ABSTRACT

RF superconducting cavities have been in use for nearly three decades to accelerate the ion beam to ever increasing higher energies in a particle accelerator. Cavities used to-date are made of niobium- either in bulk or Nb coated on copper cavities. These cavities are operated between 1.5 and 1.8 K where the BCS component of the surface resistance is reduced to minimum and the cavity is operated in the residual resistivity regime. Operating temperature can be increased if we switch over to higher Tc superconductor. The oxide superconductors which once looked most attractive with Tc above 77 k, however, proved disastrous because of weak superconductivity at the intergrain boundaries. We are thus left with the choice of A-15 superconductors as the possible materials for RF cavities. Out of a total of more than 50 known A-15 superconductors only Nb$_3$Sn, Nb$_3$Ge, Nb$_3$Al, V$_3$Ga, V$_3$Si and Mo$_3$Re with high Tc are the possible candidates for being considered as the replacement of Nb. This paper discusses a variety of routes for manufacturing these intermetallic compounds, (extremely brittle) which were developed in the wake of the production of multifilamentary wires of these A-15 superconductors for magnet applications. Some of these technologies can as well be adapted to realize A-15 RF cavities with suitable modifications. The methodology followed in these technologies and their relevance to cavity fabrication is discussed in detail. Efforts being made at LNL to develop A-15 superconducting cavities are briefly described.
1. INTRODUCTION

To attain high beam energies and the domain of higher atomic number elements, the beam is repeatedly accelerated by pumping RF voltage in an array of pill box resonators (cavities). The RF voltage is applied across the gap through which the beam passes. The beam gets a boost when the phase of the beam in the gap inside the cavity matches with the phase of the RF field. At frequencies > 10^7 Hz the alternating current (AC) flows only through a thin surface layer $\delta$ (skin depth) given by

$$\delta = C / (2\pi \sigma \omega)^{1/2}$$

At high frequencies $\delta$ may be smaller than the mean free path $\ell$ for high purity metals wherein only electrons traveling parallel to surface participate in conduction. Ultra high purity of the cavity material is thus not helpful once the skin depth $\delta$ becomes comparable to the mean free path. Copper cavities which have been used widely, are therefore operated at room temperature and not at 77 K or 4.2 K.

Problem with conventional copper cavities is that a large power is required to produce even moderate fields. This power is necessary to offset Ohmic losses in the walls of the accelerating system, the surface resistance being high. The power dissipation is related to the accelerating field through the shunt impedance $R_{sh}$ of the accelerating structure

$$P_{diss} = E_{acc}^2 / R_{sh} \quad (W/m)$$

Where $P_{diss}$ is the power dissipated in the structure / unit length, $E_{acc}$, the effective accelerating field (V/m) and $R_{sh}$, the shunt impedance per unit length (\(\Omega/m\)). If a particle beam is also present with a beam current $I_b$ and phase $\alpha$ relative to accelerating field the power dissipation becomes

$$P_{Tot} = E_{acc}^2 / R_{sh} + E_{acc} I_b \cos \alpha \quad (W/m)$$

The shunt impedance $R_{sh}$ is thus a principal Figure of Merit of an accelerating system and depends upon the geometry of the system and inversely proportional to surface resistance, $R_s$ of the interior walls and given by

$$R_s = (\pi \mu_0 f \rho)^{1/2}$$

Where $\rho$ is bulk resistivity and $f$ the operating frequency. The surface resistance, $R_s$ however happens to be high for copper viz; $8 \times 10^{-3} \Omega$ at 1 GHz, $1.4 \times 10^{-2} \Omega$ at 2.8 GHz and $2.4 \times 10^{-2} \Omega$ at 8.4 GHz. To have an idea of dissipation consider a typical SLAC copper structure with a value of $R_{sh} = 55 M \Omega/m$. To sustain a field of 10 MV/m in this structure would require a power input of 1.8 MW/m and a total of 5500 MW for the total length of over 3 Km. This is a prohibitively large power dissipation ruling out continuous operation of the accelerator. Situation is however significantly improved if a
superconducting structure is used. For example, in niobium a surface resistance of $10^{-9} \, \Omega$ is easily achieved. With Nb-structure the power consumption of SLAC is only 5.5 KW.

2. Superconducting RF Cavities and Surface Resistance

Superconducting cavities are superior to normal conducting cavities in so far as they permit continuous operation of the accelerators, improve energy conversion to beam, relax constraints on cavity design and minimize cavity impedance as seen by the beam. Different priorities are given to these advantages according to the accelerator characteristics such as duty cycle, intensity and beam dynamics properties. All the advantages of a superconducting material stems from a single property – Low Surface Resistance. The surface resistance $R_s$ is related to the power dissipation through the relation

$$P_{\text{diss}} = \frac{1}{2} \left( \frac{H^2}{R_s} \right)$$

Where $H$ is the tangential surface RF magnetic field and $R_s$ is the surface resistance ($\Omega / \text{cm}^2$). In addition, the accelerating field in the structure is limited by the break down field $H_{\text{ac}}$. Thus for a superconducting structure the material should have low surface resistance as well as high critical magnetic field.

The expression for surface resistance of a superconductor has been given by Mattis and Bardeen\(^{(1)}\) which reads as:

$$R_s = \frac{A}{T} \sigma_n \omega^2 \lambda^3 e^{-B_T/T} + R_{\text{res}}$$

![Fig.1 Surface resistance of a superconductor plotted against $T_c/T$. Experiments show a temperature independent residual resistance at the lowest temperature and does not follow the BCS straight line.](image)

Here $A$ and $B$ are constants weakly dependent on material, $\omega$ the RF frequency, $\sigma$ the normal state conductivity, $\lambda$ effective London penetration depth and $T_c$ the transition temperature. The first term in the expression is the BCS term ($R_{\text{BCS}}$) and at finite non
zero temperature is caused by the normal electron component of the superconductor. The ac magnetic field inside the cavity produces ac electric field and causes normal electrons to dissipate energy. The BCS component strongly depends on Tc and λ. It is therefore important to have high Tc and low λ. The two parameters are however contrary to one another. High Tc favours type II superconductors whereas low λ favours type I superconductors. In fact, there is no ideal superconductor available for RF cavity application. One has to make a compromise. R_{BCS} also depends upon the frequency and the normal state conductivity or the purity of the material. The purity of the material or the mean free path enters the coherence length and the penetration depth and affects the R_{BCS} in the following way:

\[
1 / \xi = 1 / \xi_0 + 1 / \ell \quad \text{and} \quad \lambda = \lambda_L \sqrt{\xi_0 / \xi}
\]

Here ξ₀ is the coherence length in pure material and ξ the coherence length in the real material. In the dirty limit (\ell \ll ξ₀) R_{BCS} is proportional to \ell^{1/2}, R_{BCS} decreases with purity. On the other hand in the clean limit R_{BCS} is proportional to \ell and the R_{BCS} surprisingly increases with the increase of purity. Consequently there is a minimum at ξ = \ell, that is, Rs is minimum when the mean free path is comparable to the coherence length. Fig.2 shows R_{BCS} plotted against the mean free path for Nb at 4.2 K and at a frequency of 1.5 GHz. The second term, R_{res}, of the BCS surface resistance expression is the so-called residual resistivity and is temperature independent. Even though the exact origin of this term (R_{res}) is not understood yet it is believed to be arising out of non ideal surface quality like surface serrations, metallic inclusions within λ and grain boundaries which are intrinsic in nature and also by flux trapping during cool down process which is extrinsic in nature and can be avoided. An analysis of the available data shows that R_{res} is at least proportional to the square root of ρₙ, the normal state resistivity. To conclude
therefore a superconductor for RF cavity application should have high Tc, high Hc and low \( \rho_n \).

3. The Ubiquitous Niobium Cavities

Niobium has been widely accepted as the material for use in RF cavities. Niobium is a borderline type II superconductor with Tc of 9.2 K, highest among the elemental superconductors, and a thermodynamic critical field of 190 mT. This makes it feasible to attain an accelerating field of 45 MV / m. Niobium is available in high purity and is ductile enough to be formed in required geometry and shape. Two options are available. The cavity is either made of copper and the inner surface is coated with niobium or the cavity is made from solid niobium using e-beam welding. Nb-coated copper cavities have been used with great success in the Large Electron Positron ring (LEP) at CERN (3). In the TESLA(4,5) linear collider where a gradient of 25 MV / m is needed only cavities made of solid Nb have been used. Very significant advancement was made at Jefferson Laboratory in Virgina, where for the Continuous Electron Beam Accelerator Facility CEBAF (6) an accelerating gradient of 8.4 MV / m was obtained in a structure consisting of 340 five-cell niobium cavities. In some specially prepared cavities a gradient of 15 – 20 MV / m was reached. Low thermodynamical critical field thus does not seem to be an hindrance. These cavities were designed by Cornell Uni. and produced by the industry. A high thermal conductivity too is required to take away the heat generated on the cavity surface to the liquid helium bath through the cavity walls. For this reason, high purity material should be used.

As for the operation of the cavity one has to look at the BCS surface resistance. For Nb the surface resistance say for 1.3 GHz is about 800 n\( \Omega \) at 4.2 K and drops to 15 n\( \Omega \) at 2 K. It is essential to operate Nb-cavities at below 2 K to obtain high accelerating gradient combined with high ‘Q’ factor. Liquid helium below 2 K is a superfluid with extremely high thermal conductivity and is thus an excellent coolant. Nb-cavity are accordingly operated at between 1.5 and 1.8 K.

The second component of the surface resistance, the temperature independent residual resistance is minimized by producing clean surface, avoiding frozen-in-flux and by removing metallurgical defects. Yet one more criteria to have low surface resistance is, as discussed in section on surface resistance, is that the BCS surface resistance is minimum where the mean free path is comparable to the coherence length \( (\xi) \). One has therefore to go to optimum purity and not to very high purity. Nb with an RRR of 300 is normally used for cavity fabrication.

Notwithstanding its wide use, Nb suffers from the high reactivity with oxygen. Since these cavities are operated at below 2 K the refrigeration efficiency of Nb structure is also poor. There is obviously need to explore new materials with high Tc and high critical magnetic field. High Tc cuprates with Tc well above 77 K were thought to be the best candidates for the cavities but proved to be disastrous because of the poor intergrain connectivity. The normal state resistivity is in the m.\( \Omega \).cm region. Further, these materials show large anisotropy in critical current and critical magnetic field. Cuprate
superconductors also are very sensitive to oxygen stoichiometry which alters the structure if a temperature excursion takes place during the operation.

4. High Tc Conventional Superconductors

Table 1 gives the list of all classes of superconductors known to-date. For one reason or the other we have just a handful of systems and the superconductors which can be considered for RF cavity application. A comprehensive discussion about the merits of various class of superconductors for cavity application has been given by Palmieri (2), the summary of which will be in place here. Alloy superconductors (such as Nb-Ti) may have higher Tc but are dirty superconductors. These superconductors have small mean free path ℓ and have thus large BCS surface resistance and large dissipation. They are also characterized by poor thermal conductivity and lead to thermal instability and quench. Alloy Superconductors are thus not suitable for cavity application.

Table 1: Various Classes of Superconductors

<table>
<thead>
<tr>
<th>Superconductor</th>
<th>Tc (K)</th>
<th>Structure / Type/ Nick Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>9.3</td>
<td>Elemental Superconductor</td>
</tr>
<tr>
<td>Nb₃Ge</td>
<td>23</td>
<td>Intermetallic A-15</td>
</tr>
<tr>
<td>Nb-Ti</td>
<td>10</td>
<td>Alloy</td>
</tr>
<tr>
<td>MgB₂</td>
<td>39</td>
<td>Alloy</td>
</tr>
<tr>
<td>NbN</td>
<td>17.2</td>
<td>B-1 (NaCl)</td>
</tr>
<tr>
<td>Ba₁₋ₓKₓBiO₃</td>
<td>30</td>
<td>Perovskites</td>
</tr>
<tr>
<td>SnₓMo₆S₈</td>
<td>14</td>
<td>C-15, Cheveral Phase</td>
</tr>
<tr>
<td>CeCu₂Si₂</td>
<td>0.6</td>
<td>Heavy Fermions</td>
</tr>
<tr>
<td>ErRh₄B₄</td>
<td>8.7</td>
<td>Magnetic Superconductors</td>
</tr>
<tr>
<td>LuNi₂B₂C</td>
<td>16</td>
<td>Borocarbides</td>
</tr>
<tr>
<td>PdH(Cu,Ag,Au)</td>
<td>17</td>
<td>Palladium Hydride</td>
</tr>
<tr>
<td>BEDT - TTF</td>
<td>14</td>
<td>Organic Superconductors</td>
</tr>
<tr>
<td>La₂₋ₓSrₓCuO₄</td>
<td>35</td>
<td>Oxide</td>
</tr>
<tr>
<td>Y₁Ba₂Cu₃O₇</td>
<td>95</td>
<td>YBCO, High Tc Superconductors</td>
</tr>
<tr>
<td>Bi₂Sr₂Ca₂Cu₃O₁₀</td>
<td>110</td>
<td>BISCO, High Tc Superconductors</td>
</tr>
<tr>
<td>Tl₂Ba₂Ca₂Cu₃O₁₀</td>
<td>125</td>
<td>Thalium Compounds</td>
</tr>
<tr>
<td>Hg₁Ba₂Ca₂Cu₃O₁₀</td>
<td>133</td>
<td>Mercury Compounds</td>
</tr>
<tr>
<td>CsₓC₆₀</td>
<td>43</td>
<td>Fullereness</td>
</tr>
</tbody>
</table>
Even though we have over a thousand known conventional superconductors only a limited number of compounds mostly belonging to either B1 structure (NaCl) or A-15 intermetallic compounds (β-W structure) have Tc in the range of 15 to 23 K and can be considered to be the candidates for RF cavity applications. Among the B1 compounds NbN (Tc = 17.3 K), NbC (Tc = 12 K), NbCN (Tc = 17.8 K) and NbTlN (17.5 K) have Tc higher than that of Nb. Limited work has been carried out on these materials at CERN and Saclay but the results have not been encouraging particularly because the accelerating field could not be increased beyond 10 MV / m. So the choice seems to be restricted to A-15 family of compounds.

5. A-15 Superconductors – Possible Alternative to Niobium

As stated earlier, A-15 superconductors continue to be used for the production of intense magnetic field in the research laboratory as also in many other applications in the industry, notwithstanding the emergence of a variety of known superconductors listed in table 1. This stems from their ruggedness once they are formed, Tc above 15K and high critical fields. The first A-15 superconductor, V₃Si (Tc = 17.1 K) was discovered by Hardy and Hulm [8]. Nb₃Sn with Tc = 18.1 K was discovered next by Matthias [9]. Tc was raised to 20 K in a pseudo binary Nb₃Al₀.₅Ge₀.₂, again discovered by Matthias in 1967. Well over 50 A-15 superconductors were found by various groups since then, till Gavaler [10] and Testardi [11] obtained a record Tc of 23 K in sputtered films of Nb₃Ge.

A-15 compounds have a formula A₃B and a structure of Cr₃Si or β-W type. The structureberitch class name is A-15. As shown in fig.3, A atoms form orthogonal chains bisecting the faces of the bcc unit cell. B atoms occupy corners and centre of the bcc structure. The Tc of most A-15 superconductors is extremely sensitive to the degree of long range order and the integrity of the chain. The spacing of A-atoms is smaller in

![A-15 crystal structure](image-url)
chains than in pure A-crystal. The ratio of atomic radii \( r_A / r_B = 0.84–1.12 \). This can lead to site interchange and thus to disorder. A long list of A-15 compounds is given in table 2 of reference 2. As seen from the table important A-15 compounds have A-atom either Nb, V or Mo. Other compounds have A-atom either Ti, Zr, Ta, or Cr but have low Tc and are not of technological interest. B atom in Nb and V based superconductors can be drawn from noble metal group, for example, Au or d-shell element between group 3 and 5. A-15 superconductors which are of technological importance are listed in table 2.

### Table 2. Important High Field A-15 Superconductors with Technological Potential

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure Classification</th>
<th>Tc (K)</th>
<th>( H_{c2} ) (T)</th>
<th>( J_c ) (A.cm(^{-2})) 4.2 K, (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_3Ga )</td>
<td>A-15</td>
<td>15.5</td>
<td>22</td>
<td>2 x 10(^6) (10 T)</td>
</tr>
<tr>
<td>( V_3Si )</td>
<td>A-15</td>
<td>17.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Nb_3Sn )</td>
<td>A-15</td>
<td>18.3</td>
<td>22</td>
<td>3 x 10(^5) (10 T)</td>
</tr>
<tr>
<td>( Nb_3(Al,B,Be) )</td>
<td>A-15</td>
<td>20.0</td>
<td></td>
<td>3 x 10(^4) (8 T)</td>
</tr>
<tr>
<td>( Nb_3Al )</td>
<td>A-15</td>
<td>18.9</td>
<td>32</td>
<td>10(^5) (22 T)</td>
</tr>
<tr>
<td>( Nb_3Ga )</td>
<td>A-15</td>
<td>20.3</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>( Nb_3(Al,Ge) )</td>
<td>A-15</td>
<td>20.5</td>
<td>41</td>
<td>1 x 10(^4) (12 T)</td>
</tr>
<tr>
<td>( Nb_3Ge )</td>
<td>A-15</td>
<td>23.2</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>( Mo_3Re )</td>
<td>A-15, bcc</td>
<td>15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All A-15 superconductors belong to type II category and are characterized by high upper critical field \( (H_{c2}) \). However flux penetration starts at \( H_{c1} \), the lower critical field which is smaller than the thermodynamical field \( H_c \). Fortunately the nucleation time of a vortex is larger than the RF period, the relevant critical field of an RF superconductor is not the usual \( H_{c1} \) or \( H_c \) but \( H_{sh} \) – the Superheating Field. Large RF magnetic fields are present in a cavity, the critical field of the cavity superconductor should therefore be large. \( H_{sh} \) approaches \( H_c \) in type II superconductors. Rough surfaces and voids provide nucleation sites to fluxoids and flux enters at field levels well below \( H_c \) or even below \( H_{c1} \). The cavity surface should therefore be very smooth and free from defects. In addition, a high degree of compositional homogeneity too is required to prevent weak spots with locally depressed energy gap and hence low \( H_c \). The requirement of high thermal conductivity becomes less stringent as the superconductor is deposited in the form of thin film.

A-15 superconductors are intermetallic compounds and are extremely brittle. These materials have been produced in the form of fine multi-filaments in copper matrix during 1970s and 80s to meet the requirements of high field magnets particularly for high energy physics. To overcome the problem of brittleness a variety of indirect techniques were
developed. For the same reason, bulk A-15 cavities are just not feasible. The only approach has to be based upon the film coating on a conducting cavity or converting the surface of the Nb or V cavities into A-15 layers. A variety of techniques to produce A-15 materials have been discussed by Sharma(12,13). Some of these techniques can as well be adapted to produce A-15 cavities. There is, however, one major difference between the approaches to multifilamentary wires and the cavities. For wires, controlled impurities or imperfections are introduced in the A-15 layer to create flux pinning sites to enhance the critical current density (Jc). On the other hand, cavity layer has to have a perfect stoichiometry (high Tc) and a perfect structure. Surface imperfections and impurities cause dissipation in the cavity surface layer and has to be prevented. For example, small grains are preferred in wires for high Jc as the grain boundaries in A-15 materials are the best flux pinning sites. For cavities one requires larger grains as the grain boundaries are weak spots which bring down the break down magnetic field. The techniques which have been employed successfully for the production of wires and tapes for magnet construction can be classified in the following way:

I. Diffusion reaction

(i) Surface Diffusion process
(ii) Composite (Bronze) Process
(iii) In situ Process
(iv) Infiltration Technique

Nb₃Sn, V₃Ga Tapes
Nb₃Sn, V₃Ga, Nb₃Al
Nb₃Sn, V₃Ga
Nb₃Sn, Nb₃(Al,Ge,Si)

II. Phase Change or Crystalization

(i) Rapid Quenching
(ii) Laser Quenching
(iii) Electron Beam Quenching

Nb₃Al(Ge), Nb₃Al
Nb₃Ga, Nb₃Al
Nb₃Ga

III. Deposition

(i) Chemical Vapour Deposition
(ii) Vacuum Evaporation / Sputtering

Nb₃Ge, Nb₃Sn
V₃Si, Nb₃Ge

IV. Co-Extrusion

Not feasible for A-15 Materials

V. Powder metallurgy

(i) Cold Process
(ii) Hot Process
(iii) Infiltration

Nb₃Sn
Nb₃Sn
Nb₃Sn, Nb₃(Al,Ge,Si)

In the following sections we will discuss techniques that are relevant to cavity coatings.
6. The Chemical Vapour Deposition Technique

Since RF is confined within a shallow depth of \( \leq 1 \mu m \), a thin film route is to be preferred to deposit A-15 layer on the cavity surface.

The chemical vapour deposition (CVD) technique is comparatively a simpler and cheaper technique and provides faster deposition rate compared to sputtering and vapour deposition techniques. CVD method seems to be ideal to coat cavities of complicated geometries with uniform stoichiometry. Here the two constituent chlorides, formed in situ, are reacted together in a reactor and are hydrogen reduced to A-15 compound on a heated substrate. He / Ar is used as a diluent gas. The parameters which influence the quality and the growth rate of the film are:

- Gas flow rates of \( H_2 \), He / Ar and \( Cl_2 \) and mixing ratio of \( H_2 / NbCl_5 + GeCl_4 \), tape moving speed, substrate material and temperature, reaction furnace temperature and the gas flow pattern around the tape.

For cavities one has to ensure the uniformity of the temperature along the entire length to have the homogeneity and the uniformity of the coating. Negative points are the formation of corrosive and toxic by-products like HCl and \( H_2 \) which have to removed thoroughly and should not be incorporated within the A-15 layer.

6.1 \( Nb_3Sn \) (CVD)

\( Nb_3Sn \) is the best known high field material among the family of A-15 superconductor with a \( Tc \) of 18.3 K and is used for the production of intense magnetic field reaching a record value of 21T \(^{(14)}\). Prior to the development of multifilamentary wires \( Nb_3Sn \) flexible tapes were produced by RCA \(^{(15)}\) of USA by the chemical vapour deposition (CVD) technique. In this technique, \( Nb_3Sn \) is deposited either on a Nb or a hastelloy tape by hydrogen reduction of tin and niobium chlorides. Chlorides are formed in situ by the chlorination of Nb and Sn metals at 900\(^0\)C inside a reactor. These chlorides are fed along with hydrogen in to the reactor where the moving tape is electrically heated to 1100\(^0\)C. He or Ar is used as a diluent gas. \( Nb_3Sn \) is formed inside the reactor as per the reaction

\[
3 NbCl_4 + SnCl_2 + 7H_2 \leftrightarrow Nb_3Sn + 14HCl
\]

The growth furnace is maintained at 700\(^0\)C to prevent deposition of \( Nb_3Sn \) on the walls of the reactor. In the RCA process, the typical reaction parameters are: ratio of Nb and Sn chlorides, 3:1; ribbon speed 15 m / hr, chlorine flow rate to Nb and Sn metal sources, 140 ml / min. High \( Jc \) values of the order of \( 10^4 \) A.cm\(^{-2} \) (4.2 K,18T) were obtained by Enstrom and Appert \(^{(16)}\) (Fig. 4) by alloying Nb with 1.3 % Si and doping with 0.1 % CO\(_2\). Alloing with Si raises the \( H_{c2} \) value from 18.5 T to 22.5 T. Our requirement for cavity is, however, for a pure \( Nb_3Sn \). No additions or dopings are to be used. Microstructure has to be tailored to obtain large grains using post reaction annealing.
Fig. 4 High values of $J_c$ and $H_{c2}$ obtained for CVD-Nb$_3$Sn tapes through alloying (1.3 % Si) and doping with CO$_2$ (0.1 %). Alloying or doping may not help cavities as it will raise normal state resistivity $\rho_n$ (Ref. 16).

6.2 Nb$_3$Ge (CVD)

Since stoichiometric Nb$_3$Ge is metastable in nature, CVD or the sputtering techniques are the only choice for making long tapes of Nb$_3$Ge. The CVD technique for Nb$_3$Ge is almost identical to that followed for Nb$_3$Sn except that now we use a vapour mixture of NbCl$_5$ and GeCl$_4$. Nb$_3$Ge is deposited on a metal surface by the hydrogen reduction of these two chlorides. He / Ar are used as the diluents to reactive gases. The technique has been employed to produce long lengths of Nb$_3$Ge tapes (17,18). Paidassi et al. (19) deposited Nb$_3$Ge on tapes kept at 840$^0$C to 960$^0$C. The tape had $T_c$ (onset) of 23.6 K with a transition width of 4-5 K and a high $J_c$ of $10^5$ A.cm$^{-2}$ (19 T, 4.2 K). Maley et al. (20) reported a maximum $T_c$ of 19.21 K, a $J_c = 8 \times 10^4$ A.cm$^{-2}$ and an $H_{c2}$ value of 31.7 T for a 910$^0$C reacted Cu-Ta substrate tape up to a length of 20 m. It is further reported that a temperature of 800$^0$C to 850$^0$C produces fine grains and a large pinning force (high $J_c$) with somewhat lower $T_c$ and $H_{c2}$. Temperatures higher than 900$^0$C, on the other hand, produce coarse grains and low pinning. For cavity we thus have to carry out the reaction at temperatures higher than 900$^0$C. Fig 5 shows typical $J_c - H$ behaviour of a CVD Nb$_3$Ge tape. Process parameters are to be optimized through trial and error so as to obtain material with perfect stoichiometry over the entire area and with large size grains.
Fig. 5 High values of $J_c$ and $H_{c2}$ are obtained in Nb$_3$Ge film coated by CVD technique on a Cu-Ta tape. A reaction temperature of higher than 900°C is required to get large grain Nb$_3$Ge coating (Ref. 20).

Fig. 6 A schematic diagram of the reactor used by Asano et al. for synthesizing Nb$_3$Ge tapes by CVD technique (Ref. 21).

Asano et al. (21) carried out detailed studies on the various deposition parameters such as the chloride gas ratios ($\text{NbCl}_5 / \text{GeCl}_4$), reaction furnace and substrate temperatures, gas flow pattern around substrate, tape speed and substrate material. Nb$_3$Ge films deposited on Hastealloy-X tapes (0.1 x 3 mm) in a reactor furnace maintained at 575-600°C and at the Nb/Ge ratio of 2.5 - 3 had an onset $T_c$ of 20 K. The substrate temperature was kept at
$870^0\text{C}$ and a dilution ratio of He / $\text{Cl}_2$ for Nb and Ge chlorination and also of $\text{H}_2 / \text{NbCl}_5 + \text{GeCl}_4$ for reduction was kept at 15. Most of the films prepared were composed of A-15 Nb$_3$Ge with a small amount of Nb$_5$Ge$_3$ phase. The technique thus appears to be viable for cavity development but the parameters have to be optimized to rid the material of any spurious phase like Nb$_5$Ge$_3$.

7. Physical Vapour Deposition (Sputtering)

It has been emphasized earlier that the thin film route is the best available option for coating A-15 materials, characterized by high melting points and a narrow range of composition. Sputtering technique has many advantages over other thin film techniques and is the most promising one for this class of materials. Sputtering is a simple and rapid way to synthesize new materials and high melting point poses no problem except in the preparation of target material. Layer by layer growth process leads to surface diffusion which controls growth of hot sputtered film. The new phases and particularly the metastable phases are obtained more readily than in the bulk form. The inhomogeneities in the target are not of consequence. Sputtered films generally do not show critical dependence upon exact composition in a compound. Moreover, sputtering is a well-established technique with the accelerator community having mastered it for the deposition of Nb. Besides LNL is a well known laboratory for its pioneering work on sputtering technique.

Co sputtering is one option to deposit films of a binary system. Here typically two constituents are sputtered simultaneously on to a substrate maintained at a controlled temperature. Stoichiometry depends upon the relative positions of the targets and the substrate which can be manipulated to yield films of desired composition. The stoichiometry over a large areas like the accelerating systems is, however, difficult to control. The better option therefore is to sputter single target of the desired stoichiometry. As for the target preparation, powder metallurgy (to be discussed in this article) is a standard procedure. Target is prepared by compacting the mixture of the constituent powders followed by sintering or melting. Thus one has to master both sintering and sputtering techniques. Sputtering offers the advantage that stoichiometry, substrate temperature, deposition rate and thickness can be varied independently.

7.1 Mo-Re (Sputtering)

Outside the regime of V and Nb based A-15 superconductors is the Mo$_3$Re system which is quite promising. It is a solid solution and thus free from bulk and surface inhomogeneities. In contrast to Nb, the solubility of interstitial elements particularly oxygen is low in this system. It is a strong coupling superconductor with low $\kappa$, high $H_{c1} (= 500 \text{ G})$. It has low value of penetration depth $\lambda$. Bulk material is in $\sigma$ phase which is tetragonal and has low $T_c = 6 \text{ K}$ but A-15 phase with high value of $T_c$ have been reported by Gavaler et al.\(^{(22)}\) and Testardi et al.\(^{(23)}\). Gavaler et al.\(^{(22)}\), report A-15 phase in the sputtered film of Mo$_{70}$Re$_{30}$ composition with a lattice parameter ‘a’ = 4.980 ±0.001 Å and the presence of bcc phase with the lattice parameter ‘a’ = 3.13 ± 0.005 Å. A $T_c$ of 13 K is
reported. Testardi et al.\textsuperscript{(23)} report a value of $T_c = 15$ K for a film deposited at 1250$^\circ$C. The structure is found to be cubic with a lattice parameter $a = 4.94$ Å.

At LNL, we carried out detailed studies\textsuperscript{(24,25)} on three compositions of Mo-Re system, namely, Mo$_{75}$Re$_{25}$, Mo$_{60}$Re$_{40}$ and Mo$_{38}$Re$_{62}$ using single target DC magnetron sputtering technique. We used sapphire, quartz, Cu and Nb substrates. The substrate temperature was varied between 600$^\circ$C and 1000$^\circ$C. Post deposition annealing too was carried out which enhanced the crystalinity and the sharpness of the transition. We obtained the highest $T_c = 12.1$ K in Mo$_{60}$Re$_{40}$ composition. The substrate temperature was kept 800$^\circ$C and post annealing was done at 800-856$^\circ$C for one hour. We always observed the phase to be bcc. The lattice parameter of most of the samples varied from 3.1167 to 3.1192 Å. The best values of $T_c$ obtained for the three compositions with process parameters are given in Table 3.

Table 3. The highest $T_c$ values obtained for film specimens of the three compositions deposited on sapphire substrate. Films prepared by single target DC magnetron sputtering technique at LNL.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$ (K)</th>
<th>$\Delta T_c$ (K)</th>
<th>RRR</th>
<th>$T_{Substrate}$ ($^\circ$C)</th>
<th>Annealing T ($^\circ$C)</th>
<th>Annealing t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$<em>{75}$Re$</em>{25}$</td>
<td>11.82</td>
<td>0.012</td>
<td>1.71</td>
<td>751</td>
<td>751-793</td>
<td>30</td>
</tr>
<tr>
<td>Mo$<em>{60}$Re$</em>{40}$</td>
<td>12.13</td>
<td>0.065</td>
<td>1.3</td>
<td>800</td>
<td>800-856</td>
<td>60</td>
</tr>
<tr>
<td>Mo$<em>{38}$Re$</em>{62}$</td>
<td>9.47</td>
<td>0.029</td>
<td>1.11</td>
<td>750</td>
<td>750-785</td>
<td>60</td>
</tr>
</tbody>
</table>

We were not able to go to substrate temperatures beyond 1000$^\circ$C and thus not in a position to confirm the results of Testardi et al.\textsuperscript{(23)} if a $T_c = 15$ K and the A-15 phase is reproducible in this system. This requirement of high substrate temperature and to be maintained uniform over large areas of the cavity structure could pose formidable problem.

**Fig.7** Typical superconducting transition curve for a Mo$_{75}$Re$_{25}$ composition. Substrate temperature 633$^\circ$C, post anneal 633$^\circ$C x 15 min, $T_c = 11.4$ K $\Delta T = 0.009$ K and RRR = 1.57 (Ref. 25)
7.2 \( V_3Si \) (Sputtering / Thermal Diffusion)

Yet another potential candidate deserving attention is \( V_3Si \), the first of the A-15 superconductors discovered with high \( T_c = 17 \) K at the perfect stoichiometry. It also happens to be a highly ordered compound with a high \( RRR \) value of 80. The work on this material has been pursued by Palmieri at LNL some years ago and a fresh push is being given now. Three different routes have been followed. The first was the cosputtering method \(^{26} \) (facing target magnetron). \( V \) and \( Si \) targets were sputtered simultaneously on a variety of substrates kept at temperatures above 500\(^\circ\)C. The \( Si \)-contents in the films were found to vary from 21 to 32 at % depending upon the targets sputtering voltages. The best sample had a \( T_c = 14.4 \) K and a \( RRR = 4.5 \). The optimum temperature for \( V_3Si \) formation is around 800\(^\circ\)C. This temperature is too high for substrates like Cu and quartz. Nb substrate could be one option but large solubility of \( V \) in to Nb is a problem. Any idea of a buffer layer between Nb and \( V \) will make the process too complicated for cavity development.

The second method followed was the reactive sputtering \(^{27} \) in a DC magnetron configuration. The target was a 50 mm x 2 mm disc of 99.7 % V and the substrate a 10 mm x 10 mm and 0.5 mm thick sapphire. The maximum sputtering temperature was limited to 500\(^\circ\)C to avoid copper contamination from the substrate holder. Two most crucial parameters to be optimized to obtain stoichiometric \( V_3Si \) are the silane pressure and the rate of deposition. A post deposition annealing at 800\(^\circ\)C x 3-4 hrs. was followed which yielded a \( T_c \) of 16.2 K and a \( RRR \) of 16.7. Typical sputtering parameters are given in Table 4.

**Table 4.** Typical sputtering parameters of the \( V_3Si \) films grown by the reactive sputtering technique at LNL. Best \( T_c = 16.2 \) K and \( RRR = 16.7 \) (Ref.27)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering Temperature</td>
<td>500 (^{\circ})C</td>
</tr>
<tr>
<td>Argon</td>
<td>( 9 \times 10^{-3} ) m bar</td>
</tr>
<tr>
<td>Silane</td>
<td>( 1.5 \times 10^{-3} ) m bar</td>
</tr>
<tr>
<td>Current</td>
<td>0.39 A</td>
</tr>
<tr>
<td>Voltage</td>
<td>480 Volts</td>
</tr>
<tr>
<td>Deposition Rate</td>
<td>0.6 nm / sec</td>
</tr>
<tr>
<td>Annealing Temperature</td>
<td>800 (^{\circ})C</td>
</tr>
<tr>
<td>Annealing Time</td>
<td>3 Hours</td>
</tr>
</tbody>
</table>

Yet another technique developed at LNL was the thermal diffusion technique \(^{28} \). \( V_3Si \) films were deposited on sapphire, Cu, Nb and \( V \) substrates. In the first series of experiments \( V \) was sputtered on sapphire substrates and then the samples were annealed in silane atmosphere at 800-900\(^\circ\)C for about 10 hours. The best \( V_3Si \) sample had a \( T_c = 16.8 \) K and a \( RRR = 9 \). Experiments on Nb and Cu substrates failed primarily due to the high temperature of annealing which lead to inter diffusion of \( V \) with the substrate material.
Diffusion of Si in bulk V using this thermal diffusion technique turned out to be successful. Choosing bulk V as the substrate one does away with the need of V-sputtering. Here the diffusion times are larger because the dominant diffusion in bulk material is via the lattice. In thin film, on the other hand, the diffusion is primarily through grain boundaries and surface which is faster. The actual diffusion of Si, using silane, may be complicated but surely higher process temperature and longer durations are required for diffusion in bulk V. These samples were annealed at 850°C in silane atmosphere for 20 hours followed by vacuum annealing at the same temperature for 40 hours. Tc turned out to be 16.0 K and 0.4 K wide. Process parameters can still be improved for better quality films.

Having seen the merits and demerits of the techniques discussed above, it has been felt that the reactive thermal diffusion is the most promising technique for developing V₃Si cavities. Work has already started (29) at LNL in right earnest. The system used for silanization of V-samples is shown in fig.8 and the heating arrangement for the samples and the 6 GHz V-cavities is shown in fig.9. We start with a base pressure of 10⁻⁸ mbar. Silanization is carried out at a temperature of 800-850°C with a silane pressure of 10⁻³ to 10⁻⁴ mbar for a period of 10 hours. Dilution of silane (SiH₄) is carried out by argon. The samples are vacuum annealed at the same temperature for a period of 20 hours to get rid of hydrogen and the composition reaching close to stoichiometry. Optimization of process parameters is very crucial to get quality films. Diffusion temperature and the rate of growth are two most important parameters.

Fig. 8. The versatile system used for cosputtering, reactive sputtering and reactive thermal diffusion used at LNL.
Quite a few samples were recently prepared which show encouraging results. Fig. 10 is a typical transition curve for a V₃Si-sample silanized at 850°C for 10 hours followed by an annealing for 20 hours. A $T_c = 15.4$ K is achieved. A V-cavity has recently been silanized at a temperature of 850°C for 4 hours and further annealed for 6 hours. The silane pressure was kept $5 \times 10^{-3}$ mbar. RF measurements are planned for evaluating ‘Q’ and the surface resistance.

It is to be remembered that the quality of the film not only depends upon the silanization parameters but also on the quality of the V-surface. A recipe consisting of buffer chemical polishing, annealing and electro polishing has been standardized through the ‘Q’ value determination at the different stages of surface preparation.
8. Liquid Surface Diffusion Technique

The technique has been successfully used to produce commercial Nb$_3$Sn and V$_3$Ga tapes for magnet applications. In fact, the first 18 T superconducting magnet built at NIRM, Tsukuba, Japan in 1976 used the V$_3$Ga tape produced by Tachikawa and Tanaka (30) using this method. This technique involves dipping of Nb or V ribbons in liquid Sn or Ga respectively and carry out the reaction at temperature determined by the respective phase diagrams of Nb$_3$Sn or V$_3$Ga.

8.1 Nb$_3$Sn (Liquid Surface Diffusion)

This technique was developed by GEC in USA for the commercial production of the copper clad Nb$_3$Sn tapes for magnet winding around the same time as RCA produced such tapes by CVD method. In this process a Nb-tape typically 12 x 0.2 mm is coated with a layer of Sn, usually by a dipping process and heat treated around 950°C. This reaction temperature is important because, as seen from the Nb-Sn phase diagram in Fig.11, low Tc Sn-rich phases like Nb$_6$Sn$_5$ (Tc = 2.6 K) and NbSn$_2$ (Tc = 2.1 K) are formed below 930°C. To obtain a phase pure Nb$_3$Sn it is therefore essential to carry out the reaction above 930°C. During the heat treatment Sn reacts with Nb and forms Nb$_3$Sn on either side of the tape leaving a thin Nb core unreacted at the centre, which provides strength to the tape. A thin layer of Sn is also left over the Nb$_3$Sn layers. For magnet application this Sn-layer facilitates soldering of copper strips on both sides for thermal stabilization. To enhance the Jc impurity additions have been made to Nb-tape as well as to Sn-bath. Benz (31) reported a high Jc = 2 x 10$^6$ A.cm$^{-2}$ (4.2 K, 10 T) for ZrO$_2$ doped Nb$_3$Sn. Small addition of copper (1 at %) to Sn-bath has also been found by Sharma and Alekseevskii (32) to increase Jc of the Nb$_3$Sn layer significantly.

![Fig. 11 The phase diagram of Nb-Sn system. Nb$_3$Sn has a wide range of composition 18-28 at %. Nb$_3$Sn is the only stable phase above 930°C](image-url)
The above process appears to be ideal for converting the surface of Nb-cavities to Nb$_3$Sn except that the Sn left unreacted on the cavity surface has to be removed. There are two possible ways to get rid of this Sn layer. One could be the removal of Sn by chemical method. The other could be to subject the cavity to prolonged heat treatment in the absence of Sn-bath so that Sn on the surface diffuses inside, leaving no free Sn on the surface. Good attempt has been made at LNL (INFN) to coat 6 GHz Nb cavities by this technique. The schematic diagram of the reactor built by LNL is shown in fig.12. Procedure has been laid to obtain Nb$_3$Sn layer with high $T_c$ and the surface free of Sn traces by a so called three step ‘hybrid’ process. The details of this work have been reported by Deambrosis et al. (33) in this Workshop. The process roughly involves preheating the Nb sample to about 975°C under vacuum better than 10$^{-7}$ m bar and dipping the sample / cavity in Sn for about 30 minutes. The specimen is then lifted out of Sn-bath and the heated at the same temperature for about 15 hours to allow the Sn on the sample surface to diffuse inside. Fig.13 shows a transition at 17.7 K for a sample prepared by dipping at 1000°C x 2hrs. and annealing (in presence of Sn-bath) at 1000°C x 14 hrs.

![Fig.12 The schematic diagram of the reactor used for Nb$_3$Sn coating by liquid diffusion technique at LNL](image)
It appears that Sn traces are still left on the surface as seen by a transition in fig. 13 at 3.6 K, the Tc of pure Sn. A hybrid method was therefore devised. In this revised technique a short annealing (~2 hrs.) was carried out in presence of the Sn-bath for obtaining perfect stoichiometry, followed by a long anneal (~10 hrs.) in the absence of the Sn-bath to avoid the presence of Sn-vapours. Transition at 3.6 K was not observed any more. Fig.14 shows a typical grain structure of the Nb₃Sn layer as revealed by the SEM. The grains seem to be well oriented perpendicular to the surface. Fig. 15 is the XRD pattern of a Nb₃Sn layer prepared by this hybrid method. Note that it is a phase pure and well crystalline material. No peaks of other phases like pure Sn or the Sn-rich phases, Nb₆Sn₅ or NbSn₂ are observed. These studies confirm the efficacy of the technique for cavity application. ‘Q’ measurements on 6 GHz cavities coated by the technique are planned.
A systematic study\textsuperscript{(34)} was carried out at the Wuppertal Uni., Germany for fabricating single cell and multicell Nb\textsubscript{3}Sn cavities by Sn-vapour deposition technique. The inner surface of the Nb-cavity was exposed to Sn vapours (10\(^{-3}\) m bar) in a UHV furnace at temperatures between 1050\(^0\)C and 1250\(^0\)C and a few µm thick Nb\textsubscript{3}Sn layer deposited. The sample preparation is rather elaborate and needs nucleation centres before the Nb\textsubscript{3}Sn
layer can be formed. Sample surface is usually anodized with a layer of Nb$_2$O$_5$ and kept in a furnace where the SnCl$_2$ is heated to 500$^0$C. A Sn layer is formed over the Nb$_2$O$_5$ surface. The substrate (cavity) is now heated to 600$^0$C where the Nb$_2$O$_5$ layer disintegrates. The oxygen is absorbed by Nb and Sn gets deposited on Nb surface. Sn vapour deposition then starts. The coating technique was applied to 22 GHz cavities (35,36) as well as to 1 and 3 GHz cavities (37,38). Nucleation centres were not required for Nb cavities with fine grains. At 1 GHz, RF losses are reduced by a factor of 10 at low field level and a factor of 4 at high field level. Situation improves at higher frequencies reaching an improvement factor of 150 at 21.5 GHz. Accelerating fields of 10 MV / m have been achieved at 4.2 K. The reactor system developed and used at the Wuppertal University is shown in fig. 16.

8.2 V$_3$Ga (Liquid Surface Diffusion)

As mentioned earlier the method was proposed and employed successfully by Tachikawa and Tanaka (30) for producing V$_3$Ga tapes at NRIM. The process consists of two steps. In the first step, a V-tape, about 50 µm thick, is passed through a molten Ga-bath heated to 500 – 600$^0$C and then through a tube furnace maintained at 800$^0$C. After the first step, V$_3$Ga$_2$ and VGa$_2$ layers, about 10 µm are formed on both sides of the tape substrate. In the second step, the tape is electroplated with Cu (5 µm) and then heat treated at about 650$^0$C to form V$_3$Ga. Copper rapidly diffuses in to V$_3$Ga$_2$ and VGa$_2$ layers to form ternary Cu-V-Ga layers of low melting point (700 – 800$^0$C) and enhances the growth of V$_3$Ga with sufficient supply of Ga from the ternary alloy. The formation of V$_3$Ga is schematically shown in fig. 17. High values of Jc were obtained and the material used in the winding of high field superconducting magnets. The method is not straightforward like for Nb$_3$Sn in so far as V$_3$Ga is not formed in the first step itself and the substrate has to be coated with Cu before final heat treatment. Further the final product is left with a Cu-Ga layer. This outer layer is not at all desirable for cavity application. We have thus not considered this material for cavity development.

![Fig. 17 Formation of V$_3$Ga by Liquid Surface Diffusion Process developed by Tachikawa and Tanaka (Ref. 30)](image)
9  The Bronze Process

The breakthrough in the use of A-15 superconductors for magnetic field production came in 1970 when the bronze process was proposed for Nb$_3$Sn by Kaufman and Pickett\(^{(31)}\) and for V$_3$Ga by Tachikawa\(^{(40)}\). Both these superconductors are produced commercially by the industry in the form of multifilamentary wires following this process. Here, for Nb$_3$Sn conductors one prepares the bronze of Cu-Sn (8 at.%) and puts the required number of Nb rods in to the bronze billet. The composite billet is reduced to wire with a few intermediate annealings. These wires are bundled repeatedly and reduced until the wire of desired dimension and number of filaments is obtained. The wire can now be used for winding a magnet or any other device. The device is now subjected to heat treatment at 700-750\(^{0}\)C for prolong period lasting several days. During the heat treatment Sn from the bronze matrix diffuses in to the Nb-cores and forms Nb$_3$Sn. The process is similar for the production of V$_3$Ga multifilamentary wires except that the Nb rods are replaced by V rods and the Cu-Sn matrix by the Cu-Ga (19at %) matrix. Final wire is flexible enough to be used for device application. Here the heat treatment temperature is slightly lower than required for Nb$_3$Sn. An annealing temperature of 650-700\(^{0}\)C has been found to be optimum for this material.

9.1  Nb$_3$Sn (Bronze Process)

Fig.18 shows schematically the bronze route process for the production of Nb$_3$Sn multifilamentary wires. The most crucial parameter to be optimized is the temperature of heat treatment which can lead to perfect stoichiometry (3:1), required layer thickness and a fine grain structure. Grain boundaries being the main flux pinning sites in a-15
materials, heat treatment is tailored to produce a structure with small grains. A typical grain structure of the Nb$_3$Sn formed at the interface between the Nb-core and the matrix is something like shown in fig.19. The grains close to Nb-core are columnar because of Sn-deficiency, the central part has equiaxed grains and close to bronze matrix are coarse grain. For high Jc conductors it is the central equiaxed grains region which is most important.

A two step heat treatment 700$^\circ$C x 4days + 730$^\circ$C x 2days of Airco bronze processed 2869 filament conductor (41) has been found most suitable treatment which leads to enhanced Jc. The first heat treatment at 700$^\circ$C leads to fine grains and the second treatment at 730$^\circ$C, though coarsen the grains improves the compositional homogeneity which in turn raises H$_{c2}$. The combination leads to an overall increase in Jc from $2 \times 10^4$ A.cm$^{-2}$ to $2.8 \times 10^4$ A.cm$^{-2}$ (4.2 K, 14 T).

![Fig. 19](image1.png)

**Fig. 19** A typical grain structure of Nb$_3$Sn in a bronze route conductor Ref. (41)

![Fig.20](image2.png)

**Fig.20** A two step heat treatment shown above leads to high Jc and better stoichiometric uniformity 700$^\circ$C reaction leads to small grains and 730$^\circ$C reaction improves compositional uniformity and thus Hc2 Ref.(41)
Commercial wires and cables are produced world wide for over three decades by this process. The Process, in principle can be employed to fabricate RF cavities. Here, the cavity is to be fabricated using Cu-Sn (13 wt%) bronze either in bulk form or by spinning bronze sheets. Work hardening of bronze during processing has to be taken care of by resorting to intermediate annealings. Nb should then be deposited on the cavity surface preferably by sputtering technique, already a well developed technique. The cavity has then to be heat treated around $750^0C$ for prolonged period whereby Sn diffuses in to Nb and reacts with it to form Nb$_3$Sn. Heat treatment parameters are to be carefully optimized so as to (1) convert the Nb-layer to Nb$_3$Sn completely, (2) obtain near perfect stoichiometric composition and (3) prevent incorporation of copper in to Nb$_3$Sn layer. There are no reports about this method ever tried for cavity fabrication by any group.

9.2 V$_3$Ga (Bronze Process)

Work on multifilamentary V$_3$Ga conductors was followed religiously only in Japan. Tachikawa at NRIM (Tsukuba, Japan) contributed most to this development. As stated earlier, the technique is quite identical to that followed for Nb$_3$Sn except that Cu-Sn matrix is now replaced by Cu-Ga matrix and Nb-cores by V-cores. There is one major difference that the value of $\gamma$ (ratio of sp. heats) for V$_3$Ga is 3.04 mJ.cm$^{-3}$.K$^{-2}$ and Tc of 15.5 K. Nb$_3$Sn on the other hand has $\gamma = 1.42$ mJ.cm$^{-3}$.K$^{-2}$ and a Tc = 18.3 K. Consequently the ratio of Jc ( proportional to $\gamma^{3/2}Tc^{5/2}$) of V$_3$Ga to that of Nb$_3$Sn turns out to be 2. Thus Jc of V$_3$Ga should be twice the Jc of Nb$_3$Sn. Further, the decomposition temperature of V$_3$Ga is 1300$^0C$ compared to 2100$^0C$ for Nb$_3$Sn. For comparable pinning strength V$_3$Ga composites have to be heat treated at a lower temperature than the Nb$_3$Sn composites. A heat treatment temperature of 625$^0C$ to 650$^0C$ has been found optimum which is smaller than 700$^0C$ to 750$^0C$ for Nb$_3$Sn. There is a cross over in the Jc – H behaviour of the two materials at 12 T. V$_3$Ga carries larger currents than Nb$_3$Sn in field higher than 12 T. Besides V$_3$Ga has the distinction of displaying less sensitivity to strain than any other A-15 conductor. Large improvement in the Jc values in V$_3$Ga have been reported by Tachikawa et al.$^{(42)}$ and Sharma et al.$^{(43,44)}$ through elemental additions to V cores or Cu-Ga matrix or to both and also by reversing the geometry of the core and the matrix. Production of MF V$_3$Ga wires was started by Furukawa in 1980s but now its place has been taken over by improved Nb$_3$Sn which also happens to be much cheaper than V$_3$Ga.

We have not considered V$_3$Ga for development as Nb$_3$Sn stands out far superior vis-à-vis cavity application

10. Powder Metallurgy

For preparing composites of high melting point materials powder metallurgy (P/M) is an established industrial process. It is an ideal method to prepare compounds which are either brittle or have a non equilibrium structure. It adapts well to the fabrication of A-15 multifilamentary superconductors and had been used successfully to produce MF wires of Nb$_3$Sn, V$_3$Ga and Nb$_3$Al with high Jc values. In the P/M technique for Nb$_3$Sn conductors, fine powders of Cu and Nb are mixed and compacted in high strength jacket
like Cu-Be and processed to fine wires. The jacket is removed and the conductor is coated by Sn. Subsequent heat treatment leads to diffusion reaction of Sn with Nb filaments which are formed during the processing of the wire. Sn can also be added to the Cu-Nb powder-composite before the extrusion. In fact, three variants of this technique are available, namely, cold powder method, hot powder method and the infiltration method. These are briefly described below.

![Uniform filaments in a Cu-Nb (30 wt %) wire prepared by cold powder method using hydride-dehydride Nb and a reduction ratio of 500 (Ref. 45)](image)

**10.1 Cold Powder Method (Nb$_3$Sn and Nb$_3$Al)**

In this method powders of the constituent metals are mixed thoroughly, compacted and jacketed in a high yield strength material like Cu-Be. The composite is reduced to fine wire size. Heat treatment leads to diffusion and the formation of A-15 phase. Fig.21 is the longitudinal microstructure of the very uniform filaments of Nb in a cold powder processed Cu-Nb (30 at %) composite wire with a reduction ratio of 500. High Jc and fine filamentary structure is found in conductors reduced in Cu-Be jackets. High Jc = $1.8 \times 10^4$ A.cm$^{-2}$ (14 T, 4.2 K) has been attained$^{(46)}$ in a composite of Cu + 35 wt % + 26 wt % Sn, cold powder processed in a Cu-Be jacket and with an area reduction ratio of 2000.

High field Nb$_3$Al composite superconductor cannot be produced by conventional method. It forms stoichiometry compound only close to its melting point. Nb powder (80 µm) + 8 wt % Al (5µm) are compacted by cold powder method and reduced to wires with an area reduction ratio of 3-4 x $10^4$. The composite wire is reacted at 1100°C for 1.5 minute followed by long anneal at 750°C for 3 days. Jc of the order of $10^4$ A.cm$^{-2}$ (20 T, 3.5 K) was achieved$^{(46)}$. 
10.2 Hot Powder Method (Nb₃Sn and V₃Ga)

Hot powder method leads to very high reduction ratios but oxygen poisoning at such temperatures is a problem. Borman and Freyhardt (47) at Gottingen University incorporated a getter having binding enthalpy for oxygen greater than for Nb (=390 kJg⁻¹) such as Hf, Ca, Al, Mg or Zr in the compact. Large area reductions are possible with extrusion above 900°C and the resultant compact with low micro hardness can be cold drawn without annealing. External Sn-plating, diffusion and reaction between 500 and 600°C, yields an overall \( J_c = 10^4 \text{ A.cm}^{-2} \) (16 T, 4.2 K) for a hot extruded Cu-30 wt % (Nb) - Sn composite. For a hot extruded Cu-30 wt %-Ga composite a \( J_c \) value of \( 4 \times 10^4 \text{ A.cm}^{-2} \) (19 T, 4.2 K) has been obtained. Billets weighing several Kgm were processed. Filament size can be controlled by the initial powder size. Complete reaction of the filaments leads to high \( J_c \).

![Fig. 22 Overall Jc of P/M processed Cu+35 wt %Nb+26 wt %Sn composite with an area reduction ratio of 2000 using Cu-Be jacket (upper curve), using Cu+35 wt %Nb+19 wt %Sn fabricated in a Cu-Zr jacket, area reduction ratio 2000 (lower curve) (Ref. 46)](image)

10.3 Infiltration Technique [Nb₃Sn, Nb₃(Al-Ge), Nb₃(Al-Si)]

In this technique (48), hydride - dehydride Nb powder (40-60 µm size) is compacted in to rods and then partially sintered at high temperature (2250°C) in vacuum, so as to produce an interconnect with a porosity of 15-20 %. The rod is then infiltrated with Sn at 350-400°C by a dipping process and jacketed in monel with a Ta barrier to prevent Sn expulsion during extrusion process. The rod is reduced to fine wire with a reduction ratio of 4000. Heat treatment at 950°C produces Nb₃Sn with a \( T_c \) of 18 K and an overall \( J_c = 10^4 \text{ A.cm}^{-2} \) (20T, 4.2 K) (49). The technique is ideal for synthesizing materials like Nb₃(Al-Ge) and Nb₃(Al-Si). The porous rod is infiltrated with Al-Ge and Al-Si eutectics. Parameters like immersion time, rate of cooling and morphology of eutectics can be
controlled to ensure deformability of the infiltrated rod. High $J_c$ is reported\(^{(50)}\) for liquid infiltrated Nb$_3$Sn superconductors by using Nb + 0.13 at % Ta powder. Fig.23 shows the overall $J_c$ plotted against strain (%) between 10 and 23 T field. $J_c$ is high enough to wind a 20 T magnet.

The technique is thus useful to produce multifilamentary conductors but may not be suitable for cavity fabrication. Forming complicated geometry may not be easy with powder metallurgy technique and then there is large porosity which is undesirable. Any such defect will cause nucleation of flux and lead to dissipation.

**11. Other Techniques**

Apart from the above discussed techniques there are quite a few others which have been successfully demonstrated to be viable for large scale production of the filamentary wires of the important A-15 superconductors. These include the In Situ technique employed to produce wires of Nb$_3$Sn and V$_3$Ga, the ECN Technique, Nb-Tube Technique and the Internal Tin Technique, all for Nb$_3$Sn. Jelly Roll Method has been successfully used for the fabrication of Nb$_3$Sn and Nb$_3$Al conductors. Laser Beam Method has been used successfully by NRIM Group, Japan to prepare long lengths of difficult types of superconductors like Nb$_3$Ga, Nb$_3$Al and Nb$_3$(Al,Ge). A good account of all these techniques can be found in a review article by Sharma (13). We have not discussed them here because they have little or no relevance to our cavity fabrication programme.
12. Summery

In the present scenario only A-15 superconductors hold the promise for being used as the material for future RF cavities. Being brittle in nature, bulk cavities can easily be ruled out. Film route seems to be the best choice. This not only provides us the practical way to deposit A-15 layer on cavity surface but also fulfill the requirement of an RF cavity in so far as the RF field is confined to within a small distance below the cavity surface. Out of a few potential A-15 compounds we at LNL have selected precisely three materials for cavity development. These are Nb$_3$Sn, V$_3$Si and Mo$_3$Re. After studying the merits and demerits of various available techniques we decided to follow a liquid diffusion technique for Nb$_3$Sn, thermal diffusion technique for V$_3$Si and the DC magnetron sputtering technique for Mo$_3$Re. A large No. of short samples have been studied for all the three systems. Process parameters have almost been optimized and Nb$_3$Sn and V$_3$Si cavities are ready for ‘Q’ measurements. Studies on Mo-Re system are confined to short samples and A-15 phase is still to be realized. The details of these studies are being presented in separate papers in these proceedings by Silvia Deambrosis.

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REFERENCES


2. V. Palmieri, Proc. Tenth Workshop on RF Superconductivity, Sept. 6-11, 2001, Tsukuba, Japan, p. 162

3. G. Guignard et al., CERN report 2000 - 008


MAG-17, 533 (1981)


23. L.R. Testardi, J.J. Hauser and M.H. Read, Solis State Commu. 9, 1829 (1971)

Italy

25. S.M. deambrosis, G. Keppel, V. Ramazzo, C. Ronkolato, R.G. Sharma and V. 


27. Y. Zhang, V. Palmieri, R. Preciso and W. Venturini, LNL-INFN (REP) 144/99

(REP) 157/2000

29. N. Pretto, Laurea Thesis, No. 449125 / MT, 2005-06, Padova University, Italy


33. S. Deambrosis, G. Keppel, N. Pretto, V. Rampazzo, R.G. Sharma and V. Palmieri, 
This proceeding

34. M. Peiniger, M. Hein, N. Klein, G. Muller, H. Piel and P. Thuns, III Int. Conf. on 
RF Superconductivity, Argonne National Laboratory, USA, Sept 14-18 (1987), 
page 503-530

35. N. Klein, Diplomarbeit, University of Wuppertal, WUD 86-7 (1985)

36. M. Hein, Diplomarbeit, University of Wuppertal, WUD 87-3 (1987)

37. M. Peiniger, Diplomarbeit, University of Wuppertal, WUD 83-1 (1983)

38. J. Ding, Diplomarbeit, University of Wuppertal, WUD 86-7 (1986)


44. R.G. Sharma, Y. Tanaka and K. Tachikawa, Cryogenics, 25, 381, (1985)


Appendix

Phase Diagrams of Important Nb and V Based A-15 Compounds

Nb-Ga System

V-Ga System

Nb-Ge System

Nb-Al System
V-Si System

Mo-Re System

Nb-Sn System