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Structural and superconducting properties of Nb–Ti alloy thin films

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Abstract. The structural instability in Ti rich compositions of Nb–Ti alloy system, which leads to various anomalies in the normal and superconducting state properties, has been extensively studied in bulk samples in the past. In this paper we report the formation of thin films of several compositions in the Ti rich region of this alloy system by RF magnetron sputtering and investigation of their electrical properties. Compositional analysis of two representative films was carried out by the RBS technique and the compositions agreed to within 2% of the targeted values. The anomalous variations in the electrical properties characteristic of the bulk, which can be ascribed to the structural instability related to the formation of athermal ω-phase, are also observed in thin films.

Keywords. Superconductivity; thin films; structural instability; Nb–Ti.

1. Introduction

Despite the promise shown by the high temperature superconductors, Nb–Ti alloys remain the most widely used materials for the high current applications of superconductivity. The commercially useful compositions of this alloy system are titanium rich and range between 35 and 45 at.% Nb (Hawsworth and Larbalestier 1980), although the transition temperature, T_c, peaks towards the niobium rich side of the compositions, viz. in the range 50–70 at.% Nb (Hulm and Blaugher 1961). The reason for this stems basically from the anomalous increase in the normal state resistivity ρ_n, defined at a temperature just before the onset of superconducting transition, as the Ti concentration increases. This increase in ρ_n more than compensates for the slight decrease in γ, the electronic specific heat coefficient and T_c, resulting in the enhancement of the upper critical field H_{c2} for the Ti rich alloys (Larbalestier 1981). The incipient instability of the β-phase in the Ti rich composition region plays an important role in the anomalous increase in the resistivity and the enhancement of H_{c2} (Prekul *et al* 1974; Collings 1980; Bychkov *et al* 1981; Hochstuhal and Obst 1982; Hariharan *et al* 1984, 1986). This instability of the β-phase is relieved by one of a variety of structural transformations (Hariharan *et al* 1986). Among them the transformation to ω-phase is most extensively studied, because of its marked effect on several physical properties. While considerable amount of work exists on the properties of these alloys in the bulk form, little work exists on the alloys in the thin film form. In this paper we report the formation of alloy thin films with the targeted compositions in the Ti rich region and the measurements of their normal and superconducting properties.

2. Experimental

Four sets of $Nb_{100-x}Ti_x$ alloy films, with $x = 58, 64, 70, 77, 81$ and 87 at.%, were prepared by RF magnetron sputtering on to glass substrates, held at room temperature. To

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produce Nb–Ti films of different compositions, deposition rates from Ti and Nb targets were calibrated experimentally under different sputtering conditions. This was carried out by varying the DC bias voltage at the Nb and Ti targets in separate runs but by keeping the other parameters like the Ar gas flow rate (11 SCCM) and Argon pressure (0·53 Pa) constant. Substrates were rotated at 3 rpm and films were deposited for 30 min. The total thickness of the deposited films was measured at each value of DC bias voltage by a Dektak 3030 A surface profiler. In order to prepare homogeneous Nb–Ti alloy films, RF plasma was struck over both Nb and Ti targets simultaneously while the substrates rotated over the targets. The deposition rates from the two targets were selected depending upon the composition of Nb–Ti film desired. The thickness of each film was measured which was in the range 150–170 nm.

Crystal structures of the films were examined by conventional X-ray diffraction analysis by using Cu-K_α radiation in the standard θ–θ Bragg Brentano arrangement. Lift off photolithography was used to pattern a four-probe geometry for resistivity and T_c studies. The RBS analysis of the two samples with the nominal compositions $Nb_{19}Ti_{81}$ and $Nb_{30}Ti_{70}$ revealed the actual compositions to be $Nb_{20}Ti_{80}$ and $Nb_{28}Ti_{72}$. All the compositions of films reported in present study are based on the targeted values.. The actual composition can be taken to be within 2% of the targeted values. The electrical resistivities of the films were measured by the standard four-probe technique by varying the temperature between 4·2 K and 300 K in a dipstick cryostat. Temperature was measured by using a silicon diode thermometer. The variations of lattice parameter, superconducting transition temperature, T_c, normal resistivity, ρ_n, and room temperature resistivity ρ_{300K} with respect to Ti concentration in films have been shown in table 1.

3. Results and discussion

The superconducting transition temperature T_c decreases with the increase in Ti content in the Ti rich Nb–Ti alloy films studied. The absolute values of T_c of our films are in accordance with the reported T_c values of water quenched bulk samples of Hulm and Blaugher (1961). ρ_n increases with the increase in Ti content. However, for a given composition, ρ_n of the thin film is found to be larger than the typical value found in the corresponding bulk alloy by as much as 20 $\mu\Omega$-cm (Hulm and Blaugher 1961; Bychkov *et al* 1981) up to a Ti concentration of 80 at.%. Beyond this there are larger deviations

Table 1. Normal and superconducting properties of $Nb_{100-x}Ti_x$.

Sample composition	ρ_n ($\mu\Omega$-cm)	ρ_{300K} ($\mu\Omega$-cm)	T_c (K)	Lattice parameter (nm)
$Ti_{58}Nb_{42}$	76·45	85·28	8·1	0·32837
$Ti_{64}Nb_{36}$	95·83	101·15	6·9	0·32957
$Ti_{70}Nb_{30}$	98·49	103·15	6·9	0·33039
$Ti_{77}Nb_{23}$	104·18	110·22	7·0	0·33045
$Ti_{81}Nb_{19}$	120·18	128·54	5·3	0·33050
$Ti_{87}Nb_{13}$	124·81	134·14	4·5	0·33401

from the bulk value which will be discussed separately. This increase in the resistivity ρ_n may be because of tensile stress developed in the films which are deposited on glass substrates at room temperature. Another possibility for the increase in the resistivity is due to grain boundary scattering from the small grain size (16 ± 1 nm) of our polycrystalline films.

The variation of ρ_n with composition of the films shows a more marked difference from that of the bulk alloys beyond 80 at.% Ti. In the bulk alloys the resistivity rises monotonically with Ti content and peaks near 78 at.% Ti (Prekul *et al* 1974; Bychkov *et al* 1981; Collings 1983). The region between 70 to 78 at.% Ti is marked by dynamical fluctuation of the diffuse ω-phase, which is due to the incipient instability of the bcc lattice and leads to monotonic increase in resistivity with increase of Ti content. As shown by Hariharan *et al* (1986), this increase in resistivity could be understood by invoking a model based on two level system (TLS); indeed the ω-phase instability related scattering of electrons is the most dominant mechanism of resistivity in Nb–Ti alloys. In bulk samples of higher Ti content, beyond about 80 at.%, the structural transformation from β to martensitic α''-phase occurs and the resistivity decreases steeply. In the case of our thin films the resistivity keeps on increasing with Ti content right up to 87 at.%. This may be because of persistence of ω fluctuation up to this concentration, and films maintain the bcc structure without undergoing structural transformation to α''-phase. Resistivity value of our $Nb_{13}Ti_{87}$ film is 134 μΩ-cm. This value is among the highest reported for Nb–Ti alloy system.

Unlike the bulk alloys, which show negative temperature coefficient of resistivity, $d\rho/dT$, near 78 at.% Ti (Hochstuhal and Obst 1982), the films exhibit positive $d\rho/dT$ for all the compositions. However, the variations of $d\rho/dT$, averaged over the intervals 10–300 K, with composition exhibit minima near 70 at.% Ti (figure 1). It is interpreted that the decreasing values of positive $d\rho/dT$ are the direct manifestations of the

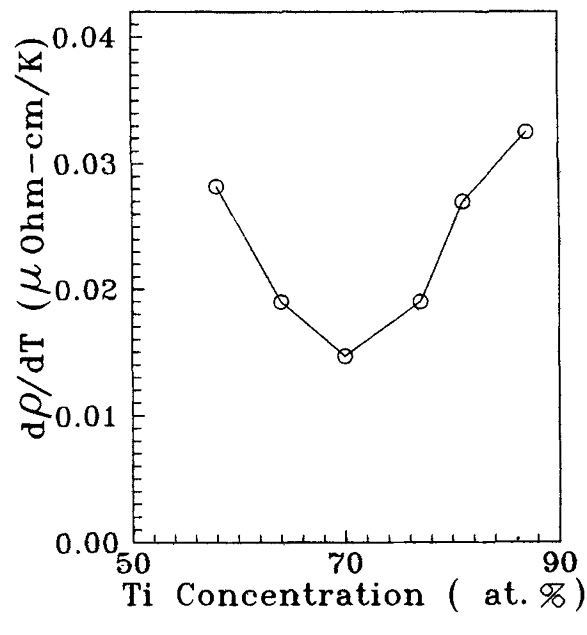

Figure 1. Variation of $d\rho/dT$ with Ti content in Nb–Ti films.

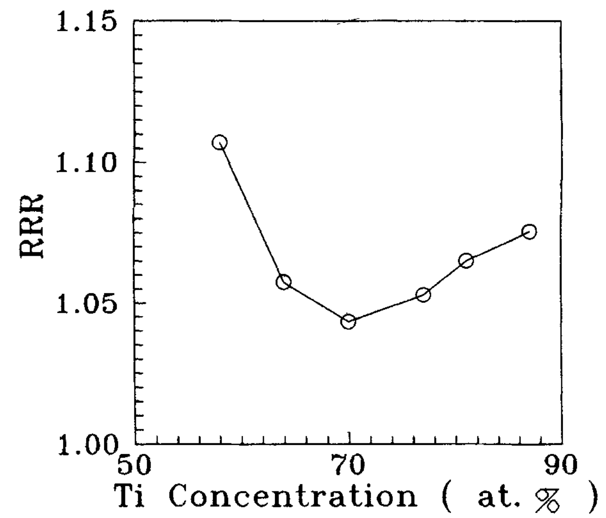

Figure 2. Variation of residual resistivity ratio with Ti content in Nb–Ti films.

dynamical ω fluctuations, which become pronounced near 70 at.% Ti, where the incipient instability of the bcc lattice is relieved by structural transformation to athermal ω-phase. Further decrease in positive values of $d\rho/dT$ with increase in Ti concentration is arrested in our thin films due to the β to athermal ω transformation. The reason that this occurs at a lower composition of Ti may be due to the influence of intrinsic stress present in the films. Thus, it is interpreted that as the Ti content of the films is increased beyond 70 at.%, the β-phase instability is progressively relieved leading to an increase in the positive value of $d\rho/dT$ (figure 1). We believe that the non-occurrence of negative $d\rho/dT$ in the films in marked contrast to the behaviour seen in bulk samples is mainly due to the tensile stress, which is of the order of 3–5 $\times$ 10^8 N/m^2 as calculated from the increase in lattice parameter compared to bulk alloys. Stress has been seen to change $d\rho/dT$ from negative to positive values in as-quenched $Nb_{22}Ti_{78}$ alloy under application of 2·4% tensile stress (Obst *et al* 1980) which is equivalent to the stress of 6·9 $\times$ 10^8 N/m^2.

The residual resistivity ratios (RRR) ρ_{300K}/ρ_n decrease initially with the increase in Ti content, reach minimum at 70 at.% and thereafter increase with further increase in the Ti content (figure 2). These variations are similar to that of $d\rho/dT$ and support the above mentioned interpretation.

4. Conclusion

We conclude that the instability is incipient for Ti compositions below 70 at.% while the instability has been relieved by the formation of the athermal ω-phase for compositions beyond 70 at.%. The films retain the bcc phase right up to 87 at.% Ti presumably with fine precipitates of athermal ω-phase. It is interesting to note that while in the β quenched bulk alloys the composition at which the instability was interpreted to be relieved occurred between 78 and 82 at.% Ti (Collings 1983), in the present study, this occurs at a lower Ti composition. It is known that stress influences the instability in the direction of relieving it in favour of a structural transformation (Obst *et al* 1980; Hochstuhal and Obst 1982). Our result in thin films are consistent with this picture.

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