Tutorial

SRF Materials other than Niobium

Anne-Marie Valente-Feliciano Thomas Jefferson National Accelerator Facility Jefferson Science Associates LLC







Motivation

- •Which Superconductors for SRF Cavities?
- ·Nb compounds: NbN, NbTiN
- ·A15 Compounds: Nb₃Sn, V₃Si, ...
- •MgB₂

- •SIS Multilayer Structures
- Concluding Remarks



Why looking beyond Nb?

Nb has the highest $\rm T_{c}$ for a pure metal and the highest lower magnetic field $\rm H_{c1}$

•Nb cavities performance have reached close to its theoretical limit (H \approx Hc = 200 mT)



•For further improved cavity RF performance, innovation needed



Looking beyond Nb - Potential Benefits

≻Higher Tc

Jefferson Lab

potentially higher Hc

Substrates with higher thermal conductivity

Potentially cryogenics cost reduction if cavity operation temperature at 4.2K or higher



Which superconductors are suitable for SRF applications?

Surface Resistance $R_{S} = R_{BCS}(T) + R_{res}$

Jefferson Lab



V. Palmieri, 10th Workshop on RF Superconductivity Proceedings, Tsukuba 2001 (Noguchi) "New materials for superconducting radiofrequency cavities"







If $T < T_c / 2$

Jefferson Lab

 $= \frac{R_n}{\sqrt{2}} \left(\frac{\eta\omega}{\pi\Delta}\right)^2 \frac{\sigma_1}{\sigma_1} = A\sqrt{\rho_n} e^{-\frac{\Delta}{K_B T}} \left(1 + O(\Delta, \omega, T)\right)$

- A & B constants weakly dependent on material
- ω = RF frequency
- pn = Normal State conductivity
- A = Penetration depth
- Tc = Transition Temperature

dependence on ρ_n and T_c represents an immediate criterion for selecting the most favorable candidates for cavities

Material with high normal state conductivity and high Tc should be selected







A.-M. Valente-Feliciano 13th International Workshop on RF Superconductivity -Beijing, October 13th, 2007



Residual Resistance R_{res}

Temperature independent

Contributions to residual losses:

Intrinsic:

Inhomogeneties, Metallic Inclusions within λ , Grain Boundaries, Oxides Extrinsic:

Trapped Flux during cooling (can be avoided)

Variety of phenomena involved **matheta** Not one formula predicting R_{res}

From literature

Jefferson Lab

Empirically, R_{res} found proportional to at least $\int \rho_n$

For two materials with the same R_{BCS} and different T_c and ρ_n , the one with the smallest ρ_n should have the smallest R_{res}

Metallic behaviour is favored



Critical Field



Boundary between Type I and Type II determined by the Ginzburg-Landau parameter

κ = λ/ξ

Ginzburg-Landau theory relates H_{c1} , H_{c2} and H_c to κ , over a restricted range of κ .

H_{sh} is the maximum permissible value of the applied field, which satisfies Ginzburg Landau equations.

$$H_{c1} = \frac{\phi_0}{4\pi\lambda^2} \left(\ln \frac{\lambda}{\xi} + 0.5 \right)$$

Jefferson Lab

SC fully in Meissner state up to $H_{\rm c1}$

For Type – II superconductors, the Meissner state can persist metastably above H_{c1} but only up to H_{sh}

 $H_{RFcrit} \approx H_{sh}$



Criteria of choice

THERE IS NO IDEAL SUPERCONDUCTOR FOR CAVITY CHOICE IS BASED ON COMPROMISE





Possible Choices among Superconducting Materials

Nb compounds
A15 compounds
MgB2

Material	T _c (K)	ρ _n (μΩcm)	H _c (0) [T]	H _{c1} (0) [T]	H _{c2} (0) [T]	λ (Ο) [nm]	
Nb	9.2	2	0.2	0.17	0.4	40	
NbN	16.2	70	0.23	3 0.02		200	
NbTiN	17.5	35		0.03		151	
Nb₃Sn	18.3	20	0.54	0.05	30	85	
V ₃ Si	17						
Mo ₃ Re	15		0.43	0.03	3.5	140	
MgB ₂	40		0.43	0.03	3.5	140	



Nb Compounds

B1 compounds - NaCl structure

Metallic atoms A form an fcc lattice and non-metallic atoms B occupy all the octahedral interstices.







Nb Compounds

Only few Nitrides and Carbides of the IV, V and VI group Transition Metals have critical temperatures higher than Niobium.

BA	Sc	γ	La	Ti	Zr	Hf	V	Nb	Ta	Cr	Мо	Ŵ	Re
В	$\{ y_i, y_j \}_{i \in \mathbb{N}}$	1.5		200	3.4	3.1	-						
С	<1.38	<1.38		3.42	<0.3	<1.20	0.03 3.2*	12	10.35		14.3	10.0	3.4
N	<1.38	<1.4	1,35	5.49	10.7	8.83	8.5	17.3	6.5	<1.28	5.0	<1,38	
P	6.67		<1.68					\sim		5 - 19 ²			
Sb		<1.02	<1.02	생겼				el de la composition Composition					
0		11/1		2.0			<0.3	1.39	- 1				1.00
S	<0.33	1.9	0.87	143	3,3		511				1.		33
Se	<0.33	2.5	1.02				1.4			12			1
Те		2.05	1.48										12

* $T_c = 3.2$ K was registered in vanadium carbide after implantation of C⁺ ions s

Jefferson Lab

Superconductivity of Transition Metals, their Alloys and Compounds, S.V Vonsovsky, Y.A. Izyumov, E.Z. Kurmaev, Springer-Verlag, 1982



The only B1 simple compound that has widely tested for accelerating cavities Mainly two different techniques have been investigated for this application:

•Thermal diffusion of N into Nb followed by rapid quench cooling •Reactive Sputtering on metallic or ceramic substrates to Nb cavities Thermal Diffusion:

Bulk Nb (RRR 300) annealed @ 1550°C for 2h

reacted in N₂ vapor(150mbar) @ 1400°C for 4h Rs=1.3 10⁻⁶ @ 4.2K and 4 10⁻⁹ @1.8K @7.9GHz

G.Gemme et al., J.Appl.Phys. 77(1), Jan. 1995

Reactive Sputtering:

Sputtering from high purity Nb target in Ar+ N₂ in DC triode magnetron sputtering system Highest Tc for substrate temp. > 500°C, P_{Ar}=8.10⁻³mbar, P_{N2}=1.10⁻³mbar

A. Nigro et al., Physica Scripta Vol. 38, 483-485, 1988





Good SC properties, even if deposited at low temperature Low secondary emission coefficient Very stable surface properties

The right B1-NbN superconducting phase is the so-called $\delta\text{-phase}$

Tc= 17.2 K for δ -phase (lattice parameter = 4.388 Å) T_{c} very sensitive to Nitrogen stoichiometry

. In sputtered films, the δ -phase can be found mixed to some other low $\mathcal{T}_{\mathcal{C}}$ phases

Even if no grain boundaries are present and δ -phase single crystal is considered the single grain resistivity is not so low.

Anomalously high resistivity of NbN in the normal state, often higher than 100 μΩcm due to both metallic and gaseous vacancies randomly distributed in both sublattices Equiatomic composition is Nb_{0.987}N_{0.987} not Nb_{1.0}N_{1.0} Common problem for B1 compounds





Ternary Nitride Nb_{1-x}Ti_xN

Presence of Ti found to reduce significantly the resistivity And facilitate formation of a pure cubic structure. The δ -phase remains thermodynamically stable even at RT. T_c as high as for good quality NbN, for Nb fraction (1-x)>0.5

extreme hardness, excellent adherence on various substrates, very good corrosion and erosion resistance, high-sublimation temperature, and relative inertness

More metallic nature and better surface properties than NbN should result in better RF performance



Jefferson



INFN : reactive sputtering with Ar/N_2 in DC Triode Magnetron Sputtering @ 600°C and 200°C

 $(Nb_{1-x}Ti_{x})N$ films with 1-x<0.5 present a lower calculated surface impedance, lower critical fields and better surface properties than NbN, especially when deposited at low temperatures.

R. Di Leo et al. J. of Low Temp. Phys, vol 78, n1/2, pp41-50, 1990





Fig. 1. Superconducting critical temperature T_c as a function of the titanium composition (x) for the $(Nb_{1-x}Ti_x)N$ films deposited at $T_s = 600^{\circ}C$ (circles) and at $T_s = 200^{\circ}C$ (squares).

Jefferson Lab

Fig. 3. Calculated BCS surface impedance $R_s(BCS)$ as a function of the titanium composition (x) for the $(Nb_{1-x}Ti_x)N$ films deposited at $T_s = 600^{\circ}C$ (circles) and at $T_{\rm r} = 200^{\circ} {\rm C}$ (squares). The continuous lines correspond to the values of the lines through the data in Figs. 1 and 2.







for a NbTiN sample, at 4 GHz.



A.-M. Valente-Feliciano 13th International Workshop on RF Superconductivity -Beijing, October 13th, 2007

CERN:

Jefferson Lab

Samples and six 1.5 GHz Cu cavities coated by reactive cylindrical magnetron sputtering Best cavity result for thicker film (4.3µm) and lower deposition temperature ($265^{\circ}C$) Rs = $330n\Omega @ 4.2K$ Q_0 at zero field is higher than the Q-value of Niobium cavities but Eacc limited under 10 MV/m As for NbN, N stoichiometry critical to obtain the right SC phase

M. Marino, Proceedings of the 8th Workshop on RF Superconductivity, October 1997, Abano Terme (Padua), (Rep) 133/98, vol.IV, p.1076



A15 Compounds - Structure

A atoms = Transition elements of group IV, V or VI B atoms = Non transition or transition elements



B atoms occupy corners and centre of BCC structure A atoms form orthogonal chains bisecting the faces of the BCC unit cell. Linear Chain Integrity is crucial for Tc



A15 Compounds - Potential candidates for RF Cavities

Nb₃Sn, Nb₃Al, Nb₃Ge, Nb₃Ga, V₃Si, Mo₃Re

• Among the Nb and V based high Tc (15 - 20 K)

Jefferson Lab

- Nb_3Ga and Nb_3Ge do not exist as stable bulk materials at 3:1 stoichiometry
- Nb_3Al exists only at high temperature causing excessive atomic disorder
- Production of above materials need non equilibrium processes
- V_3Ga , V_3Si & Nb₃Sn are stable bulk material and have high T_c
- Another A-15 compound holding promise is Mo_3Re (Tc=15K)

Sharma, International Workshop on Thin Films and New Ideas for Pushing The Limits Of RF Superconductivity, LNL-INFN, Oct.2006



A15 Compounds - Preparation Methods I

Extreme brittleness so A-15 bulk structure cannot be formed

The A-15 should be produced as thin layer on the interior of the already formed structure

Such a layer need to be only 1 or 2 microns thick Λ_L (Nb3Sn) = 65 nm

Thin film route ideal



A15 Compounds - Preparation Methods II

Co-Sputtering

- Considerable success achieved in synthesizing difficult materials like Nb_3Ge with highest Tc(~23k) or V_3Si
- Typically two constituents are sputtered simultaneously onto a temperature controlled substrate
- Stoichiometry dependent on relative positions of target and substrate (can be manipulated to get perfect stoichiometry)
- Stoichiometry control difficult over large areas like accelerating system and if stoichiometry range for A-15 phase is narrow.

<u>Sputtering</u>

To sputter from a single target of correct stoichiometry (prepared by powder sintering) Stoichiometry, Substrate Temperature, Deposition Rate, Deposition Thickness Can be varied independently



A15 Compounds - Preparation Methods III

Chemical Vapor Deposition (CVD)

MOCVD (*Metal Organic Chemical Vapour Deposition*) is a particular case of CVD in which the precursor is a metallorganic compound

Process in which one or more precursors, present in vapor phase, chemically react on an appropriate warm substrate, giving rise to a solid film

- Deposition rate and structure of the film depend upon temperature and reagent concentration
 - ⇒ Uniformity of temperature and flow of gaseous over entire cavity surface may be difficult with complex geometry

Diffusion Reaction

Technique proved successful for magnet conductor application Simple equipment compared to sputtering and CVD



A15 Compounds - Nb₃Sn

Wuppertal, end '80s :

Nb3Sn cavity (1.5 GHz) obtained trough Sn vapour phase diffusion @ 1200°C



Q vs. E_{peak} of the 1st two Nb₃Sn-coated 1.5GHZ single cell cavities in comparison to pure Nb at 4.2K and 2K from CEBAF

5-cell 1.5GHz cavity also coated: $Q_{o}{\sim}10^{9},~E_{acc}{=}7MV/m$ with $Q{=}8.10^{8}$

G. Müller et al., M. Peiniger & H. Piel, IEEETrans. On Nucl. Sc. Vol NS-32, nº5, Oct. 1985 A.-M. Valente-Feliciano 13th International Workshop on RF Superconductivity -Beijing, October 13th, 2007



A15 Compounds - Nb₃Sn through liquid diffusion

S. Deambrosis, Sharma, International Workshop on Thin Films and New Ideas for Pushing The Limits Of RF Superconductivity, LNL-INFN, Oct.2006 S. Deambrosis et al., Physica C 441 (2006) 108-113



Diffusion temperature to be kept above $930^{\circ}C$ to avoid formation of low Tc phases like Nb₆Sn₅ (2.6 K) and NbSn2 (2.1 K) Diffusion time optimize to obtain desired Nb3Sn thickness

Post diffusion heat reaction important to get rid of the outer Sn layer

Post diffusion annealing to have enlarged grains and perfect ordering

Jefferson Lab

A15 Compounds -Nb₃Sn through Multilayer Coating

Deambrosis, Keppel, LNL/INFN, International Workshop on Thin Films and New Ideas for Pushing The Limits Of RF Superconductivity, LNL-INFN, Oct.2006

Coat alternate layers of Nb and Sn and subject to diffusion reaction Preliminary results: a sharp transition and a T_c of 17 K has been obtained



Thickness Nb = 4.5 Thickness Sn Annealed after sputtering for 3 hours at 975 °C

Jefferson Lab

🍘 🤁

A15 Compounds - Nb₃Sn through MOCVD process

G. Carta et al. International Workshop on Thin Films and New Ideas for Pushing The Limits Of RF Superconductivity, LNL-INFN , Oct.2006

MOCVD technique using bis(cyclopentadienil)niobium borohydride, (cyclopentadienil)niobium tetramethyl and tributyltin hydride as Nb and Sn precursors respectively.



Sample characterization by XRD, SEM and RBS analyses: presence of niobium (I, II, V) and tin (II) oxides on the surface.

Problems: great oxophylic character of Nb

Jefferson Lab



A15 Compounds - V₃Si

S. Deambrosis et al., Physica C 441 (2006) 108-113

Highly ordered compound, RRR~80 achievable, m,ax Tc (17.1K) when stoichiometric composition (25at.% Si)

V₃Si layers by silanization of V substrate and Thermal Diffusion V substrate heated to get SiH₄ decomposition and Silicon diffusion Film grown by silanization with p (SiH₄) ~ 10^{-3} - 10^{-4} mbar Annealing in vacuum to get rid of hydrogen



Silicon content (at. %)



* Tc ~ 16 K is routinely obtained

* RF measurement on 6 GHz V-cavities will be available soon





Jefferson Lab

825°C, 4h+8h

A15 Compounds - Mo₃Re

Mo₃Re thin films by DC magnetron deposition: Mo₇₅Re₂₅, Mo₆₀Re₄₀ Solid solution, free of bulk and surface inhomogeneities, low intersticials solubility compared to Nb, low κ, high H_{c1} (500G) Bulk in σ phase, tetragonal low T_c (6K) but T_c up to 18K reported in literature with bcc structure

S.M. Deambrosis et al., Physica C 441(2006) 108-113

Jefferson Lab



Fig. 4. A Mo₇₅Re₂₅ film deposited on Cu transition curve: deposition T = 680 °C, $T_c = 11.18$, $\Delta T_c = 0.08$ K.



A15 Compounds - Results on cavities?



Cf. WE203: The progress at LNL on Nb₃Sn and V₃Si, Silvia Deambrosis (INFN-LNL, Padua University)



6 GHz Nb cavities for RF properties systematic testing for V₃Si, Nb₃Sn





Magnesium Diboride (MgB₂)

Graphite-type boron layers separated by hexagonal close-packed layers of magnesium

Superconductivity comes from the phonon-mediated Cooper pair production similar to the low-temperature superconductors except for the **two-gap nature**.

 $T_{c} \sim 40 \ K$

Compared to cuprates:

• Cheaper

Jefferson Lab

- Lower anisotropy
- Larger coherence length
- Transparency of grain
 boundaries to current flows







attractive for RF applications.

C. Buzea and T. Yamashita, Superconductor Sci. Technol. 14 (2001) R115.



MgB₂: Two Energy Gaps



A. Floris et al., cond-mat/0408688v1 31 Aug 2004

Jefferson Lab

RF response has shown lower energy gap behavior. This must be compared to $\Delta \approx 1.5$ mV for Nb. There is room for better performance than niobium, since the resistivity can also be made quite low (best values are $\leq 1 \ \mu\Omega$ cm).



MgB₂ - Potential Low BCS Rs for RF Cavity





Jefferson Lab

(2002)







A.-M. Valente-Feliciano 13th International Workshop on RF Superconductivity -Beijing, October 13th, 2007

MgB2 - A comparison with conventional SC for RF applications

	MgB ₂	Nb
T _c (K)	39	9.2
ρο (mΩcm)	0.1-10	0.05
RRR	3-30	300
$\Delta_{p,s}$ (meV)	2,7	1.2
2 $\Delta_{p,s}$ /K _B T _c (meV)	1.6, 4	3.9
× _{p,s} (nm)	50,12	40
λ (nm)	85	80
m_0H_{c2} (T)	6-50	0.2
$R_{BCS} \otimes 4K$, 500MHz (n Ω)	2.5/2.3×10 ⁻⁵	69

X. Xi, International SRF Thin Films Workshop, Padua, Italy, 2006

 $\downarrow \text{from } R_{BCS}(n\Omega) = \left(\frac{1}{T}\right) 10^5 v_{GHz}^2 e^{(-\Delta/KT_c)}$

F.Collings et al. SUST 17 (2004)

Jefferson Lab



MgB₂-Thin films growth



curve of MgB₂ < Mg vapor pressure

Jefferson Lab

optimal T for epitaxial growth ~ T_{melt}/2 For MgB₂ , 540° C → it requires P_{Mg} ~11 Torr *Too high for UHV deposition techniques (PLD, MBE...)*

At P_{Mg} = 10⁻⁴-10⁻⁶ Torr, compatible with MBE, Tsub ~ 400° *C* MgB₂ is stable, but no MgB₂ formation: Mg atoms re-evaporate before reacting with B



M. Naito and K. Ueda, SUST 17 (2004) R1

At P=10⁻⁶ Torr and T> 250°C no accumulation of Mg will take place on the substrate and the growth of the superconducting phase is very slow due to a large kinetic energy barrier.

At low Mg pressure only extremely low deposition temperatures can be used



MgB₂ - HPCVD on metal substrates

X. Xi- Penn State University



Susceptor

Jefferson Lab

Hybrid Physical Chemical Vapor Deposition

High T_c has been obtained in polycrystalline MgB₂ films on stainless steel, Nb, TiN, and other substrates.

Clean HPCVD MgB2 thin films with excellent properties:

•RRR>80

low resistivity (<0.1 $\mu\Omega)$ and long mean free path

- high $Tc \sim 42$ K (due to tensile strain), high Jc (10% depairing current)
- low surface resistance, short penetration depth
- \cdot smooth surface (RMS roughness < 10 Å with N₂ addition)

 good thermal conductivity (free from dendritic magnetic instability)

Critical engineering considerations:

generate high Mg pressure at substrate (cold surface is Mg trap) deliver diborane to the substrate (the first hot surface diborane sees should be the substrate)





MgB₂ - Microwave Performance on HPCVD Films



13th International Workshop on RF Superconductivity -Beijing, October 13th, 2007

MgB₂ - Reactive Evaporation





1000

1.0



MgB₂ - Challenges

Keys to high quality MgB2 thin films:

- High Mg pressure for thermodynamic stability of MgB_2
- oxygen-free or reducing environment
- clean Mg and B sources

Challenges

Jefferson Lab

Film properties degrade with exposure to moisture: resistance goes up, T_c goes down Clean cavity surface leads to degradation in water and moisture ... need of a cap layer?

Safety ... procedures for use of diborane

Cf.TU203 Prospects for higher Tc-Superconductors for SRf Applications, Xiaoxing Xi (Penn State University)





SIS Multilayers

Alex Gurevich, Appl. Phys. Lett. 88, 012511 (2006)

Taking advantage of the high -Tc superconductors without being penalized by their lower Hc1...

Higher- T_cSC : NbN, Nb₃Sn, etc



Jefferson Lab

Multilayer coating of SC cavities: alternating SC and insulating layers with d < λ

Higher T_c thin layers provide magnetic screening of the bulk SC cavity (Nb, Pb) without vortex penetration

- Strong increase of H_{c1} in films allows using RF fields > H_c of Nb, but lower than those at which flux penetration in grain boundaries may become a problem
- Strong reduction of BCS resistance because of using SC layers with higher ∆ (Nb₃Sn, NbN, etc)



SIS Multilayers - A minimalistic solution with Nb₃Sn



A single layer coating more than doubles the breakdown field with no vortex penetration, enabling E_{acc}~ 100 MV/m Potential to increase Q for bulk Nb of 2 orders of magnitude above Nb values



SIS Multilayers: Experiments in progress

• JLab

NbN/Al₂O₃/Nb and NbTiN/Al₂O₃/Nb coated in UHV multi-techniques and ECR deposition systems under preparation (combining magnetron sputtering, IBAD, ECR, ...)

• INFN Legnaro

Multilayers with Nb₃Sn

• INFN Naples

Multilayers with NbN, NbTiN by Sputtering

Argonne National Lab

Atomic Layer Deposition (ALD): alternating, saturating reactions between gaseous precursor molecules and a substrate to deposit films layer by layer. Films from a wide variety of elements, compounds and alloys with a thickness from a few atomic monolayers to microns

cf.TUP64

• Penn State University, Los Alamos National Lab,...

 MgB_2 as a top layer with HPCVD

KEK

Jefferson Lab

MgB₂ by PLD cf. WEP69



SIS Multilayers - The Benefits

- Multilayer S-I-S-I-S coating could make it possible to take advantage of superconductors with much higher H_c , than those for Nb without the penalty of lower H_{c1}
- Strong increase of H_{c1} in films allows using rf fields > H_c of Nb, but lower than those at which flux penetration in grain boundaries may become a problem
- Strong reduction of BCS resistance because of using SC layers with higher $\Delta(Nb_3Sn, NbN, ...)$
- The significant performance gain may justify the extra cost.

... but ...

Jefferson

Technical challenges, influence of composition on Hc1 and Hc, influence of the morphology and composition at grain boundaries, ...



CONCLUDING REMARKS

Over the years, some attempts have been made to study alternative materials to Nb for applications to SRF cavities.

Most of the sample/cavities using alternative materials have been produced by reactive magnetron sputtering or thermal diffusion. Use of Energetic Condensation Techniques like Vacuum Arc Deposition, ECR, or ALD? (production of very dense films with nmscale roughness...Some trials with Vacuum Arc @ INFN-Rome, non conclusive)

The multilayer approach opens the door to further potential improvement for SRF cavities, taking benefits from the advantages of higher T_c superconductors without the limitation of H_{c1} .

The effort for new materials research for SRF cavities application has been very limited so far... There is still a lot of work ahead!

Jefferso



Aknowledgements

Larry Phillips, JLab C. Reece, JLab V. Palmieri, LNL-INFN S. Deambrosis, LNL-INFN T. Tajima, LANL X. Xi, PSU J. Elam, ANL

- A. Gurevich, FSU
- R. Russo, INFN

