HIGH-RATE SPUTTERING OF Nb-Al-Ge AND Nb-Al SUPERCONDUCTORS

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ABSTRACT

High quality Nb-Al-Ge and Nb-Al superconductor deposits were made at a rate of 1 $\mu\text{m}/\text{min}$ using high-rate sputtering techniques. Deposits were up to 1 mm thick. High-rate sputtering reduced fabrication difficulties and significantly increased current capacities. Sputtering equipment capabilities indicate reasonable quantities of high field superconductors can be made by high-rate sputtering for practical application. The Nb-Al-Ge and Nb-Al deposits were of high quality as indicated by highly reflective metallic mirror surfaces, even in thicknesses up to 1 mm. Moreover, the deposits were completely void-free and they did not seem to be overly brittle either before or after heat treatment. Crystal structures for deposits made at 10 $^{\circ}\text{C}$ to 20 $^{\circ}\text{C}$ were not clearly defined, but probably were body-centered-cubic (bcc). Heat treatment at 550 $^{\circ}\text{C}$ to 850 $^{\circ}\text{C}$ completely transformed the bcc deposits to extremely small grains of the A-15 crystal structure. The A-15 phase formed by heat treatment for short times (e.g., 1 hr to 5 days) at 750 $^{\circ}\text{C}$ was metastable and supersaturated with Al and Ge. Deposition and heat conditions for decomposition of the metastable A-15 phase were identified. The deposits having the highest critical temperatures (18 $^{\circ}\text{K}$) consisted only of undecomposed metastable A-15 phase. In order to assess practical use of the sputtered superconductors, one- to two-meter lengths of ribbon and filamentary Nb-Al-Ge superconductor were produced on ribbon and wire substrates. It also was found that an excellent superconductor-stabilizer bond can be formed by high rate sputter-deposition of copper stabilizer onto heat treated Nb-Al-Ge and Nb-Al superconductors.

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I. INTRODUCTION

Significant advances in applied superconductivity can be expected from the use of sputter-deposited high field superconductors if recent research trends continue. For example, the critical temperature of Nb_3Ge was raised by Gavalier¹ to 22.3°K with special sputter-deposition techniques, and Nb_3Ge now has the distinction of having the highest known critical temperature. Moreover, recent results²⁻⁴ show that high-rate sputter deposition is an excellent method for producing high quality Nb-Al-Ge and Nb_3Al superconductors. Thick sputter-deposited $\text{Nb}_{12}\text{Al}_3\text{Ge}$ made at a rate of 1 $\mu/\text{min.}$ had critical currents at 4.2°K up to $4.4 \times 10^5 \text{ A/cm}^2$ at 100 kOe,² A/cm^2 at 150 kOe,³ and at 200 kOe;³ critical temperatures were up to 18.5°K.^{2,4} The high critical currents were attributed to the formation of extremely small, 350 Å diameter grains during heat treatment.^{2,4} The critical currents for Nb-Al-Ge are comparable at all fields to those for Nb_3Sn and V_3Ga , which are the current leading materials for applications above 100 kOe.

The full potential of Nb-Al-Ge and Nb_3Al superconductors has not been realized due to fabrication limitations that sputter deposition can overcome. Specifically, critical fields for Nb-Al-Ge (410 kOe)^{5,6} and Nb_3Al (295 kOe)^{8,5} are much higher than those for Nb_3Sn (225 kOe)⁷ and V_3Ga (210 kOe).^{8,7} Critical temperatures of Nb-Al-Ge (20.7°K)^{8,2} and Nb_3Al (18.7°K)^{8,9} also are higher than those for Nb_3Sn (18.3°K)^{8,7} and V_3Ga (14.5°K).^{7,9} V_3Ga is currently the best choice for applications above 150 kOe due to its greater current capacity,¹⁰ but the high cost of Ga alone is sufficient reason to encourage development of lower cost superconductors containing Nb, Al, and Ge.¹¹

II. SPUTTERING CAPABILITY

High rate sputtering has advanced to the point where rather massive deposits can be made at quite high rates. A freestanding 1.3 kg cylinder of a Cu-Zr alloy, for example, was sputter deposited at a rate of 1.7 μ /min. Another deposit of the same alloy was 5.5 kg and up to 1.2 cm thick. If the same mass (5.5 kg) of Nb-Al-Ge superconductor were to be sputter-deposited in the form of a 1000 A capacity ribbon, the conductor would be 3000 m long (assuming a current density of 4.4×10^5 A/cm² at 100 kOe and 4.3°K). The cost of sputter-deposited superconductor would not be excessive. Estimates of the material, electrical power, equipment, and operating costs suggest the price of the conductor to be about \$1.67/kA · m, including stabilizer (Table I).

TABLE I

Cost Estimate for a One Meter Length of 1000 A Capacity
Sputter-Deposited Nb-Al-Ge Superconductor & Stabilizer

Item	Cost
Nb	\$0.14
Al	0.01
Ge	0.10
Stabilizer, Al	0.25
Electrical Power	0.02
Equipment	0.15
Operating	0.75
Total --	\$1.67/kA · m

III. SPUTTER DEPOSITION OF Nb-Al-Ge AND Nb-Al

The objective of the sputter-deposition work was to form an undecomposed A-15 phase containing 75 at.% Nb for compositions where the A-15 phase is not thermodynamically stable. Such metastable compositions were expected to have the highest critical temperatures. It was found that a single, undecomposed A-15 phase of very fine grain size could be made by sputter deposition at a relatively low temperature, e.g. 20°C, and heat treatment at a moderate temperature, e.g. 750°C, Figure 1.

Deposits made at 20°C almost certainly had a distorted body-centered cubic (bcc) crystal structure. Only three very broad (bcc x-ray diffraction lines were found for Nb-Al-Ge, but Nb-Al made at 20°C was clearly bcc. A Nb₃ (Al_{0.75}Ge_{0.25}) deposit made at a temperature estimated to be between 50°C and 200°C also was clearly bcc. The deposits were made at a rate of 1 μ/min. from compacted elemental powder sputtering targets.

Heat treatment at 750°C completely transformed the bcc phase to the A-15 phase (Figures 1 and 2). Critical temperatures were low and lattice parameters of the A-15 phase were high for very short heat treatment times, e.g. 1 hr (Figure 1). The critical temperature reached a maximum of about 18°K after heat treatment for 1 to 5 days at 750°C (Figure 1). Similarly, the lattice parameter reached a minimum after 5 days (Figure 1). Diffraction lines for extra phases were barely detected in the x-ray diffraction patterns after 5 days, but they were clearly evident after 20 days at 750°C.

Decomposition of the metastable A-15 phase caused an increase in the Nb content in the remaining A-15 phase solution as indicated by the increase in the A-15 phase lattice parameter between 5 and 20 days (Figure 1). The critical temperature decreased as a consequence of the change in the A-15 phase composition away from stoichiometric Nb₃ (Al_{0.75}Ge_{0.25}) - (Figure 1). Sputter-deposited

Nb_3Al did not decompose quite as readily as $\text{Nb}_3(\text{Al}_{.75}\text{Ge}_{.25})$. Extra phases were not detected in the $\text{Nb}-\text{Al}_3$ until after 20 days at 750°C , and neither the A-15 phase lattice parameter nor the critical temperature changed between 5 days and 20 days at 750°C . Critical temperatures measured with the four-probe resistance method were quite sharp for $\text{Nb}_3\text{-Al}$ after 5 days at 750°C (Figure 3), but there was some structure to the curves for $\text{Nb}_3(\text{Al}_{.75}\text{Ge}_{.25})$ after 5 and 20 days at 750°C (Figure 4).

Several other Nb-Al-Ge compositions were deposited at low temperature (20°C) and heat treated for 5 days at 750°C for comparison of critical temperatures (Table II). The results show that all critical temperatures were above 15°K , but that $\text{Nb}_3(\text{Al}_{.75}\text{Ge}_{.25})$ had the highest critical temperatures (17.1 to 18.3°K , Table II). One deposit ($\text{Nb}_{80.56}\text{Al}_{13.85}\text{Ge}_{5.6}$) did not transform on heat treatment at 750°C , but it did transform to the A-15 phase after heat treatment for 2 hrs at 1240°C .

TABLE II

Critical Temperatures for Six Nb-Al-Ge
and Nb-Al Compositions after Deposition at
 20°C and Heat Treatment for 5 Days at 750°C

Deposit Composition	Critical Transition Temperature Range, $^\circ\text{K}$
$\text{Nb}_{75}(\text{Al}_{.75}\text{Ge}_{.25})$	17.1-18.3
Nb_3Al	17.1-17.4
$\text{Nb}_{75}(\text{Al}_{.6}\text{Ge}_{.4})$	15.6-15.9
$\text{Nb}_{71.67}\text{Al}_{23.78}\text{Ge}_{4.65}$	16.0-17.2
$\text{Nb}_{70}\text{Al}_{30}$	15.1-15.9
$\text{Nb}_{80.56}\text{Al}_{13.85}\text{Ge}_{5.6}$	(still bcc)

Heat treatment at 1240°C verified the conclusion that the single A-15 phases formed at 750°C were metastable. The diffraction lines for extra phases were much stronger and there were many more extra lines after heat treatment for 2 hrs at 1240°C than after heat treatment for 20 days at 750°C (Figure 5). According to the phase diagram,⁽¹²⁾ the A-15 phase should be less supersaturated with Al and Ge at 1240°C than at 750°C so the decomposition at 750°C is limited strictly by reaction kinetics.

Decomposition of the A-15 phase also occurred immediately in deposits made at elevated temperatures. The A-15 phase formed directly at 485°C for $\text{Nb}_{75}(\text{Al}_{.75}\text{Ge}_{.25})$, but diffraction lines for extra phases were already present, and critical temperatures were low even after heat treatment.

IV. SUPERCONDUCTOR FABRICATION

Work has been started to fabricate useful superconductors by sputter-deposition. One method tried was to pass ribbon and filament substrates from a reel on one side of the sputtering chamber, through the chamber where it was coated, and onto a second reel on the other side of the chamber (Figure 6). A one-meter long strip of 1.25 cm wide stainless steel and some two-meter long, 1.25 $\frac{1}{8}$ diameter tungsten wire substrates were successfully coated with 2 to 20 μ of Nb-Al-Ge superconductor by this method. Substrate temperatures were rather high for the initial experiments, but lower substrate temperatures are possible now so that optimum superconductor properties can be obtained.

Another potential applied superconductivity use for high-rate sputtering was found during the course of the sputtered superconductor studies. Specifically it is the formation of an excellent mechanical and electrical bond between superconductor and stabilizer. Formation of a good electrical bond between A-15 phase superconductors

and their stabilizer is often very difficult. Copper stabilizer has been well bonded to critical current samples by ion etching the heat treated superconductor prior to depositing a high conductivity coating, which then is intimately bonded to the superconductor. The coating need only be thick enough for a copper-to-copper solder joint to be made.

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- FIGURE 1. A-15 phase lattice parameter and control temperature, T_c , versus heat treatment time at 750°C for sputter-deposited $\text{Nb}_{75}(\text{Al}_{.75}\text{Ge}_{.25})$ made at 20°C . The upper T_c curve give the temperature where superconductivity is first indicated and the lower T_c curves give the temperature for a completely superconducting path through the sample, as indicated by the four-probe resistance method.
- FIGURE 2. X-ray diffraction pattern for an undecomposed, metastable A-15 phase in an $\text{Nb}_{75}(\text{Al}_{.75}\text{Ge}_{.25})$ sputter deposit made at 20°C and heat treated 1 day at 750°C .
- FIGURE 3. Critical transition temperature range for Nb_3Al sputter deposited at 20°C and heat treated 5 days at 750°C .
- FIGURE 4. Critical transition temperature ranges for $\text{Nb}_3(\text{Al}_{.75}\text{Ge}_{.25})$ made at 20°C and heat treated 5 days at 750°C (left) and 20 days at 750°C (right).
- FIGURE 5. X-ray diffraction pattern for an $\text{Nb}_{75}(\text{Al}_{.75}\text{Ge}_{.25})$ deposit after heat treatment for two hours at 1240°C showing significant decomposition of the A-15 phase.
- FIGURE 6. Assembled reel-to-reel equipment for sputter-deposition of Nb-Al-Ge and Ni-Al superconductors on ribbon and filament substrates.

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FIGURE 4. Critical transition temperature ranges for $\text{Nb}_3(\text{Al}_{.75}\text{Ge}_{.25})$ made at 20°C and heat treated 5 days at 750°C (left) and 20 days at 750°C (right).

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