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Progress Report

LASL Nb₃Ge Conductor Development

April 1—June 30, 1980

MASTER

University of California



LOS ALAMOS SCIENTIFIC LABORATORY

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LASL Nb₃Ge Conductor Development

April 1—June 30, 1980

Compiled by

M. P. Maley

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LASL Nb₃Ge CONDUCTOR DEVELOPMENT

April 1—June 30, 1980

Sixteenth Quarterly Progress Report

Compiled by

M. P. Maley

ABSTRACT

The 16th quarterly progress report of the Los Alamos Scientific Laboratory program to develop Nb₃Ge as a superconductor with potential applications to power transmission lines covers the period April 1—June 30, 1980. During this quarter an attempt to test our first 1-m-long Nb₃Ge cable at Brookhaven National Laboratory was unsuccessful owing to leaks in the cryogenic system. The tests are now scheduled for early July. Investigations of the influence of additions of boron and gallium to Nb₃Ge on its superconducting properties have been completed. Gallium additions produce a small decrease in T_c (~1.0 K) but do not appear to enhance H_{c2}. A thermal stress analysis of the cooldown of our Nb₃Ge tapes from their deposition temperature has been completed. It appears that a large bending moment generated by differential thermal contraction between the Nb₃Ge coat and the copper substrate may be responsible for longitudinal edge cracks.

The appendix describes one of the problems encountered in developing a superconductor from a copper strip coated with a thin layer of niobium-germanium (Nb₃Ge) polycrystals. The conductor was made with several thicknesses of coating, and the thick coatings developed a crack. A series of hand calculations was done to define the mechanisms involved and to try to quantify the stress levels above which the crack occurs.

I. INTRODUCTION

The Nb₃Ge conductor development program of Los Alamos Scientific Laboratory (LASL) commenced a third phase on January 1, 1979. The long-term objective of the program is to develop a conductor suitable for application to superconducting power transmission lines (SPTLs) that is significantly superior to presently available conductors. More specifically, the aim is to exploit the record-high T_c (~23 K) of Nb₃Ge to permit operation of an SPTL in the temperature range 14-16 K. In the initial phase of the program, completed in June 1976, we developed a chemical vapor deposition (CVD) process by which short samples of Nb₃Ge could be produced with superconducting properties that meet the requirements for power transmission at T = 12 K. A description of the program accomplishments through June 30, 1976 may be found in the EPRI Final Report (TD-200).¹ The second

phase, begun on July 1, 1976, concentrated on the task of modifying the basic CVD process to produce long lengths of Nb₃Ge-clad tapes with material properties matching those of our best short samples. The effort culminated in the production of a 20-m-long Nb₃Ge-clad tape. The tape consisted of a 0.64-cm-wide by 25- μ m-thick copper substrate coated uniformly with a 4.0- μ m-thick layer of Nb₃Ge. Sections taken from both ends of the tape had measured values for J_c of 2.5 and 2.4×10^6 A/cm² at 13.8 K and material parameters that varied by less than 5%. Phase II was completed on June 30, 1978 and is fully described in the EPRI Final Report EL-965,² entitled "Development of Nb₃Ge Conductors for Power Transmission Applications." Phase III, for which this is the sixth quarterly report, is aimed at the fabrication and testing of two 1-m-long sections of ac-SPTL using the long Nb₃Ge-clad tapes developed in Phase II.

This report covers the period April 1—June 30, 1980 and is the 16th quarterly report issued since the beginning of the EPRI sponsorship. In keeping with previous convention, we will refer to this report hereafter as PR-16. During this period, the first tests on our 1-m Nb₃Ge cable were scheduled for the week of June 23-27, and M. P. Maley and J. D. Thompson went to Brookhaven National Laboratory (BNL) to conduct the tests. Unfortunately, a vacuum leak in the BNL cryostat caused the run to be aborted before any current could be driven through the cable. Repair work is estimated to require 1-2 weeks, so we are now expecting to return to BNL for our tests during the first two weeks of July.

Work on making ternary additions, gallium and boron, to Nb₃Ge was completed this quarter. As reported in PR-15, we succeeded in achieving stoichiometry in several Nb-Ge-Ga A-15 samples, but we have been unable to maintain stoichiometry for gallium compositions greater than Nb₃(Ga_{0.2}Ge_{0.8}). No improvements in T_c or H_{c2} have been obtained with gallium additions and no further work is planned on this system. The addition of boron to Nb₃Ge by the CVD process also was accomplished during this quarter. The lack of a quantitative diagnostic process for determining boron content in the deposit was a hindrance in this study. However, it appears that boron additions to Nb₃Ge cause a steep monotonic decrease in T_c . We are planning to measure H_{c2} on these samples to discover whether any enhancement in H_{c2} occurs. Details of both studies are presented in Sec. II.

As discussed in PR-14 and in PR-15, we discovered, through ac-loss measurements and microscopic examination, a correlation between the presence of longitudinal edge cracks in the Nb₃Ge coats running the length of the tapes and Nb₃Ge coat thickness t . Tapes with $t \geq 4.0$ μ m invariably exhibited continuous longitudinal cracks along one edge, whereas tapes with $t \leq 3.0$ μ m did not crack. We contracted with LASL Group WX-4 to perform a thermal stress calculation on our conductor configuration to better understand the origin of this correlation. A summary of the results of these calculations is presented in the appendix. Because of the large mismatch in the coefficients of thermal expansion (CTEs) of Nb₃Ge and the copper substrate, large stresses are expected during cooldown from the deposition temperature ($\sim 850^\circ$ C). In an unconstrained configuration, these stresses would be relieved by yielding of the soft copper substrate. Because our tapes have Nb₃Ge coating completely surrounding the copper, this relief mechanism is blocked. The calculation indicates that a large bending moment is generated at the corners of the tape as the copper attempts to shrink away from the outer shell of Nb₃Ge. Such a bending moment would produce a tensile strain on the Nb₃Ge material at the corners proportional to the distance from the neutral axis and may explain the presence of cracking in the thicker tapes.

II. TERNARY ADDITIONS TO Nb₃Ge

A. Nb-Ge-Ga System

Work has been completed on the Nb-Ge-Ga ternary system, with somewhat unexpected results. The variations of T_c and a_0 for stoichiometric alloys are shown in Fig. 1. The variations of these parameters with composition seem quite reasonable; the unexpected behavior is the failure to produce stoichiometric alloys for compositions greater than Nb₃(Ga_{0.2}Ge_{0.8}). Based on the lattice spacing of Nb₃Ga, as well as

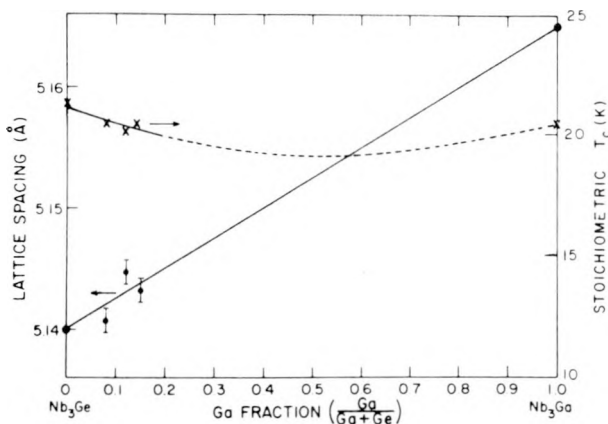


Fig. 1.
Plots of lattice spacing and T_c versus gallium fraction for stoichiometric $Nb_3(Ge_xGa_{1-x})$ alloys.

on published results showing that high- T_c Nb_3Ga can be prepared by solid-state quenching, we expected Nb_3Ga to be more stable than Nb_3Ge . This led to the expectation that Nb_3Ge would become more stable and hence easier to prepare as gallium was added. The most likely reason that this was not the case relates to the five-component Nb-Ge-Ga-Cl-H system. The presence of $GaCl_3$ and its dimer $(GaCl_3)_2$ as well as any Nb-Ga-Cl compounds not yet known must significantly alter the equilibrium products formed at the gas-solid interface in the five-component system. At present, further empirical work is likely to be unproductive and should wait until thermodynamic calculations have been carried out on this system. It is hoped that such calculations can be performed in collaboration with Prof. Karl Spear of Pennsylvania State University within the next 6 months.

B. Nb-Ge-B System

The usual atomic size for boron is significantly smaller than for germanium, and $Nb_3(Ge-B)$ alloys are expected to become rapidly unstable as germanium is replaced by boron. The preparation of this system is complicated further by the lack of a reliable, readily available analysis technique for boron. X-ray fluorescence and available electron microprobes cannot detect the extremely low energy x rays emitted by boron. As a result, all data must, for the present, be presented as a function of delivered gas phase composition. This has the additional disadvantage of preventing any estimate of whether alloys are stoichiometric or not, because solid compositions cannot be inferred from gas phase compositions, and, in addition, no prediction for the cell size of Nb_3B is available.

Gas phase boron concentrations from 0.04% to ~50% were studied, with most of the effort concentrated in the range of 0-10% boron. The A-15 phase was observed over the entire range of ternary compositions studied. This covered the range of boron:germanium ratios from 0.002:1 to 9:1 (gas phase compositions). However, when the remaining amount of germanium was removed, the A-15 structure could not be prepared, and only the niobium and NbB_2 structures were observed. The effect of boron addition on T_c is shown in Fig. 2. A rather sharp initial drop from 22 K is observed, followed by a much more gradual reduction. The most significant feature of this curve is the absence of any sort of peak at low boron concentrations. This suggests that the alloys may be shifting away from the stoichiometric composition continuously as boron is added. Additional samples remain to be measured, and the results will be presented along with H_{c2} data in the next report.

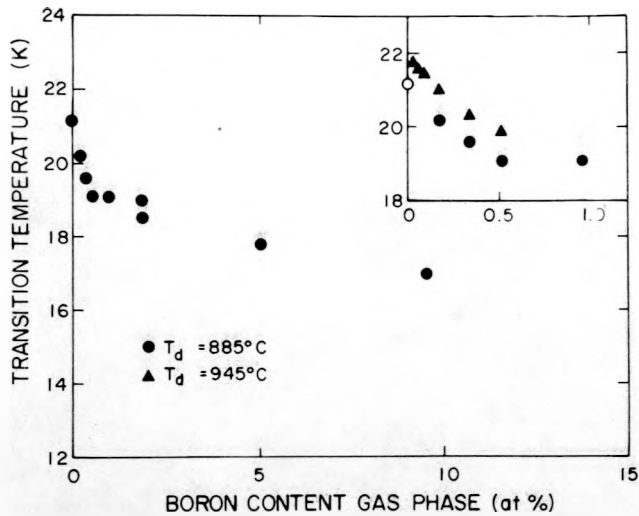


Fig. 2.
A plot of transition temperature versus boron content in the gas phase for $\text{Nb}_3(\text{Ge}_x\text{B}_{1-x})$ alloys.

PERSONNEL

L. R. Newkirk and F. A. Valencia are responsible for development and testing of the conductor, M. P. Maley and J. D. Thompson for ac-loss measurements and cable fabrication, and R. J. Bartlett and R. V. Carlson for critical current and bend test measurements.

REFERENCES

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2. "Development of Nb_3Ge Conductors for Power Transmission Applications," EPRI-EL-965, Final Report for Project 7855, prepared by Los Alamos Scientific Laboratory, January 1979.

APPENDIX

Nb₃Ge CONDUCTOR THERMAL STRESS CALCULATIONS

by

Gloria A. Bennett

I. INTRODUCTION

One of the problems encountered in developing a superconductor constructed from a copper strip coated with a thin layer of niobium-germanium (Nb₃Ge) polycrystals was cracking in the coating. The copper strip was 25×10^{-6} m thick, 6.35×10^{-3} m wide, and 25 m long, and had a coating $3-6 \times 10^{-6}$ m thick, as illustrated in Fig. A-1.

The copper strip was pulled through an 875°C oven in a hydrogen atmosphere, where the Nb₃Ge coating was sputtered onto the strip. A uniform coating formed along the width but thickened at the edges, giving the strip a "dog-bone" cross section. The strip and coating left the oven and were cooled to room temperature, undergoing considerable thermal contraction. In thick coatings, a V-shaped crack occurred at the edge and along the length of the strip as shown in Fig. A-2.

A series of hand calculations was done to define the mechanisms involved and to try to quantify the stress levels above which the crack occurs.

II. THERMAL STRESS CALCULATIONS

The material properties used in subsequent thermal stress calculations were obtained from references (room temperature data for the thermal expansion coefficient and Young's modulus of copper from Ref. 1, a temperature-averaged thermal expansion coefficient for Nb₃Ge from Ref. 2, and the room temperature Young's modulus of Nb₃Sn from Ref. 3). Assuming free thermal shrinkage of independent strips,⁴ we calculated the width changes of the copper and the coating as 98×10^{-6} and 39×10^{-6} m, respectively. If single independent strips were fixed at both ends, the resulting thermal stresses in the copper and coating would be -2.64×10^9 Pa (-383 000 psi) and -9.65×10^8 Pa (-140 000 psi).

If equal length strips are fixed to each other only at the ends and then confined as shown in Fig. A-3, the shrinkage of the assembly must be between the previously calculated values for copper and coating. This arrangement allows only axial stresses to develop. Given a 1-m-depth strip, a 2870-N (645-lb) force develops, causing a total shrinkage of 85×10^{-6} m. The deformation experienced by this assembly, as compared to the independent fixed-end case, results in less shrinkage in the copper, changing its stress from compression to 3.45×10^8 N/m² (50 100 psi) tension, and more deformation in the coating, increasing its compressive stress to -1.14×10^9 N/m² (-165 100 psi).

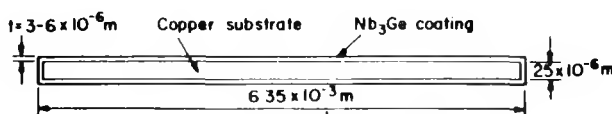


Fig. A-1.
Nb₃Ge-coated copper strip cross section.

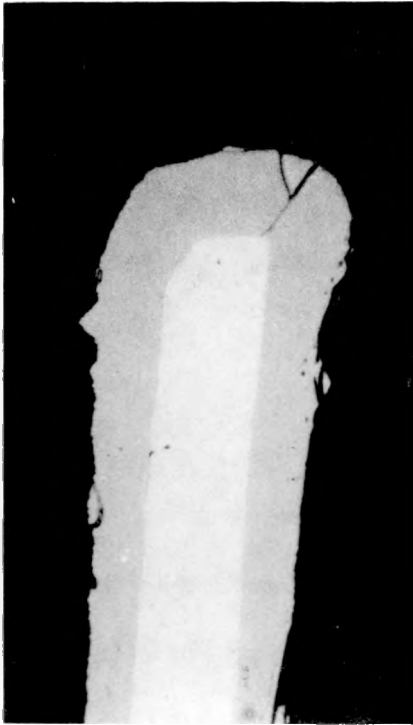


Fig. A-2.

Cracked Nb₃Ge coating on the copper strip.

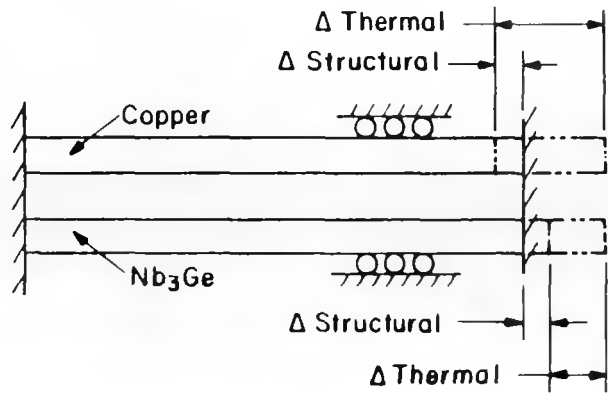


Fig. A-3.

Thermal and structural deformation of copper and Nb₃Ge strips.

Note that the deformation of the coating caused by thermal shrinkage (39×10^{-6} m) and the deformation caused by structural confinement (46×10^{-6} m) are of similar magnitudes. The additional stress in the coating caused by structural confinement might be partially relieved by allowing one of the ends to rotate.

III. BIMETALLIC STRIP

Assuming that the copper and Nb₃Ge strips are bonded before cooling and are allowed to bend satisfies the conditions that apply to composite beams and bimetallic strips. The composite beam of copper coated with Nb₃Ge is symmetrical about the horizontal midplane and also about a vertical center line, resulting in four identical quadrants. The effects of the coating on both edges of the strip are ignored, allowing a quadrant to be treated like the bimetallic strip shown in Fig. A-4.

The calculations were done using equations for composite beams and bimetallic strips⁵ that undergo stress within the proportional limit of each material. The equations give the resulting stress in the outer fibers of both layers, using equivalent sections and constants that depend on layer thickness and Young's modulus.

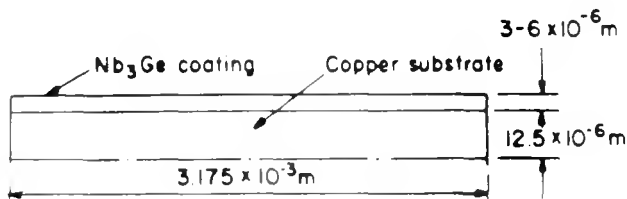


Fig. A-4.

Quadrant used for bimetallic strip calculations.

The results show that for thin (3×10^{-6} m) coatings there is a compressive stress in both layers, -2.75×10^8 N/m² ($-40\ 000$ psi) in the copper and -3.11×10^8 N/m² ($-45\ 150$ psi) in the coating. These values show that some stress relief occurs if the strip is allowed to bend and the end is free to rotate, when compared to the stresses produced by the confinement shown in Fig. A-3. Thick coatings (6×10^{-6} m) cause the stress in the coating to change to tension of $+4.32 \times 10^7$ N/m² ($+6250$ psi) and the compressive stress in the copper to increase to -3.11×10^8 N/m² ($-45\ 100$ psi).

Increasing the thickness of the coating from 3×10^{-6} to 6×10^{-6} m alters the stiffness of the section enough to change the stress in the coating from compression to tension. An optimum thickness coating of 5.5×10^{-6} m causes no stress in the coating outer surface, just balancing the compressive stress caused by the thermal shrinkage and the tensile stress caused by the bending of the strip. Coatings thicker than 5.5×10^{-6} m result in tensile stresses and should be avoided.

IV. BEAM CALCULATIONS

The Nb₃Ge coating on the edge of the bimetallic strip is modeled as a beam on an elastic copper foundation.⁵ The stresses calculated from the bimetallic strip for thin coatings are resolved into forces and used as the input loads on the beam. It is assumed that boundary conditions at the end of the beam are fixed. Because the beam is symmetrical about the horizontal midplane, only half of the beam is modeled. The equations for a finite length beam with a fixed left end and a guided right end⁴ are assumed to apply.

The resisting loads, moments, and deflections are calculated for a uniform load case to simulate the copper shrinkage; a concentrated load case is calculated to simulate the shrinkage of the coating. Figures A-5 and -6 show the dimensions and loads used on the beam calculations. The deflections from both cases are added together, assuming that the superposition principle still holds. The resulting beam deflection lies between the calculated shrinkage for free copper and coating strips and is half the quantity calculated for the bonded strip. The calculated deflection for a free end beam would be larger, suggesting that the ends of the beam are not fixed rigidly, but undergo some rotation.

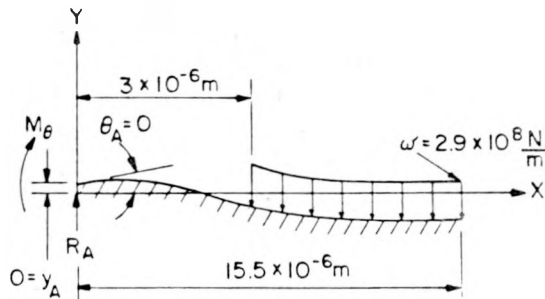


Fig. A-5.
Distributed load imposed on a beam on elastic foundation.

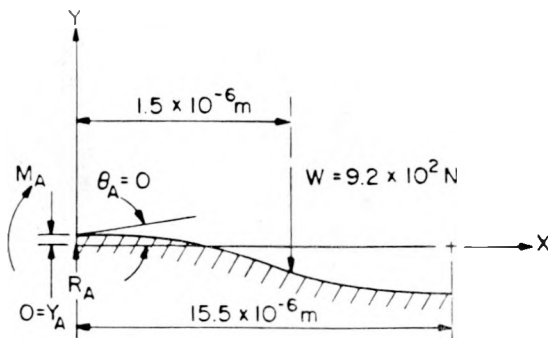


Fig. A-6.
Concentrated load imposed on a beam on elastic foundation.

V. FRAME ANALYSIS

The Nb_3Ge coating along the edge and both surfaces of the copper strip is treated as a frame in an effort to include the effects of the corner. Figure A-7 illustrates the frame labeled with the appropriate dimensions, loads, and reactions. The specific dimensions used in the calculations are taken from the photomicrographs shown in Figs. A-2 and -8 for the cracked and uncracked geometries.

The assumptions made about the behavior of the copper and coating are that the copper shrinkage can be simulated as a uniformly distributed load across the top of the symmetrical frame. Also, the cross sections of each frame member are assumed constant along the entire length. Because the Young's modulus for Nb_3Sn was substituted for Nb_3Ge , the Poisson's ratio for fused quartz glass⁶ is used as an approximation for the brittle coating. Both data were used to calculate an isotropic value for the shear modulus of the coating.

The frame shown in Fig. A-7 gives a third-degree indeterminate problem that requires using Castigliano's theorem⁴ and three of the boundary conditions. The closed-form solution involves deriving expressions for the resultant moment, shear, and axial loads in terms of the frame geometry and the imposed unit loads. The equations are written in matrix form, and the coefficient matrix is inverted to solve for the resultant loads. These solutions and the unit loads are used to calculate the deflection of the frame at the center of the span. That deflection is used to adjust the imposed unit loads up or down to arrive at the desired magnitude deflection.

The resultant moment, shear, and axial loads are used to calculate the combined stress at the outer surface and at the neutral axis of the frame upright and cross members. Stress at the outer surface includes an axial component, no shear, and the maximum bending component, whereas the neutral axis

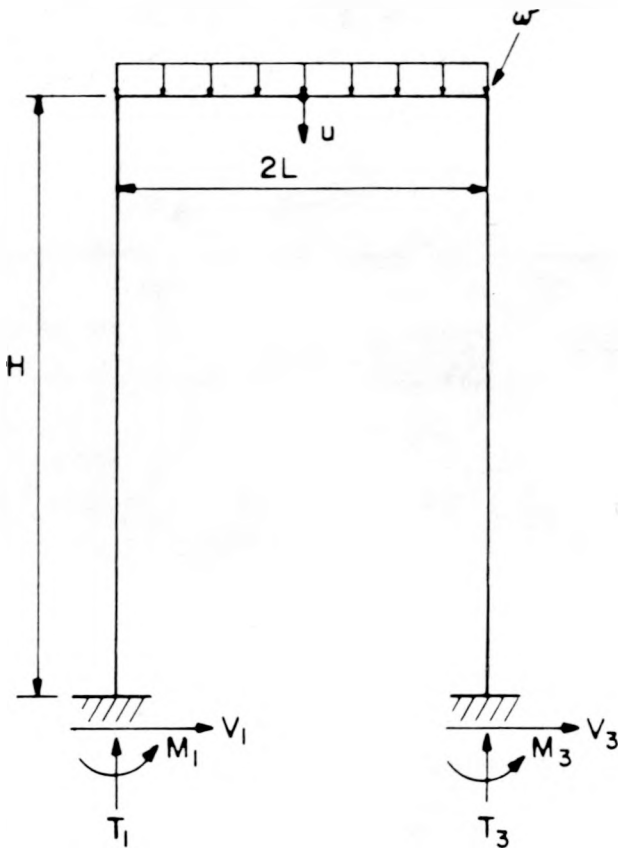


Fig. A-7.
Frame with uniform distributed load.

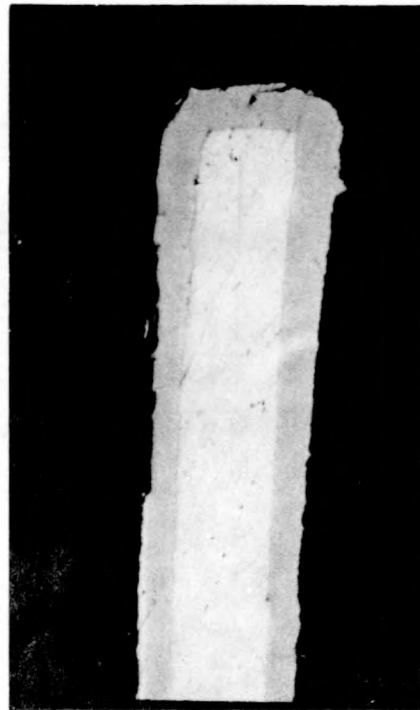


Fig. A-8.
Uncracked Nb_3Ge coating on the copper strip.

stress includes an axial component, no bending, and maximum shear contributions. The results show that the surface element in the upright member experiences a tensile stress for both the cracked and uncracked geometries. The surface element on the cross member and both neutral axis elements experience combined compressive stresses. The difference in the calculated stresses for the cracked and uncracked geometries is small, suggesting that several of the assumptions are too restrictive. The copper shrinkage exerts a shear force on the frame upright in addition to the distributed load assumed, and the upright cross section changes rapidly. Correcting both these assumptions would probably increase the difference in stresses between the cracked and uncracked geometries.

VI. CONCLUSIONS

The Nb₃Ge coating cracks from thermal stresses caused by the large thermal expansion coefficient mismatch. Based on the bimetallic strip calculations, coatings thicker than 5.5×10^{-6} m result in tension, and thinner coatings yield compression along the width of the strip. The frame calculation illustrates a tensile stress caused by the bending moment at the corner, regardless of coating thickness.

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