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**Mechanical Behavior and Stress Effects in
Hard Superconductors—A Review**

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OAK RIDGE NATIONAL LABORATORY

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MECHANICAL BEHAVIOR AND STRESS EFFECTS IN HARD
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C. C. Koch and D. S. Easton

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MECHANICAL BEHAVIOR AND STRESS EFFECTS IN HARD SUPERCONDUCTORS — A REVIEW

C. C. Koch and D. S. Easton

ABSTRACT

The mechanical properties of type II superconducting materials are reviewed as well as the effect of stress on the superconducting properties of these materials. The bcc alloys niobium-titanium and niobium-zirconium exhibit good strength and extensive ductility at room temperature. Mechanical tests on these alloys at 4.2 K revealed serrated stress-strain curves, nonlinear elastic effects and reduced ductility. The nonlinear behavior is probably due to twinning and detwinning or a reversible stress-induced martensitic transformation. The brittle A-15 compound superconductors, such as Nb₃Sn and V₃Ga, exhibit unusual elastic properties and structural instabilities at cryogenic temperatures.

Multifilamentary composites consisting of superconducting filaments in a normal metal matrix are generally used for superconducting devices. The mechanical properties of alloy and compound composites, tapes, as well as composites of niobium carbonitride chemically vapor deposited on high strength carbon fibers are presented. Hysteretic stress-strain behavior in the metal matrix composites produces significant heat generation, an effect which may lead to degradation in the performance of high field magnets. Measurements of the critical current density, J_c , under stress in a magnetic field are reported. Modest stress-reversible degradation in J_c was observed in niobium-titanium composites, while more serious degradation was found in Nb₃Sn samples.

The importance of mechanical behavior to device performance is discussed.

1. INTRODUCTION

The mechanical behavior of superconducting materials has been of interest and concern to researchers in this field over the last two decades since the discovery and use of "hard" high field superconductors. The inherent brittleness of many of the high field superconductors —

for example, compounds with structures of type A-15, B-1, or C-15 — required the development of unique processing techniques for fabrication of usable conductors. Fundamental studies of the effects of mechanical stress on superconducting properties provide insight into the nature of superconductors. In recent years, an increased interest in the mechanical behavior of commercial superconductors has occurred because of the large mechanical forces expected in proposed superconducting devices such as magnets for plasma confinement and energy storage, rotating machinery and electrical transmission lines. At several laboratories, facilities have been developed to study the effects of mechanical stress *in situ* on superconducting properties. Results from such measurements have become available within the last year; thus, it is appropriate to review the existing knowledge of mechanical behavior and stress effects in hard superconductors. The term "hard" used in this review is an imprecise but useful term often applied to type II superconductors which have high values of the upper critical field, H_{c2} and high values of J_c , the critical current density. These superconductors are the ones of present or potential usefulness for electrical engineering applications. This review will cover the mechanical properties of superconducting alloys and compounds at ambient and low temperatures, the effects of stress on superconducting properties, and their implications for superconducting applications.

2. MECHANICAL BEHAVIOR OF ALLOY SUPERCONDUCTORS

For the purposes of this review the hard superconducting alloys are bcc niobium-titanium and niobium-zirconium. The presently most available commercial superconductor is niobium-titanium, which superseded niobium-zirconium alloys about ten years ago, partly for its better mechanical properties as well as its higher values of H_{c2} .

2.1 Elastic Behavior of Hard Superconducting Bcc Alloys

Elastic constants on single crystals of the commercial superconducting alloy Ti-40 at. % Nb were determined at 298 K by Reid et al.¹ The results of these measurements were $c_{11} = 156.5$ GPa, $c_{12} = 111.6$ GPa, $c' = (c_{11} - c_{12})/2 = 22.47$ GPa, and $c_{44} = 39.63$ GPa. From these values the following moduli were calculated: bulk modulus, $K = 126.6$ GPa; shear modulus on $\langle 111 \rangle$ slip systems, $G = 26.26$ GPa; and Zener's anisotropy factor, $A = c_{44}/c' = 1.763$. Thus the elastic properties are only slightly anisotropic and isotropic elasticity theory should apply to calculations such as those for dislocation strain fields. Attempts to measure the elastic constants at lower temperature were unsuccessful due to an unexplained high attenuation of the shear waves below ~ 270 K. No change in the bcc crystal structure was observed by x-ray diffraction techniques at temperatures as low as 78 K. The polycrystalline Young's modulus can be estimated from this single crystal data using the averaging techniques of Voigt² or Reuss.³ Experimental results on polycrystalline samples in uniaxial tension should lie between these two extreme analyses with the measurements on wire samples with cellular fibers parallel to the tensile axis more closely approximating the Voigt average.² The values are $E_{\text{Voigt}} = 90.47$ GPa and $E_{\text{Reuss}} = 84.31$ GPa.

Elastic moduli of polycrystalline niobium-titanium alloys have been measured by acoustic techniques and from stress-strain curves (Table 1). Room temperature values vary with niobium concentration (Fig. 1). The values depend on the microstructure, that is, the sample heat treatment. A broad minimum in E is observed at the titanium-rich part of the alloy system. The values measured for E at 4.2 K are about 12-15% higher than the room temperature values.^{4,5}

Nelson et al.¹³ measured Young's modulus for a series of zirconium-rich alloys (0-25 at. % Nb) on polycrystalline and single crystal samples using the composite resonator acoustic technique. The room temperature values of E for Zr-25 at. % Nb (~ 0.68 GPa) are similar to the value for a Ti-25 at. % Nb alloy (Fig. 1) and the increase in E with decreasing temperatures is comparable. Both alloy systems exhibit a minimum in E

Table 1. Young's Modulus for Niobium-Titanium Alloys

Alloy (at. % Nb)	E (GPa)	Reference	Remarks
40.0	69	4	
38.5	55	5	
42.5	93	6	
49.0	97	6	
61.0	102	6	
74.0	106	6	
82.5	109	6	
91.0	109	6	
36.0	74	7	
38.5	78	7	
23.0	63	8	95% cold work
34.0	72	8	95% cold work
34.0	78	8	annealed 1000°C
44.0	81	8	95% cold work
44.0	88	8	annealed
36.0	82	9	
38.5	83	9	
36.0	86	10	
34.0	91	11	measured at 4.2 K
34.0	81	11	normalized to room temperature
6.5	78	12	as quenched
8.0	62	12	as quenched
8.0	98	12	annealed
11.5	78	12	as quenched
18.0	95	12	as quenched
21.0	78	12	as quenched
25.5	66	12	as quenched
25.5	81	12	annealed
29.0	78	12	annealed
38.0	79	12	as quenched
43.5	84	12	as quenched
43.5	90	12	annealed

Fig. 1. Young's Modulus of Niobium-Titanium Alloys at Room Temperature. Key: bulk samples: $\times$ — — — $\times$ (annealed), Fedotov; $\times$ - - - $\times$ (as quenched), Fedotov; + (arc melted), Nedyukha and Chernyy; I, Reid et al.; $\square$, Ledbetter; $\circ$ (95% cold worked), Albert and Pfeiffer; $\bullet$ (recrystallized at 1000°C), Albert and Pfeiffer; and Δ , Easton and Koch. Wire samples: I, Reid et al.; ∇ , Rutherford Laboratory; $\blacksquare$, Easton; and α , (4.2 K, normalized to 298 K), Schmidt. $10^9 \text{ Nm}^{-2} = 1 \text{ GPa}$.

with composition in the range of 20–30 at. % Nb. In the work of Nelson et al. the alloys with 12–25 at. % Nb were two phase, bcc + omega. It was concluded that the omega phase had a slightly higher modulus than the bcc phase since thermomechanical treatments which increased the amount of omega phase also increased E .

However, Sekula and Redman¹⁴ found E to decrease by about 9% from room temperature to 77 K in measurements made from uniaxial stress-strain curves.

2.2 The Shape Memory Effect and Pseudoelasticity in Hard Superconducting Bcc Alloys

Two related phenomena — the shape memory effect (SME) and the pseudoelastic effect — are observed in a wide range of alloy systems in which reversible martensitic transformations occur (e.g, see Ref. 15). The SME is described by the observation that a specimen containing deformation-induced martensite will change its shape to the original (predeformation) dimensions when the reverse martensitic transformation is activated by heating above some reversion temperature. In the pseudoelastic effect, a shape change (strain) occurs by development and growth of martensitic plates during continuous application of stress, which revert and disappear when the load is removed. The effect often produces a nonlinear stress-strain curve with a hysteresis loop in stress reversal. These effects differ from system to system and can be produced by the stress-induced reorientation of the twin domains within martensitic plates in addition to the stress-induced formation of the plates themselves. Such effects have been observed during deformation both above and below M_s (the temperature below which martensite forms).

One example of each effect has been reported for niobium-titanium alloys. Baker¹⁶ described evidence for the shape-memory effect in a Ti–22 at. % Nb (35 wt % Nb) alloy. (This is a composition which has been used as a commercial superconductor.) In this alloy, an orthorhombic martensite, α'' , phase is formed at $M_s \approx 175^\circ\text{C}$ when the material is quenched from the single-phase β (bcc) field (temperatures $> \sim 700^\circ\text{C}$). If the fully martensitic alloy is deformed below M_s it recovers

its original shape when heated above the reversion temperature, $A_s \approx 184^\circ\text{C}$. In the fully martensitic condition the strain is accomplished by the preferential growth of those α'' variants which result in stress relief (the orientation relationship between the β and α'' predicts 12 equivalent α'' orientations from a single β orientation).

Easton and Koch¹⁷ presented evidence for the pseudoelastic effect in Ti-36 at. % Nb and Ti-38.5 at. % Nb alloys (commercial compositions) at low temperatures. Uniaxial tensile stress-strain curves at 4.2 K exhibited nonlinearity with recovery of strain on unloading (Fig. 2). At higher strains load drops were observed and serrated stress-strain curves were obtained. More discussion of these serrations will be presented in Sect. 2.3.

Fig. 2. Stress-Strain Curve of a Ti-38.5 at. % Nb Alloy at 4.2 K. $1 \text{ Nm}^{-2} = 1 \text{ Pa}$

Noise was heard in these experiments. Almost immediately upon application of stress at 4.2 K clicks could be heard. The frequency of clicks was greatest at low stresses, both during loading and unloading. If a sample were loaded to a given stress and then unloaded, no clicks were heard until the stress had dropped below a certain value. When the test temperature was raised, the audible clicks and the serrations in the stress-strain curve disappeared at temperatures above ~ 30 K. This behavior is the same phenomenologically as that observed in alloys which exhibit pseudoelasticity.¹⁸

Such evidence and the observations of ductility⁹ (see Sect. 2.3) point to the presence of either a stress-induced martensitic transformation or reversible twinning. It is possible that this martensite is the α'' phase. Consider the M_s vs composition curve for niobium-titanium alloys, presented in Fig. 3 from the data of Duwez,¹⁹ Brown et al.,²⁰ and Baker.¹⁶ A reasonable extrapolation of the M_s curve to 36–39 at. % Nb indicates the M_s temperature could occur near 4.2 K. Since the M_d temperatures (the temperature below which deformation induced

Fig. 3. M_s Curve for α'' in Niobium-Titanium Alloys.

martensite forms) usually lies above M_s , it is plausible that stress-induced α'' could occur in these alloys. It is also possible that the martensite is stress-induced hcp α (the equilibrium phase) or some other intermediate phase. Since any such stress-induced phase would revert to the usual phase below room temperature, metallurgical studies of these alloys under stress at low temperatures are required and several groups^{21,22} have initiated such studies.

The nonlinear stress-strain curve and hysteresis loops are also observed in Nb-Ti-Cu (and other matrices, such as CuNi and Al) multifilamentary composites even at room temperature. This is due to the composite behavior itself, which will be discussed in Sect. 2.4. However, it should be emphasized that at helium temperatures the niobium-titanium *itself* is capable of exhibiting this pseudoelastic behavior.

The authors found similar effects (serrated stress-strain curves and hysteretic, nonlinear recovery of strain on unloading) in both a composite consisting of Nb-25% Zr filament in a copper matrix and a bare filament of the niobium-zirconium with the copper removed. Although no evidence of the shape-memory effect in niobium-zirconium could be found in the literature, no comprehensive study has been made in this area.

2.3 Plastic Behavior of Hard Superconducting Bcc Alloys

This section discusses the "plastic" properties of niobium-titanium, niobium-zirconium, and related alloys. These properties include those defined by conventional engineering stress-strain curves, such as the elastic limit, yield strength, ultimate tensile strength, and percent elongation at fracture. Plastic properties data are available for a range of niobium-titanium and niobium-zirconium alloys at ambient and lower temperatures. Data on bcc superconducting alloys is presented in Table 2. Body-centered-cubic metals and alloys typically exhibit a marked temperature dependence of their mechanical properties.²³ This temperature dependence includes a large (2-3 times or more) increase in yield and ultimate tensile strength as the temperature is decreased and also include a loss of ductility at low temperatures. This general behavior is observed

Table 2. Plastic Properties of Bcc Superconducting Alloys

Alloy	Test Temperature (K)	Condition	Yield Strength (MPa)	Tensile Strength (MPa)	Reduction In Area (%)	Elongation (%)	Reference
Nb-25 at. % Zr 0.25-mm-diam wire	289	cold-worked	1610		51		Fox + Pryle ³⁸
	77	cold-worked	1980	2440	35		Fox + Pryle
	4.2	cold-worked	a	3030	21		Fox + Pryle
0.13-mm-diam wire	298	cold-worked	1770	1910	16		Fox + Pryle
	77		2430	2520	16		Fox + Pryle
	4.2		a	4040	14		Fox + Pryle
Ti-40 at. % Nb 0.17-mm-diam wire	300	cold-worked	880	980		0.3	Verkin et al. ³⁴
	77	cold-worked	1520	1570		0.55	Verkin et al.
	21.3			2280		0.3	Verkin et al.
Ti-50 at. % Nb 0.15-mm-diam wire	300		1620	1620		0.2	Verkin et al.
	77		1850	1980		0.45	Verkin et al.
	4.2		1860	1910		0.30	Verkin et al.
Ti-38.5 at. % Nb	298			780		2.2	Reed et al. ³⁶
	77			1020		2.2	Reed et al.
	4.2			1280		2.2	Reed et al.
Ti-36 at. % Nb 0.213-mm-diam wire	300	cold-worked		1110	22	2.3	Easton + Koch ¹⁷
	4.2	cold-worked		2160	7	4.5	Easton + Koch
Ti-36 at. % Nb 0.267-mm-diam wire	300	cold-worked		1030	20	1.2	Easton + Koch
	77	cold-worked		1730	17	2.4	Easton + Koch
	4.2			2210	8	4.8	Easton + Koch
Ti-36 at. % Nb 0.318-mm-diam wire	300	cold-worked		1380	15	4.1	Easton + Koch
	4.2	cold-worked		2160	12	4.8	Easton + Koch
Ti-36 at. % Nb 1.98-mm-diam	300	800°C anneal		500	71	8.8	Easton + Koch
	4.2			1510	11	<0.2	Easton + Koch
Ti-38.5 at. % Nb 1.98-mm-diam tensile sample	300	800°C anneal		500	77	9.6	Easton + Koch
	77			1100	47	3.3	Easton + Koch
Ti-34 at. % Nb 0.25-mm-diam	300	cold-worked	860-870	880	7	<0.2	Easton + Koch
						3.0-3.5	Hillmann ¹⁰
Tensile Sample	300	cold-worked 50%	400 ^b	720		9.0	Hillmann
Tensile Sample	4.2	cold-worked 50%	1230	1450		0.5	Hillmann
Ti-25 to 50 at. % Nb 0.25-mm-diam wire	300	cold-worked		6070			Bychkova et al. ³⁹
Ti-25 at. % Nb		10 hr at 450°C		1460			Bychkova
Ti-25 at. % Nb	300	cold-worked		660			Bychkova et al. ⁴⁰
Ti-65 at. % Nb Wire	300	cold-worked		790			Alekseevskii et al. ⁴¹
	77			1370			Alekseevskii et al.
	20			1880			Alekseevskii et al.
Nb-33 at. % Zr 0.17-mm-diam wire	300	cold-worked		1920			Easton ¹⁰
	4.2			2900			Easton

^aNot defined - nonuniform deformation.^bElastic limit.

in the niobium-titanium and niobium-zirconium alloys. The largest quantity of data, and those most easily reproduced, are for the ultimate tensile strength. Even though this parameter is sensitive to composition and metallurgical history, selected values have been plotted vs test temperature in Fig. 4 for niobium-titanium and niobium-zirconium alloys. It is clear that, in general, niobium-zirconium alloys exhibit higher ultimate tensile strengths than niobium-titanium alloys. Yield strengths at low temperatures are difficult to measure and/or define due to the limited ductility and the nature of the stress-strain curve.

Fig. 4. Selected Ultimate Tensile Strength Values of Niobium-Titanium and Niobium-Zirconium Alloys Versus Temperature. $1 \text{ Nm}^{-2} = 1 \text{ Pa}$

2.3.1 Serrated Stress-Strain Curves

Most investigators report serrated stress-strain curves at low temperatures in these alloys. An example of a serrated stress-strain curve is presented in Fig. 5 for Ti-36 at. % Nb.¹⁶ Various explanations have been given for serrated stress-strain curves which occur at low

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Fig. 5. Load-Elongation Curve of a Ti-36 at. % Nb Alloy at 4.2 K.

temperatures. These include twinning,²⁴ stress-induced phase transformations,²⁵ "burst" dislocation formation,²⁶ and "adiabatic deformation." Basinski^{27,28} has shown that adiabatic deformation is a common feature of many metals at liquid helium temperatures. Since the specific heat of metals becomes quite small at low temperatures, an energy input — such as strain energy — can produce a local rise in temperature. If the flow stress decreases rapidly with temperature, the decrease in flow stress caused by local heating may exceed the increase due to work-hardening. This instability produces a load drop, the sample cools, and the process repeats itself and gives rise to the serration.

Evans²⁹ attributed the serrated stress-strain curves in Ti-40 at. % Nb at 4.2 K to adiabatic deformation. Hillmann³⁰ attributed the serrations he observes at 4.2 K in Ti-34 at. % Nb alloys to a localization of slip on the principal slip planes, {110}, due to the restricted ability for cross-slip at low temperatures. He suggests such slip processes would give rise to the serrations but does not rule out the possibility of twinning and/or adiabatic deformation. However, Albert and Pfeiffer³¹ propose that it is slip exclusively on {100} planes which is responsible for the load drops. They do not elaborate on the mechanism(s) responsible. The common slip plane for bcc metals is {110}, but Albert and Pfeiffer assume the {100} slip planes are active because of the $\langle 100 \rangle$ fiber texture of the samples and the fact that shear fracture occurs at a 45° angle to the tensile axis. However, this geometrical argument is not unique, and the possibility of twinning as a deformation mode is not considered so that this assumption is of doubtful validity.

Yajima and Ishii find serrated stress-strain curves, which they attribute to twin deformation,³² in Nb-26 and 42 at. % Zr at temperatures below 201 K. Twinning is a common mode of deformation in bcc metals and alloys at low temperatures. Flewitt and Palmer³³ find the upper temperature limit of twin formation varies with zirconium concentration in niobium-zirconium alloys, reaching a maximum slightly above room temperature for a Nb-25 at. % Zr alloy. Single surface trace analyses were consistent with a {112} habit plane for the twins at all temperatures and compositions. They observed microstructural evidence for detwinning after raising the temperature. At 4.2 K twinning became the deformation mode for plastic yielding.

Serrated stress-strain curves are also observed in the measurements of Verkin et al.³⁴ on Ti-40 at. % Nb and Ti-50 % Nb wires at 4.2 K. They saw a decrease in the ultimate tensile strength as the temperature decreased from 22 K to 4.2 K. This effect was also reported by Albert and Pfeiffer³¹ for the Ti-34 at. % Nb alloy after 40% cold work, but not in a sample deformed only 50%. Reed and Mikesell³⁵ have seen this effect in several copper-base fcc alloys. They proposed that the stress

needed to nucleate twins decreases with decreasing temperature and that deformation at 4.2 K occurs mainly by twinning.

The only study found which did not report serrated stress-strain curves in niobium-titanium alloys at 4.2 K was that of Reed et al.⁵ However, subsequent measurements revealed serrations³⁶ and the reasons for this disagreement are not known. Serrations are usually only detected if a "hard" testing machine is used³⁷ so that experimental conditions must be considered in any conclusions regarding the occurrence or not of serrations at low temperatures.

Serrated stress-strain curves were reported by Schmidt¹¹ for Ti-34 at. % Nb wires (0.26 mm diam) at 4.2 K. In some cases he observed serrations during unloading as well as during loading. Easton and Koch¹⁷ reported serrations at 4.2 K in Ti-36 at. % Nb and Ti-38.5 at. % Nb samples in the form of 2-mm-diam tensile samples and in several sizes of wire etched from multifilamentary conductors. They also observed serrations with both increasing and decreasing load. Noise, as audible "clicks," accompanied the occurrence of the serrations. The clicks preceded the first serrations on loading. On unloading neither clicks nor serrations were noted until the stress had dropped to a given level, then both occurred.

While any of the mechanisms listed above for serrated stress-strain curves at low temperatures could explain the serrations on loading, only a reversible, stress-induced (martensitic) phase transformation or stress-reversible twinning can explain the serrations on unloading. It is thus concluded that the serrations in niobium-titanium alloys are due to one of these two phenomena. *In-situ* x-ray diffraction or electron microscopy will be required to decide which mechanism is operable.

2.3.2 Ductility

In general, there is a loss of ductility in niobium-titanium and niobium-zirconium alloys at liquid helium temperatures. The degree of this effect depends on specimen size, condition, and ductility parameters (Table 2). Percent reduction of area, measured after fracture, exhibited a marked decrease. In tensile specimens, percent elongation also

decreased.⁹ However, in wire samples elongation values at 4.2 K were either comparable to those at 298 K or greater (Table 2). One reason for this apparent anomaly is as follows. Most of the deformation at 4.2 K occurs with the discontinuous load drops. If this is twinning or martensite formation, the twin (martensite) plate can propagate across the sample diameter and produce deformation. Such deformation might be restricted in larger samples and the twin (martensite) plate intersections can initiate cracking.

The appearance of the fracture surface changes with test temperature (Fig. 6). At room temperature the familiar ductile "cup and cone" fracture is observed. This mode of fracture persists at 77 K although less necking is observed. At 4.2 K a shear fracture at $\sim 45^\circ$ to the tensile axis occurs (Figs. 6 and 7). However, the microscopic features of this fracture indicate the mechanism can be classified as ductile fracture of the shear rupture type. Scanning electron micrographs [Fig. 8(a)] of the fracture surface reveal a finely dimpled surface characteristic of microscopic ductile failures. Small areas in the fracture surface do show evidence of brittle failure [Fig. 8(b)]. Evidence for inter- and transcrystalline brittle fracture was presented by Flewitt and Palmer³³ for niobium-zirconium alloys at lower test temperatures. Scanning electron micrographs of fractured surfaces on samples with low ductility (low temperatures) exhibit some cleavage facets of $\{100\}$ type. Some cracks are apparently nucleated by $\{112\}$ twins. Such cracks first propagate on $\{110\}$ planes before reverting to the $\{100\}$ cleavage plane. A ductile-brittle transition temperature was determined by studying the nature of the fracture surfaces and found to be a maximum for the Nb-25 at. % Zr composition. Takaai⁴² observed the ductile-to-brittle transition temperature in Nb-30 at. % Zr to be about 250°C. Additions of titanium (~ 10 at. %) decreased the transition temperature to about -50°C. Further zirconium additions had similar effects. There was no obvious correlation between oxygen content and ductility for concentrations up to about 880 ppm. However, Courtney and Wulff⁴³ found oxygen contents of about 3000 ppm severely embrittled Ti-45 at. % Nb samples.

Fig. 6. Tensile Specimens of Ti-38.5 at. % Nb Alloy Fractured at Various Test Temperatures. (1) Before testing, (2) 300 K, (3) 77 K, (4) 4.2 K.

Fig. 7. Fracture Surface of a 2-mm-diam Ti-38.5 at. % Nb Specimen Tested at 4.2 K. 22 $\times$. Reduced 28.5%.

Fig. 8. Specimen of a Ti-38.5 at. % Nb Alloy. (a) Typical 4.2 K fracture surface. SEM 3000 $\times$. (b) Small portion of specimen showing some evidence of brittle fracture. SEM 10,000 $\times$. Reduced 60%.

2.3.3 Microstructures

There have been several electron microscopy studies of the room temperature deformation structures of niobium-titanium and niobium-zirconium alloys. Neal et al.⁴⁴ observed a well-defined dislocation cell structure in Ti-40 at. % Nb cold-worked at room temperature. Pfeiffer and Hillmann⁴⁵ observed elongated dislocation cell structures, which they define as "substrips" or "microstrips" in Ti-22 at. % Nb and Ti-34 at. % Nb alloys. The fiber texture was $\langle 110 \rangle$ and the substrip width was 9 to 50 nm. Reuter et al.⁴⁶ also observed the $\langle 110 \rangle$ fiber axis texture in a Ti-45.7 at. % Nb alloy wire deformed 99.9% by cold work. This severe deformation could be attained in spite of the presence of 2390 ppm of oxygen in the sample. A diffuse dislocation tangle cell structure was seen, having a 0.2 μm average cell diameter. Witcomb and Dew-Hughes⁴⁷ observed a heterogeneous microstructure in cold-worked (>90%) Ti-35 at. % Nb strip containing 400 ppm N and 3000 ppm O. Some regions examined contained a uniform high dislocation density while other regions exhibited the cellular structure with a cell diameter about 0.3 μm . Baker⁴⁸ noted a significant difference between the microstructures of Ti-40 at. % Nb sheet samples with and without nitrogen doping (480 ppm N). The undoped samples exhibited a diffuse cellular structure with a ≥ 0.25 μm cell diameter. The nitrogen-doped samples had a much more uniform dislocation density, and no evidence for the cell structure was observed.

Walker et al.⁴⁹ presented microstructural results on cold-rolled Nb-25 at. % Zr sheet. They found tangles and stringers of dislocations in the as-worked condition. Heating between 500-900°C produced a well-defined cell structure. The typical bcc rolling texture was obtained with (100) planes parallel to the rolling plane and [100] directions parallel to the rolling direction. Milne⁵⁰ studied 0.25-mm-diam wires removed from multifilamentary Nb-25 at. % Zr conductors. A fibrous, diffuse dislocation structure was observed, which sharpened into a well-defined cell structure during annealing. Narlikar and Dew-Hughes reported⁵¹ a cellular structure in cold-worked (>90%) Nb-25 at. % Zr, with a cell size about 0.5 μm . They noted a

similar cell structure, with a slightly smaller average cell diameter ($\sim 0.4 \mu\text{m}$) in cold-worked Nb-25 at. % Ti. However, Finlayson and Milne⁵² saw no evidence for the cellular structure at room temperature in either Nb-26 at. % Zr or Nb-32 at. % Zr cold rolled up to 96%. From these observations, it was concluded that cross-slip is difficult in these alloys.

Flewitt and Palmer²⁵ have carried out a detailed microstructural analysis of niobium-zirconium alloys with zirconium content 16 to 40 at. %. Their TEM results reveal slip on $\{110\}$ planes with some additional slip on $\{112\}$ during room temperature deformation. Some evidence for wavy coarse slip lines is also presented. As the deformation temperature was raised above ambient, more wavy slip lines was observed along with the higher ductility. At temperatures above about 100–200°C (depending on zirconium concentration) a cellular dislocation distribution was observed (Fig. 9). At temperatures below room temperature, slip was chiefly on $\{110\}$ planes with dislocations

Fig. 9. The Effect of Temperature and Composition on Dislocation Structure in Niobium-Zirconium Alloys. (After Flewitt and Palmer.²⁵)

confined to bands with a uniform distribution within the bands. Additions of zirconium gave the same effect on dislocation structure as lowering the temperature in the composition range 0–25 at. % Zr. The reverse was observed for alloys from 25–40 at. % Zr (Fig. 9). Twinning became an important mode of deformation at lower temperatures. The effect of temperature and composition on twinning is illustrated in Fig. 10. As 4.2 K is approached twinning became the major deformation mode for yielding and at 4.2 K yield and fracture were coincident. Some crack nucleation was observed at twin intersections and thus twinning influences the fracture process as discussed above.

From the above survey of plastic properties of bcc hard superconductors it is apparent that strength and ductility are sensitive to test temperature, composition, interstitial impurity level, sample size, and metallurgical structure.

Fig. 10. The Effect of Temperature and Composition on Twinning in Niobium-Zirconium Alloys. (After Flewitt and Palmer.²⁵)

At room temperature, niobium-zirconium alloys are stronger and perhaps somewhat less ductile than niobium-titanium alloys. At liquid helium temperatures both systems exhibit limited ductility and show serrated stress-strain curves, twinning, and perhaps stress-induced martensitic transformation.

2.4 Mechanical Behavior of Composite Bcc Superconductors

Thermal mechanical, and/or electromagnetic instabilities make it impossible to use the full current-carrying capability of hard superconductors in applications such as high field magnets.⁵³ Practical superconductors therefore require stabilization by incorporation of one or more normal conductors with the superconductor. In the case of the bcc superconducting alloys, the composite usually takes the form of multiple filaments of superconducting wire encased in a normal matrix. The matrix material is typically a high-conductivity metal such as copper or aluminum. For a more complete decoupling of the filaments they are usually twisted or transposed for pulsed-field applications. A more resistive copper-nickel alloy matrix is also used under pulse-field conditions. State-of-the-art conductors now are complex composites consisting of up to 10,000 or more 10 to 20- μ m-diam filaments, often in a mixed copper-copper-nickel alloy matrix. The mechanical properties of the composite are the relevant quantities to be considered for superconducting applications.

Many review articles⁵⁴⁻⁵⁶ have appeared during the last 10 to 15 years on the mechanical behavior of composite materials. No attempt will be made here to review this broad subject but a few comments relevant to superconducting composites will be made before the experimental situation is presented. In general it has been possible to predict mechanical properties of composites from the corresponding properties of the component materials.⁵⁴ The basis of this approach is continuum mechanics and the result is the well-known "rule of mixtures" relationship for a property in terms of the volume fractions of each phase in the composite. The assumptions which are usually made in order to apply this analysis are:⁵⁵

1. isostrain conditions exist in each phase at all stresses,
2. the fibers are aligned parallel to the loading axis,
3. a "perfect" bond exists between the fiber and matrix,
4. the properties of the phases are unaltered in the combined state,
5. no transverse stresses develop as a result of fiber matrix interaction, and
6. no residual stresses exist in either component prior to loading.

While the rule of mixtures has been verified experimentally in many systems,⁵⁴ the above assumptions do not always hold true in practice. When this occurs, significant deviations from the rule of mixtures are observed.⁵⁴ The tensile stress strain of a composite (strong fibers, weak matrix) goes through four stages⁵⁶ (Fig. 11):

1. fibers and matrix deform elastically;
2. fibers deform elastically; matrix plastically;
3. fibers and matrix deform plastically; and
4. the composite fractures.

Fig. 11. The Stress-Strain Behavior of Continuous Fiber, Metal Matrix Composites.

In stage 1, the composite Young's modulus E_c is given by

$$E_c = E_f V_f + E_m (1 - V_f) ,$$

where

E_f, E_m = moduli of the uncombined fiber and matrix, respectively,
and

V_f = volume fraction of fibers.

Composites for structural applications have high modulus filaments that improve the elastic properties; however, since the modulus of niobium-titanium is lower than that of copper (0.82 compared to 1.17 GPa), composites of these materials exhibit unique behavior in that the modulus of the composite is lower than that of the matrix.

In stage 2 a "secondary" Young's modulus is defined by

$E_c = E_f \cdot V_f + (\partial\sigma/\partial\varepsilon)_m \cdot (1 - V_f)$ where $(\partial\sigma/\partial\varepsilon)_m$ = slope of the matrix stress-strain curve in the uncombined state at a strain level in stage 2.

The ultimate tensile strength of the composite σ_c is given by

$\sigma_c = \sigma_f V_f + \sigma'_m (1 - V_f)$, where σ_f is the ultimate strength of the fibers and σ'_m is the stress in the matrix when the fibers are strained to their ultimate tensile strain.⁵⁴ Stages 1 and 2 are of most interest for superconducting applications, and in particular Stage 2 which produces a pseudoelastic effect phenomenologically similar to the effect discussed in Sect. 2.2. If a composite is loaded into stage 2 and then unloaded, the fibers (still elastic) will contract and place the matrix into compression. The fibers will show a residual tension on unloading to a macroscopic stress of zero. Therefore, a hysteretic loop will be obtained under the above stress cycle. Several assumptions listed above for the rule of mixtures do not hold for multifilamentary niobium-titanium-copper, aluminum composites. In most composites the fibers are helically twisted. The case of fibers aligned to varying angles from the tensile (composite) axis has been treated both theoretically⁵⁷ and experimentally.⁵⁸ The composite tensile strength drops off rapidly with angle between the aligned continuous fibers and the tensile axis.⁵⁸ A marked reduction in tensile strength (~50%)

was observed in a silica fiber-aluminum matrix composite when the above angle approached about 10° . However, Heim,⁵⁹ considering the effects of twisted filaments, calculated the stress distribution in niobium-titanium filaments over the wire cross section with respect to axial strain. For an assumed conductor geometry and with a copper-to-superconductor ratio of 4, filament diameter = 0.5 mm, 84 filaments, and twist pitch of about 80 per m (2 per in.), he obtains about 6% correction factor from the case where twist is ignored. He proposes that appropriate analyses can thus be made by using Young's modulus which is 0.94 E of niobium-titanium in the above case.

The rule of mixtures also assumes that the composite components are not in a state of residual stress before testing. Heim⁵⁹ has also shown that the typical wire manufacturing process can leave both the filament and matrix with large residual stresses. Thus the details of final thermomechanical processing as well as stresses generated by the differential thermal contraction of the niobium-titanium and copper ($\sim 1:2$) during cooling can complicate the assumed stress distribution in the composite.

In spite of the complexities in superconducting composites described above, the stress-strain data generated so far agree fairly well with the rule of mixtures. Easton and Koch⁹ found values for Young's modulus that obeyed the rule of mixtures to within experimental error for a variety of multifilamentary conductors. While values for ultimate tensile strength did not show such simple agreement, they also approximated rule of mixtures behavior (Fig. 12). The temperature dependence of the composite and component stress-strain curves is illustrated by comparing room temperature measurements (Fig. 13) with measurements taken at 4.2 K (Fig. 14). At ambient temperature, the composite behaves as predicted. The higher values of ultimate tensile strength and elongation of a composite at strains greater than the fracture strain of the filament have been attributed⁶⁰ to a restraint by the matrix on localized necking of the filaments. Thus the filaments in a composite can show increased elongation compared with individual wires where necking occurs at lower strain values since fracture follows necking with little further uniform deformation.

Fig. 12. Relationship Between Ultimate Tensile Strength and Volume % of Niobium-Titanium Filaments in a Copper Matrix.

Fig. 13. Room Temperature Stress-Strain Curves of Matrix, Filament and Composite for a 2.8:1 Niobium-Titanium-Copper Composite.

Fig. 14. 4.2 K Stress-Strain Curves of Matrix, Filament and Composite for a 2.8:1 Niobium-Titanium-Copper Composite.

At 4.2 K (Fig. 14) the situation is markedly different. Here the niobium-titanium filament shows greater apparent elongation than the composite. However, some of this elongation is not permanent plastic deformation, but results from the reversible pseudoelastic behavior discussed in Sect. 2.2.

Most (or all) of the observed plastic deformation occurs with the discontinuous load drops. If these load drops are due to mechanical twinning or to an elastic martensitic phase transformation the resulting shape deformation as surface kinks may be prevented by the matrix, thus preferentially introducing fracture. Serrations are often observed in the composite stress-strain curve at 4.2 K, although not to the extent seen in the niobium-titanium filaments. This is further indirect evidence for the constraining effects of the matrix on the deformation mode in the filaments at 4.2 K.

Verkin et al.³⁴ made stress-strain measurements at 300, 77, 22, and 4.2 K on composite cables of 0.17-mm-diam niobium-titanium

filaments clad with copper and placed six to a cable of 0.82-mm OD. Ultimate tensile strength and percent elongation values agree almost exactly with data of Easton and Koch¹⁷ on a conductor with similar copper-to-superconductor ratio (~ 2.8). Verkin et al. also observed serrations in the stress-strain curves at 4.2 K.

Hillmann³⁰ presented room-temperature mechanical properties data on niobium-titanium-copper composites with 61 or 120 filaments per conductor as well as several single core conductors. The volume fraction of superconductor in the composites varied from 16 to 50%. He finds larger values for the fracture stress than would be predicted by the rule of mixtures. He cites several factors which complicate this simple rule including the stress state and the nature of the bond between superconductor and matrix.

Reed et al.⁵ measured the tensile properties of a multifilamentary niobium-titanium-copper composite and its components at 298, 77, and 4.2 K. The Young's moduli of the components were lower than values for bulk samples (see Sect. 2.1), but the rule of mixtures predicts well for the components and composite. Values of the composite tensile strength predicted by the rule of mixtures fell about 25% below the measured composite values. This was rationalized by assuming that the copper in the composite was in a more work-hardened condition than the copper wire used for comparison. Serrations were not observed at any test temperature down to 4.2 K. (Subsequent work³⁶ by the NBS Boulder Group did report serrated stress-strain curves at 4.2 K in niobium-titanium composites.) This group found the yield strength to increase slightly and the percent elongation at fracture to decrease with increasing strain rate at 4.2 K. Hysteresis in stress-strain cycles was observed with anelastic recovery effects increasing with increasing applied stress.

Fisher et al.⁶¹ studied the influence of cyclic stresses at 4.2 K on transport properties of superconducting composites. The samples were constant-strain cycled in pure tension-compression modes to strains of the order of 0.1 to 0.5% and up to about 2000 cycles. Most of this work involved measurements of changes in resistivity and critical

current density and will be reviewed in Sect. 4. However, measurements of the current indicated that filament fracture occurred with a tension strain of 0.5% at 565 cycles.

The Bauschinger effect has been invoked⁵⁹ to describe the inelastic behavior of superconducting composites. The Bauschinger effect describes the experimental observation that the elastic limit in compression is reduced following tensile prestrain. For niobium-titanium copper composites in stage 2 of the stress-strain curve, the copper yields in tension. During unloading, the constraint of the still elastic fibers places the copper in compression. A hysteresis loop is generated according to the simplified composite analysis presented above. The Bauschinger effect determines the shape of the loop, however. Heim⁵⁹ claimed his composites were in a residual stress state due to the manufacturing process such that the precompression of the copper decreased the copper elastic limit to essentially zero before testing. However, Easton and Koch⁹ have found in many multifilamentary composites a clearly defined elastic region (stage 1) from which good Young's moduli can be obtained. The final processing steps must be critical in this regard. After repeated stress cycling around a hysteresis loop, both Heim and Easton find no significant change in loop character with further cycling. The stabilization (that is, closure of hysteresis loops) has been observed⁶² in other composite systems such as tungsten-copper after several strain cycles into stage 2. The dislocation dynamics and microstructure of the niobium-titanium-copper composite (matrix) requires further investigation for a clear picture of the microscopic mechanism responsible for the stress-strain hysteresis loops.

3. MECHANICAL BEHAVIOR OF COMPOUND SUPERCONDUCTORS

The *compound* superconductors to be considered in this review are the high field A-15 materials (such as Nb₃Sn, V₃Ga, and Nb₃Ge), the refractory metal nitrides and carbonitrides, NbN and Nb(C,N), and the Laves phases V₂(Hf,Zr). One consistent feature of all superconducting compounds at ambient and lower temperatures is their inherent brittleness. Thus, unlike the alloys discussed in Sect. 2, little

information on plastic properties is available so most of the mechanical behavior to be discussed will involve elastic properties and composite performance.

3.1 Elastic Properties of Compound Superconductors

3.1.1 Compounds with the A-15 Crystal Structure

Because of their potential technological importance as high field superconductors and the fascinating anomalous elastic behavior and structural instabilities observed in them, the elastic properties of A-15 superconductors have been extensively studied. No attempt will be made here to review the vast literature on the subject, particularly since the reader may be referred to several recent and comprehensive review papers in this area.⁶³⁻⁶⁵ L. R. Testardi sums up the situation, "...Indeed, as a class and as a phenomenon there are few materials for which so much detailed information is now available."⁶⁴ However, we will briefly outline some of the major experimental observations which bear on the stress effects in these superconductors to be discussed in Sect. 4. Most of the elasticity and structural studies have been carried out on either V_3Si or Nb_3Sn due primarily to the availability of single crystals of these materials. Ultrasonic experiments in both V_3Si (ref. 66) and Nb_3Sn (ref. 67) revealed anomalous, though differing, elastic constant dependence on temperature. Unlike most materials (for example, niobium-titanium) which show a stiffening of the lattice on cooling, V_3Si and Nb_3Sn exhibit a lattice softening as evidenced by a near vanishing of the elastic (shear) moduli $(C_{11} - C_{12})/2$ as the temperature is decreased from ambient to a low critical temperature. In V_3Si the decrease in $(C_{11} - C_{12})/2$ is stabilized to a low constant value at either T_c (~ 17 K) or, in samples which undergo a martensitic phase transformation, there is an arrest at the structural transformation temperature T_m (~ 21 K) (ref. 66). In Nb_3Sn $(C_{11} - C_{12})/2$ also decreases to a low value with decreasing temperature but at T_m (~ 43 K) rises again to a high stable value below T_m (ref. 67). The reasons for these differences are not understood. The structural changes are martensitic

transformations from the cubic A-15 crystal structure to a tetragonal structure. The tetragonal distortions are small; for V_3Si , $c/a \approx 1.0024$ ($T_m = 18-25$ K)⁶⁸; for Nb_3Sn , $c/a \approx 0.9938-0.9964$ ($T_m \approx 43$ K).⁶⁹ The martensitic transformation results in a twin-related domain structure in the tetragonal state which gives rise to a shape deformation of the sample surface similar to that observed in other martensitic transformations. Martensitic transformations have also been observed in V_3Ga (ref. 70) and $Nb_3Al_{0.75}Ge_{0.25}$ (ref. 71). The transformations are not observed in all samples of a given material.⁶⁸ The occurrence of the transformation has been related to a defect structure and it has been reported^{64,68} that nontransforming V_3Si samples have lower resistivity ratios, $\rho(300\text{ K})/\rho(20\text{ K}) \approx 10-20$, compared to values of $\approx 40-80$ for transforming samples. This has recently been rationalized⁷² by assuming that point defects give rise to microdomains of tetragonal distortions that stiffen the cubic lattice for shear-type motion and stabilize the cubic phase.

One would expect the mechanical stress to affect the above structure-sensitive phenomena, and this is the case. Uniaxial stress (~ 20 MPa) along [001] directions in single crystal V_3Si caused a change in the morphology of the domains of the tetragonal phase.⁷³ The domains rotate such that the a_0 axis in each is parallel to the applied stress. Stress did not change T_m (to a resolution of 0.1 K) but reduced the volume fraction of tetragonal phase present. At high stress values (~ 30 MPa), the transformation was totally suppressed. At this stress level the strain is about 10^{-3} , comparable to the strain produced during transformation without applied stress. Thus, an applied strain similar in size to the transformation strain suppresses the transformation.

The elastic moduli in V_3Si increase with stress as measured in uniaxial tension⁷⁴ or by ultrasonic experiments.⁶⁴ The tetragonal distortion given the crystals by the applied strain stabilizes the cubic phase and the attendant phase stability increases the shear modulus over the unstrained condition by a factor of two.

While most of the experiments on elastic behavior and structural stability in A-15 superconductors have been carried out on single crystals, the elastic constant softening^{75,76} and structural transformation^{76,77} have been observed in a variety of polycrystalline materials.

Old and Charlesworth measured Young's modulus of bulk Nb_3Sn by an ultrasonic technique and found it to be 179 GPa at room temperature.⁷⁸

Hydrostatic pressure also influences the elastic moduli. At room temperature the bulk modulus and the shear moduli, C_{44} and $(C_{11} - C_{12})/2$, increase with hydrostatic pressure⁷⁹ in V_3Si . Below about 80 K the shear modulus (which is responsible for the instability) decreased under pressure. In nontransforming samples the negative pressure dependence reaches a maximum value at $T = 15\text{--}20$ K and then remains approximately constant. In a transforming sample the pressure dependence became positive again at about 50 K, no measurements were made below 37 K. Hydrostatic pressure decreases T_m in V_3Si by 1.5×10^{-9} K/Pa.⁸⁰ Recent studies^{81,82} of V_3Si under hydrostatic pressure at room temperature indicate that in addition to the contraction of the unit cell, structural or defect changes may occur.

Anharmonic effects are observed in A-15 materials. Patel and Batterman,⁷⁴ using an x-ray diffraction technique, found a nonlinear stress-strain relationship for a V_3Si single crystal under uniaxial compression in the [001] direction. The relationship between the applied stress, σ_{zz} , and the measured transverse strain, ϵ_{yy} , is illustrated in Fig. 15 for a sample tested at 25 K ($T > T_m$). The results imply that the crystal is stiffer at higher stresses. Below the transformation temperature T_m , the reorientation of the tetragonal twin domains under stress provides a possible source for pseudoelastic behavior. Recently, anharmonicity was investigated by Smith et al.^{83,84} in V_3Si and Nb_3Sn by measuring thermal expansion. In V_3Si samples, with 25 and 26 at. % Si, a large, anomalous, negative thermal expansion coefficient was observed below about 60 K. An anomalous positive thermal expansion coefficient was seen in a transformed Nb_3Sn sample below T_m (43 K) but no anomalous behavior was noted in a nontransforming sample.

3.1.2. Elastic Behavior of Other Compound Superconductors

In contrast to the A-15 superconductors, elastic property data are limited for other compound superconductors. Lattice instabilities occur

Fig. 15. Non-Linear Stress-Strain Behavior of a V_3Si Single Crystal Under Uniaxial Compression in the (001) Direction at 25 K. (After Patel and Batterman.⁷³)

in the C-15 superconductors (Laves phases). Lawson and Zachariasen⁸⁵ report a cubic to orthorhombic transformation starting at about 120 K in HfV_2 while Moncton⁸⁶ found a cubic to rhombohedral transformation in ZrV_2 , also at about 120 K. This is a curious result, since the pseudobinary alloys $Hf_xZr_{1-x}V_2$ form complete solid solutions at ambient and higher temperatures in the C-15 phase. These pseudobinaries are potentially useful superconductors due to their high values of H_{C2} (~ 23 T at $X = 0.5$). Finlayson et al.⁸⁷ have made internal friction measurements in both HfV_2 and ZrV_2 and find large peaks, which they tentatively attribute to mechanical effects such as phase boundary or defect motion at temperatures below the phase transition. Doherty and Gibbons⁸⁸ previously observed a similar effect in ZrV_2 but at higher temperatures (peak about 120 K).

The B-1 superconductors [NbN , NbC , $Nb(C,N)$] are of interest because of their high transition temperatures (to 18 K) and H_{C2} (15 to 20 T) values. The Young's moduli for these materials are expected to be high.

The room temperature modulus for NbC is 488 GPa (ref. 89). Techniques have been developed for producing NbC and Nb(C,N) superconductors on carbon fibers by chemical vapor deposition.^{90,91} The high strength and modulus of the carbon fiber substrates are expected to provide desirable mechanical properties. These materials will be discussed further in Sect. 3.3.

3.2 Plastic Behavior of Compound Superconductors

All the potentially useful superconducting compounds are brittle at ambient and lower temperatures and fracture occurs in the elastic strain regime. Thus, fracture tensile strains of about 0.1–0.3% are typically observed. While speculation as to the relative ductility of the various A-15 compounds has been common, no systematic comparison has been made to our knowledge. In fact such a comparison would be difficult since fracture strain in the elastic regime is sensitive to surface flaws, cracks, and sample alignment, which causes a scatter in the data that might mask any trend among these inherently brittle materials. The brittleness in these compounds is presumably from the difficulty of dislocation motion at and below room temperature. This in turn is generally believed due to the nature of bonding in the compounds, which must be either directional (covalent) or reflect the high degree of long range order. However, at high temperatures (relative to the melting temperature) plastic behavior can be observed in brittle compounds. Levinstein et al.⁹² plastically deformed V_3Si single crystals at 1520°C and studied the dislocation structure by etch-pitting techniques. The observation of dislocation arrangements suggested that the slip system in V_3Si is $\{100\} \langle 001 \rangle$.

When the $Hf_xZr_{1-x}V_2$ C-15 phases were first found to be high field superconductors it was suggested⁹³ that they might have desirable mechanical properties due to their lower microhardness values ($\sim 270\text{--}450 \text{ kg/mm}^2$) compared with those of A-15 compounds ($\sim 1000 \text{ kg/mm}^2$). This assumption of possible better ductility has been subsequently repeated.⁹⁴ We find no evidence for such a conclusion; rather we found the $Hf_xZr_{1-x}V_2$ C-15 phases to be brittle at ambient temperatures — as are

other C-15 phases. There is not necessarily a one-to-one correlation between hardness and ductility — many soft materials are completely brittle. Hardness is a complex quantity controlled by bonding while ductility reflects the ability for dislocation motion to occur.

3.3 Mechanical Behavior of Composite Compound Superconductors

Besides the need for combining high conductivity normal material with the superconductor for stability, it is mandatory to prepare the brittle compound superconductors in composite form in order to handle them. The first Nb_3Sn conductors developed at Bell Telephone Laboratories in the early 1960s^{95,96} were made by packing a mixture of niobium and tin powder in a niobium tube and drawing the composite down to wire. Solenoids were wound from the wire and then reacted to form the Nb_3Sn phase.

Problems with brittleness and porosity of the wire formed in this manner led to the development of flexible tape conductors that were reacted prior to winding. These tapes were made either by chemical vapor deposition⁹⁷ or diffusion of tin into a niobium substrate.⁹⁸ Copper or aluminum as well as strengtheners such as stainless steel were laminated with solder to the tape conductors. Benz^{99,100} has described and analyzed the mechanical behavior of diffusion processed Nb_3Sn -copper-stainless steel tapes. A typical symmetrical tape composite is illustrated in Fig. 16.

A large compressive stress develops in the Nb_3Sn layer as the composite is cooled from the bonding temperature (353 K) to the operating temperature (4.2 K) because the thermal expansion coefficients of the copper and stainless steel are much larger than for Nb_3Sn . Thus, an external tensile force applied to the composite at 4.2 K can reach substantial values before the stress on the Nb_3Sn changes from compressive to tensile. The stress where this occurs has been defined as the "design stress level" and given as a safe operating stress. The average stress on the total conductor which causes fracture of the Nb_3Sn was defined as the failure stress. Elastic behavior is assumed in the Nb_3Sn up to failure.

$$\epsilon_i = y_i / r_0$$

Fig. 16. A typical Nb₃Sn tape composite. (After Benz.⁹⁹)

Bending also causes strain. For a radius of curvature r_0 , mechanical strain ϵ_i is equal to y_i/r_0 where y_i is the distance from the neutral axis of bending. If $t_{\text{Nb}_3\text{Sn}}$ is defined as the thickness of the Nb + Nb₃Sn central layers, then $\epsilon_i = t_{\text{Nb}_3\text{Sn}}/2r_0$. If the fracture ductility in tension of Nb₃Sn is about 0.2%, bends around a radius less than 250 times $t_{\text{Nb}_3\text{Sn}}$ will initiate fracture in the outer layers of Nb₃Sn. Nonsymmetric composites can also be analyzed in the same manner with the Nb₃Sn layer kept at the neutral axis by balancing the thicknesses of the composite layers. That is, $E_{\text{Cu}} t_{\text{Cu}} = E_{\text{ss}} t_{\text{ss}}$ where E_{Cu} , E_{ss} are the moduli of copper and stainless steel and t_{Cu} , t_{ss} are the layer thicknesses.

Benz found failure stresses to be higher than the calculated values.¹⁰⁰ In an analysis of Nb₃Sn-aluminum-stainless steel composites, Henning et al.¹⁰¹ found that while bare Nb₃Sn fractures at about 0.2%, the fracture strain of the Nb₃Sn in the composite increases to about 0.3%. They claimed that this was due to the initial biaxial compressive stresses producing lateral constraints on the Nb₃Sn. Using the above definitions, Henning et al.,¹⁰¹ Benz,¹⁰⁰ and the Brookhaven Group¹⁰² found the experimentally measured failure stresses had identical or higher values than predicted values. The few instances that the measured values were lower were attributed to prior damage due to handling of the composite.

In recent years Nb_3Sn (ref. 103) and V_3Ga (refs. 104, 105, 106) have been produced in multifilamentary form by variations of the "bronze" method whereby niobium (or vanadium) rods are inserted into a copper-tin (copper-gallium) matrix and codeformed to fine twisted filaments as in the niobium-titanium composites discussed in Sect. 2.4. The composites are then given a reaction heat treatment to form Nb_3Sn (or V_3Ga). The composite behavior outlined in Sect. 2.4 should also apply to these multifilamentary materials with additional complications due to the extreme brittleness of the A-15 compound layer and the presence of an unreacted niobium (or vanadium) core. Tensile data on these materials has only recently become available. Old and Charlesworth⁷⁸ made room temperature tensile tests on multifilamentary Nb_3Sn prepared by the bronze method with the number of filaments ranging from 37 to 5143, with nearly totally and partially reacted niobium, and with initial niobium volume fractions in the bronze from 11% to 25%.

Two markedly different types of stress-strain curves were observed in these materials (Fig. 17). In curve A the composite exhibits elastic

Fig. 17. Two Types of Room Temperature Stress-Strain Behavior in Nb_3Sn Multifilamentary Composites. (a) $>16\%$ Nb, (b) $<15\%$ Nb. (After Old and Charlesworth.⁷⁸)

behavior up to about 0.15% strain, where yielding occurs. The wire then deforms plastically until fracture at total strains between 0.5 and 0.8%. In type B behavior, the yielding at 0.15% strain was followed by a plastic region up to 0.9% strain. Further deformation then continued at an essentially constant load until fracture at about 10% strain.

Attempts to use the simple law of mixtures criteria failed to explain this behavior. However, it was found that samples containing 16% or more niobium (before reaction) followed type A behavior and those with less than 15% exhibited type B stress-strain curves. Optical metallography revealed localized transverse cracks in type B samples at strains about 0.9%. In type A samples such cracks spread across the sample and failure occurred, whereas in type B samples the damaged regions increased with strain until the entire length of the wire was cracked at fracture. Acoustic emission studies indicated that cracking started at about 0.7% strain. This is much higher than the about 0.2% fracture strain in bare Nb_3Sn and, if accurate, may be due to the complex stress state in the filaments. However, Vandervoort¹⁰⁷ also studied room temperature deformation in a multifilamentary Nb_3Sn conductor with acoustic emission and reported some filament fracture prior to the 0.2% strain level, and nearly all the filaments fractured by 1.6% strain. A compressive stress-strain curve also indicated initial filament fracture at about 0.2% strain and buckling with a majority of the filaments fractured at 0.6% strain. At present we are not able to judge whether the differences in Old and Charlesworth's or Vandervoort's data reside in real material differences or in the sensitivity and/or interpretation of the acoustic emission data.

McDougall¹⁰⁸ made tensile measurements on multifilamentary Nb_3Sn at room temperature and at 4.2 K. The reaction temperatures and times were varied to give Nb_3Sn layers ranging from about 11 to 28% of the wire volume. The critical strain for failure decreased with increasing volume of compound. A volume of about 20% separated samples with high strains to failure from those with low fracture strains (Fig. 18). This behavior is characteristic of composites in which brittle interfacial layers separate ductile filaments from a matrix.

Fig. 18. Fracture Strain in Nb₃Sn Multifilamentary Composites as a Function of Volume of Compound. (After McDougall.¹⁰⁸)

The failure of the Nb₃Sn layer was analyzed in terms of interface separation caused by plastic deformation of the bronze matrix and niobium core. Any interface separation acts as a stress concentrator (notch) and induces fracture in the compound. It is unlikely that the proposed fracture model is necessary to explain cracking in the inherently brittle Nb₃Sn. The nature of the stress distribution within the Nb₃Sn layers is probably the determining factor. However, McDougall shows that increased compound thickness reduces the critical strain to failure for single and repeated stress of the composite. He finds the stress-strain curves at room temperature to have the inflections noted above. A doubly inflected stress-strain curve was observed at 4.2 K and is interpreted to be due to an increase in the niobium modulus relative to the bronze.

Larbalestier et al.¹⁰⁹ have made tensile measurements at 4.2 K on a commercial multifilamentary Nb₃Sn composite (3780 filaments) consisting of 11 vol % Nb before reaction. Various reaction treatments in the temperature range 665–780°C were given. No two samples had identical

stress-strain curves but the following general features were observed. The proportional limit occurred at about 0.1% strain and was followed by a linear stress-strain region up to 0.8–1.0% strain. Failure strains ranged from 4.6 to 13.8%. Cracks were observed by metallographic techniques at strains less than 1.0%; however, most of them did not penetrate the niobium core. There was a large variation in initial elastic modulus (5.5 to 255 GPa).

Easton¹⁰ has observed stress-strain behavior at 4.2 K in commercial multifilamentary Nb₃Sn composite conductors similar to the above examples, which exhibited large strains to failure (~10%). Ultimate tensile strength was 420 MPa and Young's modulus for this composite was 162 GPa.

Thus, it appears that although most commercial materials exhibit extensive strain before fracture (type B behavior of Old and Charlesworth), cracking of the Nb₃Sn layers occurs at low values of strain (~0.2–0.7%).

A unique class of multifilamentary A-15 superconductors has been developed by Tsuei and co-workers.¹¹⁰ These were copper-base alloys prepared by casting followed by cold work and reaction heat treatment. This procedure forms discontinuous filaments of Nb₃Sn in a bronze matrix — typically about 15% of the volume consisting of Nb-Nb₃Sn filaments. No tensile data are available on these conductors but bend tests showed no degradation in superconducting properties and the mechanical properties are expected to be dominated by the behavior of the matrix.

Tanaka and Furuto¹¹¹ made room temperature tensile tests on multifilamentary V₃Ga composites. They observed an elastic limit at about 0.08 to 0.1% strain and a second inflection in the stress-strain curve at 0.9–1.1% strain. Fracture strain was not reported. Scanning electron microscopy revealed cracking in the V₃Ga filaments after a bending strain of 0.8%.

Composites of Nb(C,N) chemically vapor deposited on high strength carbon fibers are being developed as superconducting materials.⁹¹ Preliminary tensile data¹¹² on such composites are presented in Table 3.

Table 3. Tensile Data for Carbon and Niobium Carbonitride Fibers

Sample	Ultimate Tensile Strength, GPa		Fracture Strain at 4.2 K (%)
	300 K	4.2 K	
Carbon fibers (Thornel 300)	1.62	1.58	4.9
Coated with NbN. ₅₈ C. ₄₁	7.9	0.41	1.5

4. EFFECT OF STRESS ON SUPERCONDUCTING PROPERTIES

4.1 Effects of Stress on the Superconducting Properties of Alloy Superconductors

The influence of mechanical stress on superconducting properties can assume several forms and levels of importance. The defects (dislocations, point defects, stacking faults) created by plastically deforming superconductors influence superconducting properties to varying degrees. The transition temperature (T_c) and the thermodynamic critical field (H_c) can be slightly altered by internal stresses which may change the electronic structure or phonon spectrum.¹¹³ In most cases such changes are small — a few tenths of a degree at most. Thermodynamic treatments of stress effects have been applied to specific elements with some success but only recently¹¹⁴ has a theory been developed which *semiquantitatively* predicts the pressure dependence of T_c in the transition metals. Substantial changes in T_c can occur with stress if a stress-induced phase transformation takes place.¹¹⁵

Finlayson and Milne¹¹⁶ found unusually large effects of plastic deformation on T_c of a Nb-32 at. % Zr alloy cold-rolled at room temperature. The transition temperature increased steadily with deformation; a maximum increase of 0.5 K at 93% reduction of area. Similar deformations in niobium-titanium alloys and pure niobium did not produce such shifts in T_c . This result is still not explained, but the authors suggested the possibility of a low temperature phase

transition promoted by the internal strains, or a change in the phonon or electronic spectrum due to the defect structure.

The upper critical field, H_{c2} , depends upon an intrinsic contribution, consisting of those electronic and phonon parameters which influence T_c , and an extrinsic contribution which depends upon electron mean free path and is thus proportional to normal state resistivity. To the extent that normal state resistivity is increased by mechanical deformation, H_{c2} would be raised. However, in concentrated alloy superconductors such as niobium-titanium and niobium-zirconium the resistivity is sufficiently high that even severe cold deformation does not increase H_{c2} dramatically and therefore is of little practical significance.

The critical current density, J_c , is the most structure-sensitive superconducting parameter since it depends on the interaction between the fluxoid lattice and crystal defects. The introduction of a fine dislocation cell structure by heavy cold deformation is one of the major factors in producing high values of J_c in commercial superconductors. The role of defects created by mechanical stress in increasing J_c and the fluxoid pinning problem in general have been treated extensively in a number of reviews (for example, ref. 117) and will not be discussed here. Similarly, the influence of the superconducting state on deformation mechanisms has been previously reviewed¹¹⁸ and will not be presented here.

We are mainly concerned with the effect of stress on $J_c(H)$ under operating conditions, that is, at 4.2 K. To determine this effect requires the simultaneous measurement of J_c in a magnetic field under controlled stress-strain conditions at the temperature of liquid helium. Equipment for such measurements has become available only in recent years and the number of such experiments reported is limited. Ekin et al.¹¹⁹ measured the effect of stress on J_c in a niobium-titanium-copper (1/1.8) composite wire containing 180 filaments at 4.2 K in transverse magnetic fields to 8 T. A definite degradation of critical current with stress was observed which was first evident at stresses equal to about 1/3 the fracture stress. There was about 15-20% decrease in critical current at 3/4 of the fracture stress. A large

part of the degradation was recoverable on stress removal as indicated by the dashed curves in Fig. 19. The percentage degradation

Fig. 19. Degradation in the Critical Current of a Niobium-Titanium Multifilamentary Composite as a Function of Magnetic Field and Stress. (After Ekin et al.¹¹⁹)

at a given stress showed only a slight dependence on magnetic field (for example, at 8 T the degradation was about 4% greater than at 4T).

Easton¹²⁰ has made J_c (stress) measurements on a wide variety of commercial niobium-titanium composites at 4.2 K in magnetic fields to 7 T. The critical current density, J_c , was defined as an equivalent sample resistivity of $1 \times 10^{-11} \Omega \text{ cm}$ and referred to the entire conductor cross sectional area. Critical current density was reduced with stress-strain (Fig. 20). With the exception of a composite with an aluminum alloy matrix, the degradation in J_c was <15% at strains to 2.0%. The aluminum-alloy matrix sample showed degradation of about 40% at 1.0% strain but aluminum-alloy matrix materials tested subsequent to the above measurements exhibited degradation comparable to copper matrix samples. The J_c value at zero strain was almost fully

Fig. 20. The Effect of Strain on the Critical Current Density of a Number of Niobium-Titanium Multifilamentary Conductors.

recoverable (within 1%) upon release of stress in all samples — with the exception of the one aluminum-alloy matrix sample discussed above.

Ekin and Clark¹²¹ have reported J_c values at 5 T on multifilamentary niobium-titanium stabilized by high purity aluminum (RRR $\approx$ 5000) or OFHC copper (RRR $\approx$ 70). Both conductors consisted of niobium-titanium tubes embedded in a 5056 aluminum alloy matrix with the stabilization material on the inside of the tubes. Value for J_c decreased when the wires were given strains greater than about 0.5%. The degradation was almost totally reversible and didn't become significant until strains of 1.5% or more were applied. The degradation of the aluminum and copper stabilized wires were identical to within 1%. The critical current was defined by three criteria; either an electric field level of 3×10^{-6} V/cm or resistivity levels of 10^{-10} Ω cm or 10^{-11} Ω cm (normalized to the niobium-titanium cross-sectional area in the composite). The electric field criterion was used in most cases, but only small differences in J_c resulted from the various methods of defining J_c .

Klamut and Suenaga,¹²² Ekin,¹²³ and Easton¹²⁰ found no influence of filament twist pitch on degradation of J_c with stress in niobium-titanium composites with copper matrices. However, Easton¹⁰ found a variation in the degradation of J_c with twist pitch in aluminum-alloy matrix composites (Fig. 21).

Fig. 21. The Effect of Stress on J_c for Niobium-Titanium-Aluminum-Alloy Conductors with Different Twist Pitches.

Fisher et al.⁶¹ studied cyclic strain effects on J_c in a niobium-titanium-copper composite consisting of 18, 0.2-mm-diam filaments with a copper/superconductor ratio of 2.7. The samples, which were soldered along the axis of a massive copper bar, underwent constant strain cycling up to 1360 cycles. A given cycle consisted of a tensile and compressive stress which completed a stress-strain loop to a constant strain value. The changes in the unstrained critical current density at 3.94 T during the cycling schedule are illustrated in Fig. 22. In the first 200 cycles ($\epsilon_{\text{tension}} = 0.35\%$, $\epsilon_{\text{compression}} = 0.03\%$) I_c decreased about 3.2%. No change was noted after the next 195 cycles

Fig. 22. The Effect of Cyclic Stress on J_c of a Niobium-Titanium-Copper Conductor. (After Fisher et al.⁶¹)

($\epsilon_{\text{tension}} = 0.45\%$, $\epsilon_{\text{compression}} = 0.10\%$). The sample was then warmed to 120 K over a 20-hr period and then cooled back to 4.2 K for further cycling. I_c recovered by about 0.1% during the warming period. Cycling 365 times ($\epsilon_{\text{tension}} = 0.57\%$, $\epsilon_{\text{compression}} = 0.21\%$) resulted in apparent fracture of the niobium-titanium filaments. This was revealed by a linear voltage from $I = 0$ in the V - I curves as well as an increase in resistance at I_c . It was assumed this resistance was due to current sharing between the filaments and copper matrix because of the fracture.

The degradation of J_c in niobium-titanium composites by either static or cyclic stress-strain is not understood. Several possible explanations have been eliminated. The reduction in filament cross section under strain could account for only about 1% of the degradation. However, any permanent dimensional changes could be responsible for the residual degradation observed on stress removal. Ekin¹²³ showed that the degradation could not be attributed to either heat generation due to creep or to degradation of the matrix properties. Since the

degradation is reversible, the cause must be elastic or pseudoelastic. As suggested earlier, a reversible martensitic phase transformation or reversible mechanical twinning may be likely mechanisms.

4.2 Stress Effects on the Superconducting Properties of Compound Superconductors

Müller and Saur¹²⁴ made the first measurements of the influence of mechanical stress-strain on T_c of the A-15 compounds. The change in T_c due to stress (torsion, bending, and uniaxial compression) was studied in tapes and wires of Nb₃Sn prepared by either the tin diffusion process or powder metallurgy, as well as in diffusion-reacted V₃Ga. Substantial decreases in T_c were noted with $\Delta T_c \approx -1.5$ K for samples strained in torsion. Tin layers on the sample surface produced a hysteresis effect, that is, a measurable $-\Delta T_c$ when stress was removed. Removal of the tin layers by etching eliminated the hysteresis in ΔT_c . Recently Pupp et al.¹²⁵ studied the influence of stress produced by bending Nb₃Sn films deposited on flexible quartz substrates. An average change in T_c with tensile stress, $\Delta T_c / \Delta \sigma \approx -5 \times 10^{-4}$ K/MPa was determined. They also reanalyzed the results of Müller and Saur (Fig. 23). McEvoy¹²⁶ measured the stress dependence of Nb₃Sn single crystals strained in the [001] direction. He found a $-\Delta T_c$ which depended on whether or not the stress was applied above or below the martensitic phase transformation temperature T_M . This was rationalized as being due to the effect of stress on domain rotation in the tetragonal phase. Larger $-\Delta T_c$ occurred if the stress were applied above T_M . Weger et al.¹²⁷ measured the effect of stress on T_c of V₃Si single crystals. They found a linear decrease in T_c with increasing compressive stress applied along the [100] direction ($-\Delta T_c \approx 0.5$ K at about 0.1 GPa). The change in T_c for stress applied along the [111] direction was negligible. A hydrostatic pressure of 40.5 MPa increased T_c by 0.13 K.

Müller and Saur¹²⁸ measured changes in J_c in diffusion layers of Nb₃Sn and V₃Ga under applied stress (either tension, torsion, or bending). J_c measurements were made in fields up to 0.8 T and large

Fig. 23. Change in T_c of Nb_3Sn as a function of tensile stress. (After Pupp et al.¹²⁵)

decreases ($\sim 2-3$ orders of magnitude) were observed. It was suggested that fracture of the A-15 layers was responsible for the severe degradation in J_c .

Buehler and Levinstein¹²⁹ studied the effect of uniaxial tensile stress on T_c and J_c of Nb_3Sn -cored wire. The T_c of a niobium-sheathed wire monotonically decreased with applied stress, whereas T_c first increased and then decreased for a Monel (copper-nickel)-niobium-sheathed wire (Fig. 24). This result is explained by the Monel-sheathed wire putting the Nb_3Sn in compression when cooled to 4.2 K (due to different thermal expansion coefficients). The maximum T_c occurs at the zero stress crossover between compression and tension. The J_c at 8 T was found to first increase with applied tensile stress and then decrease in both the Monel and niobium-sheathed samples. Complete recovery of the zero-stress J_c values were obtained for the Monel sheathed wires even after J_c was reduced by 10% under stress. Less recovery was observed in the niobium-sheathed samples.

Fig. 24. The Effect of Applied Tensile Stress on T_c of Nb_3Sn Wires. (After Buehler and Levinstein.¹²⁹)

Pulver¹³⁰ measured T_c , H_{C2} , and J_c in V_3Si single crystals and V_3Si and Nb_3Sn diffusion wires under uniaxial tension. The values of all the critical parameters were reduced by the tensile stress. Brand and Webb¹³¹ found that the suppression of the cubic to tetragonal transformation by uniaxial stress in V_3Si single crystals decreased J_c . Fluxoid pinning at the tetragonal-cubic phase boundaries (or internal twin boundaries) was suggested as the reason for enhanced J_c in the transformed crystals.

A second transition temperature (lower than the primary one) has been observed in pressed powders of several high T_c A-15 compounds¹³² as well as a number of C-14, C-15, and A-12 superconductors.¹³³ Alternating current susceptibility measurements indicate the lower T_c phase is present on the surface of the strained powders. The change in T_c is proportional to the T_c of the material (Fig. 25).

Smith¹³⁴ determined the hydrostatic pressure dependence of T_c in a number of A-15 compounds and reviewed the experimental and

Fig. 25. The Change in T_c Due to Stress as a Function of T_c for a Number of Materials. (After McCarthy.¹³³)

theoretical results available to him. The T_c of V_3Si and V_3Ga increase with hydrostatic pressure while T_c of Nb_3Sn and Nb_3Al decrease. None of the theoretical models for T_c explained the pressure dependence.

The bend test has been the most common mechanical test for stress effects on J_c in commercial or developmental compound superconductors. In its standard form, the superconducting tape, wire, or cable is bent around various diameter mandrels at room temperature, straightened, and then its J_c measured at 4.2 K. This test simulates any stress-induced damage which might be incurred during fabrication of a device at room temperature. In general, the bend radii for tapes which exhibit the first signs of degradation follow the simple elasticity analyses of Benz¹⁰⁰ and Henning et al.¹⁰¹ The fracture strain for the compound (~ 0.1 – 0.3%) is approximately constant so that the critical bend radius depends upon the layer thickness — that is, its outer fiber's distance from the neutral axis of bending.

It has been shown¹⁰² that if J_c measurements are made with the sample still bent at a given radius, then larger critical bend radii

are obtained than in the case of samples measured after straightening. This implies that some recovery takes place on straightening. However, Randell et al.¹³⁵ found more reproducible behavior in multifilamentary material if J_c was measured on the bent conductor (Fig. 26). The

Fig. 26. The Degradation of I_c as a Result of Bending Strain in a Nb_3Sn Conductor. o-twisted, ●-not twisted. (After Randell et al.¹³⁵)

difference between the conductors is due to the smaller strains induced in the twisted filaments at a given bend diameter.

A characteristic of both tensile and bend data is the apparent increase in current density with stress prior to degradation. Randell et al.¹³⁵ attribute this to "enhanced flux pinning by the induced strain." Oberly et al.¹³⁶, Hillmann et al.,¹³⁷ Easton and Schwall,¹³⁸ Suenaga and Sampson,¹³⁹ and Deis et al.¹⁴⁰ also observe the initial J_c enhancement in bend tests. Bend strains (total composite) up to 0.5–1.0% can be given to multifilamentary Nb_3Sn composites before any appreciable degradation of J_c is observed.^{108,135–142}

Bend tests have also been carried out on V_3Ga (refs. 105, 111, 139, 143), Nb_3Al (ref. 144), V_3Si (ref. 145), $VHf_{0.35}Zr_{0.65}$ (ref. 94),

and Nb_3Ge (ref. 146). In all cases degradation occurs at bend radii where the compound layer presumably reaches the fracture strain (~ 0.1 – 0.3%). As mentioned in Sect. 3.2, it has been repeatedly suggested that the C-15 $\text{V}_2(\text{Hf},\text{Zr})$ compounds should show more ductility than other compound superconductors because of their lower hardness values. However, bend tests on 100 μm thick $\text{V}/\text{Hf}_{0.35}\text{Zr}_{0.65}$ tape indicate degradation in J_c to begin at a bend diam of 1.5 cm (ref. 94). This means a strain of about 0.7% at the outer surface of the tape, but since the C-15 compound was in the center, closer to the neutral axis, a smaller strain would exist in it. Thus, until more detailed tests are carried out, we tentatively conclude that the C-15 $\text{V}_2(\text{Hf},\text{Zr})$ compounds do not possess significantly better mechanical properties than the other high field compound superconductors.

Tensile tests have been conducted on tape composites at both room temperature^{102,147} and 4.2 K (ref. 102) and subsequent critical currents, J_c , have been measured. Degradation of J_c with tensile strain followed the predictions of Benz¹⁰⁰ and Henning et al.¹⁰¹ for fracture strain in the compound.

Within the last year, data have become available on the effect of tensile strain on J_c of multifilamentary compound superconductors. McDougall¹⁴⁸ apparently was the first to report such measurements in multifilamentary Nb_3Sn . He measured the degradation in J_c stressed at 4.2 K, and found the critical strain at the onset of degradation to be about 50% less at 4.2 K than after straining at room temperature. He found the reaction conditions for Nb_3Sn formation influenced the strain at which degradation in J_c occurred. The conditions that produced a larger Nb_3Sn grain size produced smaller strains for the onset of degradation. Cracking along the grain boundaries was observed. Single filament samples were more resistant to strain degradation than were multifilamentary composites. The critical strain to failure was linearly related to the niobium core diameter when the Nb_3Sn layer thickness and character (grain size, etc.) were kept constant. Removing the bronze matrix on the single filament wires decreased the critical degradation stresses by about 1/2.

Filaments from mechanically tested samples (removed by etching away the matrix) were studied with scanning electron microscopy (SEM). At strains of about 0.1% the filaments appeared polished suggesting slip in the adjacent matrix. Grain boundary cracks were observed at strains of about 0.4% for 8 μm filaments reacted at 650°C for 1 hr. This strain corresponded to the observed degradation in J_c . Recovery of J_c occurred after stress removal. The reversible degradation of J_c was attributed to subcritical grain boundary cracks which close on stress removal. Small subcritical cracks might also increase the fluxoid pinning and thus be responsible for the observed initial increase in J_c with stress. In general, increasing the filament diameter increased the mechanical support for the Nb_3Sn .

Ekin¹⁴⁹ and Ekin and Clark¹²¹ studied the influence of stress on J_c at magnetic fields to 9.0 T in multifilamentary Nb_3Sn . At high stresses, large resistivities were observed by the voltage-current characteristic ($<10^{-11} \Omega \text{ cm}$). This presented a problem for the definition of J_c which has subsequently been discussed by Clark and Ekin.¹⁵⁰ A constant axial electric field (3 $\mu\text{V/cm}$) was used in this work but other definitions of J_c such as various voltage criteria could lead to a wide variation of J_c values at the same measurement. Ekin observed much less degradation in reinforced cables than in unreinforced monolithic conductors, due to the smaller strains in the Nb_3Sn at a given applied stress. The monolithic conductor showed permanent J_c degradation at higher stresses while recovery of 30–70% of the degradation was seen in the cable conductor. Degradation in J_c depends on the applied magnetic field; 5–10% more degradation at 9.0 T than at 7.0 T.

Easton and Schwall¹³⁸ compared the degradation in J_c due to tensile stresses at 4.2 K with the results of bend tests at room temperature. An example of the degradation of J_c with tensile strain for a variety of multifilamentary Nb_3Sn conductors is presented in Fig. 27. While strains in the room temperature bend tests of about 0.6% in the outer fibers caused essentially no reduction in J_c , tensile strains of 0.3% produced degradations in J_c of 12–30%. At strains above 0.7%, $V-I$ curves showed that large voltages developed even when I was nearly zero.

Fig. 27. The Effect of Strain on J_c for a Number of Nb_3Sn Multifilamentary Conductors.

Unlike similar measurements in niobium-titanium conductors, a large amount of scatter in the J_c degradation was observed, even on samples taken from the same conductor. The initial increase in J_c with stress-strain was observed in some samples but not even in all from the same conductor. Easton¹⁰ also found greater stress-produced degradation in J_c for a sample with no filament twist pitch than in an identical conductor with a twist pitch of 10 mm.

Hillmann et al.¹³⁷ also carried out tensile and bend tests on multifilamentary Nb_3Sn conductors. They considered the influence of the compressive strains of the bronze matrix on the Nb_3Sn superconducting properties. This in turn depended on the Nb_3Sn layer thickness and composition of the conductors. Hillmann et al. concluded that the compressive strains led to degradation of T_c , H_{c2} , and J_c . At high magnetic fields (~ 8 T), J_c was lower for samples reacted at lower temperatures, probably due to the lower H_{c2} and T_c values. Thinner layers of Nb_3Sn produced lower T_c values. Single core Nb_3Sn -Nb composites showed lower T_c values than the multifilamentary material.

When the bronze matrix was removed by etching from both types of conductor, T_c increased by as much as 1.5–1.8 K. Tensile tests and bend tests showed an increase in J_c and T_c with initial tensile stress, apparently due to the reduction of the compressive stress. Further tensile stressing led to degradation, but recovery in J_c occurred even after 20% degradation. Cracks in the Nb₃Sn layer were not observed at strains below about 1%.

Larbalestier et al.¹⁰⁹ studied the influence of tensile stress on J_c of multifilamentary Nb₃Sn. The J_c measurements were all made at a field of 3 T. No degradation was observed at stresses up to 100 MPa. At stresses of 250 MPa a reversible degradation was observed, but at higher stresses permanent degradation set in. The value of J_c was too low to be useful for stresses as high as 400 MPa. Several load cycling experiments were also carried out. Slight increases (~1–2%) in J_c degradation were observed after 3 cycles to 280 MPa with no further changes after 10 cycles. At higher stresses (for example, 335 MPa) larger changes in J_c degradation (~13%) were seen after 10 cycles. Less degradation in J_c was indicated than found by some of the other investigations.^{138,149} However, since Larbalestier's data were taken at 3 T, the field variation of the degradation observed by Ekin¹⁴⁹ may account for these differences; that is, less stress-induced degradation may be expected at lower magnetic fields. Fisher and Kim¹⁵¹ investigated the effects of cyclic strain on a composite containing about 25,000 Nb₃Sn filaments in a copper matrix. They found the endurance limit during elastic load-unload cycles to be greater than anticipated. I_c did not degrade for 3850 cycles at strains in the 0.1 to 0.2% range.

The mechanism for the irreversible J_c degradation in multifilamentary Nb₃Sn is probably due to cracking of the filaments when their fracture strain is exceeded. Support for this conclusion comes from several experiments^{123,148} using SEM on filaments etched from the matrix after strains into the irreversible J_c degradation regime. However, the mechanism for the reversible J_c degradation has not yet been defined. Several suggestions for the mechanism have been proposed. McDougall¹⁴⁸ suggested that the reversible degradation, as well as the initial

increases in J_c with stress, is caused by subcritical microcracks along the grain boundaries, which close when the applied stress is removed. Ekin¹²³ proposes that the reversible behavior might be due to either (1) a shift in T_c or H_{c2} by stress-induced band structure changes and/or martensitic phase transformations, or (2) a stress-induced change in the fluxoid pinning structure. Hillmann et al.¹³⁷ attribute the decrease in J_c under stress to the corresponding stress-induced degradation of T_c and H_{c2} . No speculation as to the microscopic mechanism for these changes was given.

Luhman and Suenaga¹⁵² studied the effects of removing the bronze matrix on T_c and J_c in single core bronze-processed Nb₃Sn. The parameters T_c , H_{c2} , and J_c at high fields (>10 T) increased on removal of the cladding. This was attributed to a removal of compressive stresses which degrade T_c on the Nb₃Sn. Increases in T_c of about 1.2–1.5 K were found and the transition widths decreased from about 1.4 to 0.4 K. The decrease in T_c increased with increases in the relative amount of bronze cladding. The change in T_c was about 10 times greater than predicted from the pressure dependence of T_c in Nb₃Sn. Suggested explanations for this effect were a stress-induced change in order or a stress-induced phase transformation. These results may help explain the reversible tensile stress degradation in Nb₃Sn. However, while J_c increased at high fields (>10 T) after cladding (stress) removal, the reverse was observed at lower fields (<10 T). Since the experiments on the tensile stress degradation of J_c have been conducted only at fields <10 T, a simple correlation of T_c and J_c degradation may not yet be made.

5. THE INFLUENCE OF STRESS EFFECTS ON SUPERCONDUCTING APPLICATIONS

The design of large superconducting magnets for fusion research and energy storage must consider the limitations imposed by stress effects on superconducting properties. Stress-strain limitations vary from design to design, but typical values for maximum stress and strain are 70–200 MPa and 0.1–0.2% strain.^{153,154} At these levels the static degradation of niobium-titanium conductors is negligible.

However, if pulsed coil operation results in cyclic stress, at long cycle times fatigue failure of the niobium-titanium filaments may become important. Some (~ 10 – 15%) degradation can be observed in certain Nb_3Sn composites even at the low design strains ($\sim 0.15\%$) indicated. The degradation in J_c under static stress is then chiefly a problem of providing sufficient mechanical support to the superconductor to minimize the effect of any stress-strain. However, this is not a trivial engineering or economic problem and any lessening of the stress-strain specifications on the superconductor could result in large savings in capital investment.¹⁵³

Stress-induced heat generation in composite superconductors has been studied by Easton et al.¹⁵⁵ and Kroeger et al.¹⁵⁶ The source of this heat under pulsed field (therefore stress) conditions is the hysteretic stress-strain loops which develop due to the composite nature of the conductors (Sect. 2.4). Kroeger et al.¹⁵⁶ compared the heat generated by stress, obtained from temperature rises, with the work done on the specimen, calculated from the area under stress-strain curves (Fig. 28). The cases of initial loading, that is, in which the sample is first plastically deformed, and cyclic loading, in which the hysteresis loop has been stabilized by repeated stress cycling are both presented in Fig. 28. Smaller values of heat were generated as measured calorimetrically than indicated from the stress-strain curves for initial loading because some of the work goes into elastic stored energy. The good agreement between the two measurements for cyclic loading (Fig. 28) confirms the assumption that after the hysteresis loop is stabilized, all of the mechanical work is converted to heat in the system. Of a number of conductor variables such as number and size of the filaments, twist pitch, and ratio of normal to superconducting material, only the matrix composition appeared to influence the heat generated. An aluminum alloy matrix composite exhibited substantially lower heat generation than those with copper matrices. Kuchnir¹⁵⁷ measured stress heating in a thermally insulated niobium-titanium-copper composite, and found equal temperature rises occurred when the composite was (1) loaded to some stress level, and (2) unloaded to zero stress.

Fig. 28. Comparison of Heat Generated by Stress as Obtained from Temperature Rises to the Work Done on the Specimen Found from Stress-Strain Curves for a Niobium-Titanium-Copper Conductor. In the initial loading case the sample is plastically deformed; in cyclic loading the hysteresis loop has been stabilized by repeated stress cycling.

The phenomenon of "training" has frustrated designers of magnets over the years. Training — the successive increase in critical current density with prior testing — has been attributed to a number of causes including a minimization of induced currents,¹¹³ conductor movement, cracking of the impregnant (epoxy), or general movement of the coil.¹⁵⁸ In spite of a large effort to develop optimum techniques for coil potting, Wilson states (in a recent review on stabilization of superconductors for use in magnets) that "....degraded performance and training are still shown by high current density magnets."¹⁵⁹

Recently, mechanical effects in the conductor itself have been suggested as the mechanisms responsible for training. Heim⁵⁹ proposed that the inelastic deformation of the copper matrix was responsible for training. He recommended a procedure of post wind preload to erase the mechanical history effects which, due to the Bauschinger effect, had kept the conductor in a condition at or near the matrix

yield point. This would involve prestressing the copper to levels above the operational stress. However, Schmidt^{11,160} gives arguments against plastic deformation of the copper matrix as the solution for training. His reasons include: (1) training is observed in bare niobium-titanium wires, (2) experimentally, he found the quench to occur before the copper matrix reached critical temperature, $T_c(J_c, B)$, and (3) that in superconducting magnets, training cannot be prevented by slow energizing.

Evans²⁹ proposed that training is associated with serrated yielding, since significant temperature rises have been recorded during serrated yielding.^{27,28} Schmidt¹¹ dismisses this possible mechanism since he claims the serrations only occur in the plastic portion of the niobium-titanium stress-strain curve at 4.2 K at strains greater than about 1%. However, Easton and Koch¹⁷ believe that microyielding (and thus heating) not shown by a stress-strain curve can occur at low strains as indicated by acoustic noise. The resolution of the usual stress-strain equipment is not sufficient to detect the microplastic processes which are presumably responsible. Schmidt¹⁶⁰ has studied the stress-strain behavior at 4.2 K in niobium-titanium with acoustic emission techniques and suggests that microplastic processes (twinning, dislocation motion) are responsible for the training observed in his experiments.

6. CONCLUDING REMARKS

A good start has been made in understanding the mechanical properties of hard superconductors and stress effects on superconducting behavior. Problem areas have been defined but much research needs to be done. The mechanisms for degradation of J_c in both niobium-titanium and Nb_3Sn must be studied by microstructural techniques. The nature of cyclic stress effects requires further research. The various mechanical effects that may produce heating and instabilities in magnets require study. The association of materials scientists with device engineers and designers will be needed to solve the complex problems in this area. The best solution to the stress effects problem would be the development of a high field superconductor with good strength and especially good

ductility even at 4.2 K. Such a superconductor would need to be combined in a composite such that the inelastic effects that generate heat are minimized. Lacking such an ideal conductor, careful mechanical-superconducting measurements should be continued on state-of-the-art conductors to set the limitations on the applications of superconducting devices. It is becoming generally recognized^{153,161,162} that mechanical effects may be the most severe limitation on the successful use of superconductors in large devices.

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