Theta_D/2$, where Θ_D is the Debye temperature, but for most simple metals thermal expansion gives $\rho \propto T^n$, with $n > 1$, at constant p [12] (see data in Ref. [14]). Reducing data to constant-V (isochoric) conditions restores linearity for most simple metals, but many transition metals remain non-linear. A common reason is Mott-Fermi thermal smearing of energy levels [12,15]: when the density of states changes rapidly with energy at the Fermi level, changes in T modify the effective number of charge carriers and the scattering probability, giving a non-linear $\rho(T)$. We show below that when Ti as treated as a transition metal with Mott-Fermi smearing of the band structure, excellent fits to the experimental data are found with only small variations in ρ_{sat} between materials.

Third, even when Eq. (1) fits the data well, fitted values for ρ_0 and ρ_{ep} rapidly become anomalous with alloying. For highly resistive alloys the fitted ρ_0 may be extremely high, implying an unrealistically short Λ, while the fitted ρ_{ep} may be an order of magnitude larger than for pure Ti. This is surprising; neither band structure nor phonon spectrum should be strongly affected by replacing 5–10% of the Ti atoms by Al. We show here that a modified model, partially retaining Matthiessen's rule, fits experimental data equally well. In contrast to the earlier model, Eq. (1), it also reproduces the T dependences of both ρ and $d\rho/dp$, for both Ti and the alloys investigated, yielding physically reasonable values for all fitted resistivity terms and their p derivatives. The model also correctly predicts the p dependence of the superconducting transition temperature, T_c.

Resistivity saturation is not well understood. While early authors [16–20] analyzed non-linear data in terms of band structure effects or scattering by multiple ionic energy levels, Mooij's paper [5] initiated an intense research activity and many approaches were suggested, as reviewed by Allen [21,22]. Gurvitch [23] derived Eq. (1) by assuming a minimum time between electron scattering events, equivalent to a minimum Λ, and similar expressions follow from considerations of s-d scattering [24], by expressing the conductivity in Boltzmann theory in powers of a/Λ [22] and in models predicting additional non-classical conduction channels [25]. Importantly, values for ρ_{ep} found by fitting Eq. (1) to data for elements usually agree well with calculations [26] for the non-saturated state. Interest in saturation effects increased again after the discovery that ρ did *not* saturate in some ceramic superconductors [27], fullerides [28] and other "bad metals", although saturation sometimes reappeared at constant V [29]. (Reviews are given by Allen [30] and Gunnarsson et al. [31].) For heat transport by phonons, a mean-free-path-limited "minimum thermal conductivity" [32] is observed in both glasses [32,33] and crystals [32,34] and the similarity between the electronic and lattice effects has been emphasized [35]. Both saturation effects have important implications in technology, geo- and astrophysics. E.g., resistivity saturation in Fe alloys implies a high thermal conductivity in the Earth's core [36], constraining estimates of the thermal evolution of our planet and other astronomical objects.

Although both Eq. (1) and the concept of saturation are widely accepted and used in analyses and calculations [37,38] there is still no general theory. Saturation appears at similar magnitudes of ρ in crystalline, disordered and amorphous metals, irrespectively of whether scattering is dominated by static (impurities) or dynamic (phonons) disorder. It is obviously related to Mott's minimum metallic conductivity [39]; observed values for ρ_{sat} suggest that Λ is usually of order 4–10 Å at saturation [5,11,23,40] rather than Mott's $\Lambda_{min} \approx a$. However, even the concept of Λ is probably invalid under such conditions and recent calculations [38] show that Fermi surfaces blur or collapse

under saturation conditions. Although many recent papers discuss possible models for saturation and "bad metals" [31,41–49] there is still little genuine understanding, no accepted theory and no general method to calculate ρ and its T dependence for highly resistive materials. While progress in first-principles calculations may soon change this situation we limit the theoretical discussion in this paper to simple Debye models and the simplest extensions of free-electron-like theories. The excellent agreement found between simple theory and the parameters obtained by fitting our new empirical model to the data is extremely interesting and may possibly help in advancing present understanding of resistance saturation effects.

2. Experimental details

Ti samples were prepared from cold-drawn wire, 2 mm in diameter, of iodide Ti (99.9% purity) with a measured residual resistivity ratio $\rho(298\,K)/\rho(4.2\,K) = 13.9$. Alloy samples were cut from arc-melted ingots made from 99.9% Ti and 99.99% Al at the Central Research Institute for Ferrous Metallurgy, Moscow, Russia. The average Al concentrations in the alloys were 2.43 wt % (4.23 at %) and 4.99 wt % (8.53 at %), respectively, as measured by electron probe microanalysis (X-ray spectroscopy). We refer to these alloys as alloys A (2.43% Al) and B (4.99% Al). Both alloys crystallize in the Ti α structure, which is stable to at least 9 at % Al [9–11], and both are disordered substitutional alloys with virtually the same lattice constant as pure Ti [11]. All samples were machined to nominal dimensions 0.5 mm in diameter and 10 mm in length and used without further annealing to avoid oxygen contamination. Current and potential leads were made from 0.125 mm in diameter Ti wire (99.6% purity, Goodfellow, Cambridge, U.K.), spotwelded to the samples. The resistance, R, was measured by the fourprobe DC method, switching the current direction to minimize thermoelectric effects. The current used was 100–200 mA and R was calculated from the ratio of the voltages measured over the sample and over a standard resistor of 100 mΩ connected in series.

All experimental data have been corrected for geometrical effects due to thermal expansion, using recommended data [50] for pure Ti. We have used the same expansion data for all samples, all materials, and under all conditions, even at high pressure. This does not add significantly to the experimental error because the correction is small (< 0.4%) over the range studied and the thermal expansion properties of Ti-Al alloys do not differ much from those of pure Ti.

High-p experiments at and above room temperature (RT) were performed in a piston-and-cylinder device, 70 mm in inside diameter, using an oven very similar to those used in earlier studies [51–53]. Temperature gradients were minimized by using separate end heaters. The pressure was measured using a free-standing Manganin coil [54]; wire from the same spool has been calibrated against the melting pressure of Hg. The pressure transmitting medium used above 290 K was DC200 silicone oil which solidifies [55,56] near 1 GPa at RT but has the advantage of being thermally stable up to 700 K where pyrolysis starts [52,56]. Changing p with a solid pressure medium creates stress, damaging the sample, the oven, the Manganin coil and the fragile current and potential leads to the sample. When changing p above 0.5 GPa the oven was, therefore, heated to near 500 K to keep the oil liquid in and near the oven. In early experiments, oil with a viscosity of 100 cSt was used to ensure leakage-free operation, but because effects of solidification were noted [55] most experiments were carried out using oil viscosities of 10–50 cSt.

The low-T behaviour of Ti and alloy A was investigated in separate high-p experiments down to below 80 K, using a 45 mm inside diameter piston-and-cylinder device cooled by a He compressor system [57]. In these experiments p was measured using a calibrated Zeranin coil instead of Manganin and the pressure medium was a 50/50 mixture of n- and *iso*-pentane, hydrostatic down to about 150 K [54].

In all high-p experiments T was measured using type K thermocouples. Wire from the same spools had been calibrated against a