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# Thin vanadium–aluminium alloy film resistivity saturation

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Studies of the resistivity and structure of vanadium–aluminium alloy films have been performed. $V_{0.93}Al_{0.07}$ alloy films have been evaporated with an electron gun in an ultrahigh vacuum ($p \sim 10^{-7}$ torr) on to quartz substrates at room temperature. Resistivity against temperature has been studied *in situ* in vacuum of $10^{-10}$ to $10^{-8}$ torr in the temperature range 300 to 850 K. A resistivity saturation effect has been observed. The analysis of this effect has been conducted on the basis of the shunt resistance model.

## 1. Introduction

The electrical properties of high-resistance conductors with resistivities of the order of $150\,\mu\Omega\,\text{cm}$ differ significantly from those of typical metals and semiconductors. The transition metal alloys form most of the highly resistive conductors. Some intermetallic compounds of $A_{15}$ structure known as superconductors with a high temperature of transition to superconductivity belong to the above.

The temperature dependence of the resistivity ($\varrho$) for highly resistive conductors cannot be explained within the Bloch–Blotzmann theory. Mooij [1] has observed that resistivity anomalies exhibit universal features which are subject to certain rules, described by Allen and Chakraborty [2] as the Mooij laws. The temperature coefficient of resisitivity (TCR) of highly resistive conductors, $\alpha = (1/\varrho)\,\mathrm{d}\varrho/\mathrm{d}T$, is much lower at room temperature than that expected from the Block–Grüneisen theory. It seems that there is a correlation between $\alpha$ and $\varrho$. The TCR is generally negative for conductors of resistivities greater than $\varrho^* \sim 150\,\mu\Omega\,\text{cm}$ and opposite for the other ones.

The Bloch–Boltzmann theory based on the near-free electron (NFE) model is no longer valid when the mean free path (MFP) of electrons ($\lambda$) approaches the interatomic spacing ($a$). It may apply to alloys with a high defect concentration. The inequality $\lambda < a$ being impossible is known as the Ioffe–Regel criterion [3]. A similar statement is claimed by Mott [4]. The concept of the minimal MFP was introduced for the first time by Mooij [1] to describe the anomalies in the temperature coefficient of resistance and then developed by Fisk and Webb [5]. A resistivity approaching a constant value of $\varrho^* \sim 150\,\mu\Omega\,\text{cm}$ was observed for $Nb_3Sb$ and $Nb_3Sn$ and this phenomenon was called by Fisk and Webb [5] a resistivity saturation.

Gurvitch [6] generalized the Mott formula for the case of different electron densities ($n$) and lattice constants ($a$) and gave an expression for the saturated resistivity as follows:

$$\varrho^* = \frac{1.29 \times 10^{18}}{n^{2/3}a} \quad \mu\Omega\,\text{cm} \qquad (1)$$

where $n$ is measured in $\text{cm}^3$ and $a$ in Å (1 Å = 0.1 nm). Wiesmann *et al.* [7] showed that the highly resistive conductor resistivity can be described within the shunt resistance model in a wide temperature range by the expression

$$\frac{1}{\varrho(T)} = \frac{1}{\varrho_i(T)} + \frac{1}{\varrho^*} \qquad (2)$$

where $\varrho_i(T)$ denotes the ideal resistivity derived from the Bloch–Boltzmann theory based on the NFE model and $\varrho^*$ means the saturated resistivity. The shunt resistance model is frequently applied [6, 8–10] to studies of highly resistive conductor resistivity saturation.

Resistivity saturation is an important and difficult problem in electrical conductivity theory. This problem was tackled not too long ago. The models invented [11–15] have not yielded a theory completely describing the anomalous behaviour of highly resistive conductor resistivity. The Belitz–Schirmacher [16] theory seems to be the most exact one. It treats the conductor as a strongly disordered system with high concentrated potentials which are responsible for electron scattering and according to Anderson [17] make the electrons localized.

In this theory the phonons in a conductor which contains a great number of defects (usually in metal alloys) enhance electron scattering and alternatively tunneling. When the MFP of electrons approaches the de Broglie wavelength ($\lambda_F$), the conductivity is dominated by tunnelling. The resulting competition between scattering and tunnelling gives rise to anomalous behaviour of the temperature dependence of resistivity.

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Highly resistive conductors generally have a short MFP of electrons. This fact leads to the failure of thin films of highly resistive conductors to exhibit the electrical size effect which is commonly observed for thin films of low resistivity metals with a long MFP (comparable with the film thickness).

Studies of resistivity against temperature for highly resistive conductors in the form of thin metal alloy films are often difficult and require the measurements to be conducted over a wide temperature range, which is an obstacle in maintaining an ultrahigh vacuum especially at higher temperatures. An ultrahigh vacuum is also required to prevent chemical reactions between the thin-film alloy components and residual gases such as oxygen, nitrogen and hydrogen, especially at higher temperatures. Vanadium–aluminium alloy film is one of the materials requiring an ultrahigh vacuum. The electrical properties of V–Al alloy, particularly $V_3Al$, are usually studied from the superconduction viewpoint. The few papers [1, 18] on alloy resistivity in the high-temperature range indicate a necessity to undertake further studies.

## 2. Experimental details

Thin vanadium–aluminium films were evaporated on to quartz substrates at room temperature in a vacuum ($p \sim 10^{-7}$ torr) in a UNI5P system (Riber). V–Al films were deposited by means of an electron gun with a controlled beam. The electron gun system possessed two seats containing separately the alloy components. 5N aluminium and 99.7% vanadium (Kock Light Laboratories) were used. Both the alloy components were evaporated simultaneously, the duration of the electron beam at each seat being regulated.

One evaporation process yielded five films (on one substrate) of different thicknesses, depending upon the time of screening the part of the substrate with a shutter. The deposition time ranged from a few tens of seconds up to several minutes.

Fig. 1 shows the substrate with the alloy films and vanadium electrodes (evaporated in a separate process). The film resistance was measured in a vacuum of $10^{-8}$ to $10^{-10}$ torr as a function of temperature. The substrate temperature ranged from 300 to 850 K and was monitored with an Fe–K$\alpha$ thermocouple. The film thickness ($d$) was measured by Tolansky's method [19]. The films were 1 mm wide ($w$) and 5 mm long ($l$), the latter being the distance between the voltage electrodes. The film resistance ($R$) for each temperature was measured after 20 min of isothermal annealing. The film resistivity was determined from the expression

$$\varrho = \frac{Rdw}{l} \tag{3}$$

In the chamber there were two additional substrates, one made of copper, the other of glass. The former served as a sample for electron microprobe studies. The latter made it possible to obtain the separate alloy-component films, i.e. vanadium film and aluminium film. The thicknesses of these films, measured by Tolansky's method [19], served for determination of the deposited alloy composition.

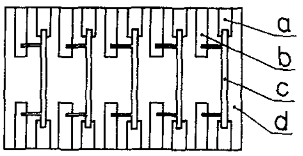

*Figure 1* Substrate with the evaporated electrodes and films: (a) current electrodes, (b) voltage electrodes, (c) films, (d) quartz substrate.

V–Al alloy film structure was examined with an Em-301 Philips electron microscope. Examination showed that the films were polycrystalline. Based on the diffractograms obtained it was found that the alloy films were a solid solution of aluminium in vanadium. As known from V–Al phase equilibria [20] the maximal solubility of aluminium in vanadium at 500° C is 40.5 at %.

## 3. Experimental results

The resistivity of $V_{0.93}Al_{0.07}$ alloy films against temperature was studied. The resistivity measurements were conducted in vacuum of $10^{-10}$ to $10^{-8}$ torr in the temperature range 300 to 850 K. The film composition was determined with an electron microprobe. A typical temperature dependence of resistivity, $\varrho$, for the most representative film is shown in Fig. 2.

The film in the as-prepared state exhibited the resistivity represented by Point A. The points on the curve AB are the experimental points corresponding to the film resistivity after subsequent isothermal annealing processes. After annealing the film was cooled down to room temperature (Point C). Points on the curve CD came from another series of isothermal annealing. The respective series of anneals are marked with different symbols and consecutive numbers (1 to 9). Each

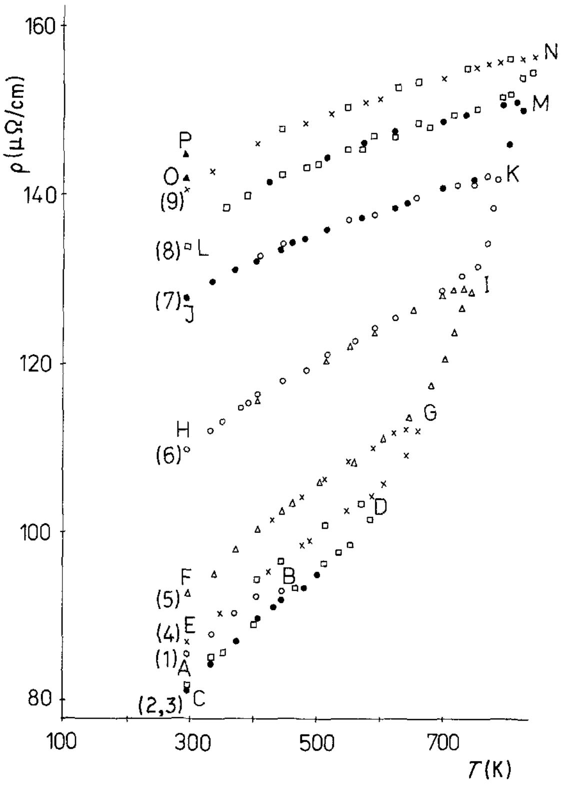

*Figure 2* Temperature dependence of resistivity $\varrho$ for the film ($V_{0.93}Al_{0.07}$, $d$ = 94.5 nm). For explanation see text.

series started at room temperature and ended at a higher temperature when compared to that of the previous series.

## 4. Discussion

$V_{0.93}Al_{0.07}$ alloy film, due to its aluminium content of 7 at %, is a highly resistive conductor. The resistivity of the film in the as-prepared state was 86.1 $\mu\Omega$ cm, which was a few times higher than that of pure vanadium films [21] as well as that of the bulk vanadium (20.11 $\mu\Omega$ cm at room temperature [22, 23]).

The first series of annealing (Curve AB with open circles) caused an irreversible drop in resistivity due to recrystallization and lattice defect reduction, and thus a lowered conduction electron scattering. The resistivity of the film cooled down to room temperature (Point C) was lower and equal to 81.5 $\mu\Omega$ cm. The second series of annealing processes (marked with closed circles in the figure) gave reversible changes of resistivity. After cooling down to room temperature the film exhibited almost the same resistivity. The third series of annealing (illustrated in Curve CD with squares) made the resistivity changes irreversible. The film resistivity after cooling down to room temperature is given by Point E in the figure and was equal to 87.2 $\mu\Omega$ cm. Irreversible changes in resistivity due to these annealing processes were the result of the lattice defect increase caused by gas absorption which did not compensate for the defect reduction due to film recrystallization. Both alloy components easily reacted with residual gases such as oxygen, nitrogen and hydrogen, especially when the film temperature increased. The influence of gases on resistivity was particularly observed for Curve OP, the resistivity rise being caused by passing to atmospheric pressure. The fourth series of annealing (Curve EG), similarly to the next ones (from 5 to 9), caused a further and irreversible rise of resistivity. The temperature dependences of resistivity became more non-linear with increasing temperature of annealing.

Curves LM and ON exhibited a resistivity saturation effect. In order to describe the resistivity of films exhibiting the saturation effect Wiesmann *et al.* [7] proposed the empirical shunt-resistor model. The resistivity ($\varrho$) against temperature ($T$) for Curves LM and ON can be described by an equation derived within the Wiesmann model. The expression (Equation 2) for $\varrho_i(T)$ in the model of nearly free electrons exhibits a linear character at higher temperatures and may be rewritten in the form

$$\varrho_i(T) = \varrho_0 + \beta T \qquad (4)$$

where $\varrho_0$ denotes the approximate residual resistivity and $\beta$ is a constant. After substituting Equation 4 into Equation 2 the following expression linear with temperature can be obtained:

$$\left(\frac{1}{\varrho(T)} - \frac{1}{\varrho^*}\right)^{-1} = \varrho_0 + \beta T \qquad (5)$$

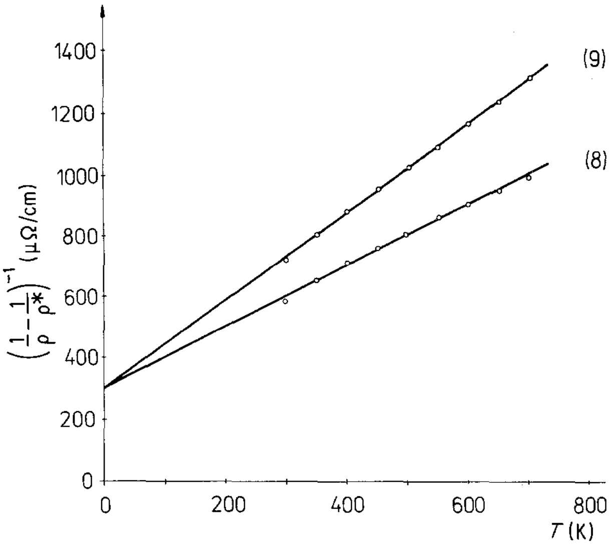

*Figure 3* Temperature dependence of $[(1/\varrho) - (1/\varrho^*)]^{-1}$ for the film after the eighth and ninth series of annealing.

The above equation constitutes an important criterion, allowing us to check if a given temperature dependence of a conductor resistivity exhibits the resistivity saturation effect, i.e. in other words it renders it possible to find the saturation resistivity ($\varrho^*$), if any, for which a linear dependence (Equation 5) may be achieved.

The calculations performed for Curves LM and ON yielded a value of $\varrho^*$ equal to 175 $\mu\Omega$ cm. Plots of Equation 5 obtained for this value of $\varrho^*$ are linear (Fig. 3).

As seen from Fig. 2 there was a drop in $\mathrm{d}\varrho/\mathrm{d}T$ and TCR with increasing resistivity due to subsequent annealing processes. It remains in agreement with the Mooij laws [1].

Similar saturation effects in resistivity and TCR and a drop in $\mathrm{d}\varrho/\mathrm{d}T$ due to resistivity increase caused by annealing were observed in the case of the remaining films of this series. It must be concluded that the content of 7 at % Al (dissolved in the vanadium lattice) in $V_{0.93}Al_{0.07}$ alloy introduced a significant defect concentration. The defects reduced the mean free path of electrons from $1.2 \times 10^{-9}$ m for pure vanadium [21] down to the value close to the interatomic distance. This reduction seems to be the most reasonable explanation of anomalies in the electrical properties of $V_{0.93}Al_{0.07}$ alloy, and moreover it remains in agreement with the views of various authors [1, 4–6].

## 5. Summary

The results of studies performed for thin vanadium–aluminium films let us draw the following conclusions:

1. Thin V–Al films with an aluminium content of a few per cent or more are highly resistive conductors satisfying the Mooij laws.
2. The above films exhibit a resistivity saturation effect, being in agreement with the Wiesmann model [7].
3. Films with a resistivity higher than the saturation resistivity exhibit a negative TCR.
4. The reason for the resistivity saturation effect lies in a reduction of the mean free path of electrons down to values close to the interatomic distances.

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