

TMC - A low-cost high-field conductor

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TMC superconductors were intensely studied worldwide before the discovery of high temperature superconductors. In this contribution I try to remind our superconductor community that TMC is a cost efficient solution for the generation of magnetic fields starting already above 5 T up to the 30/40 T range.

TMC and superconductivity



TMC = Ternary Molybdenum Chalcogenide



$$T_c \leq 15 \text{ K}$$

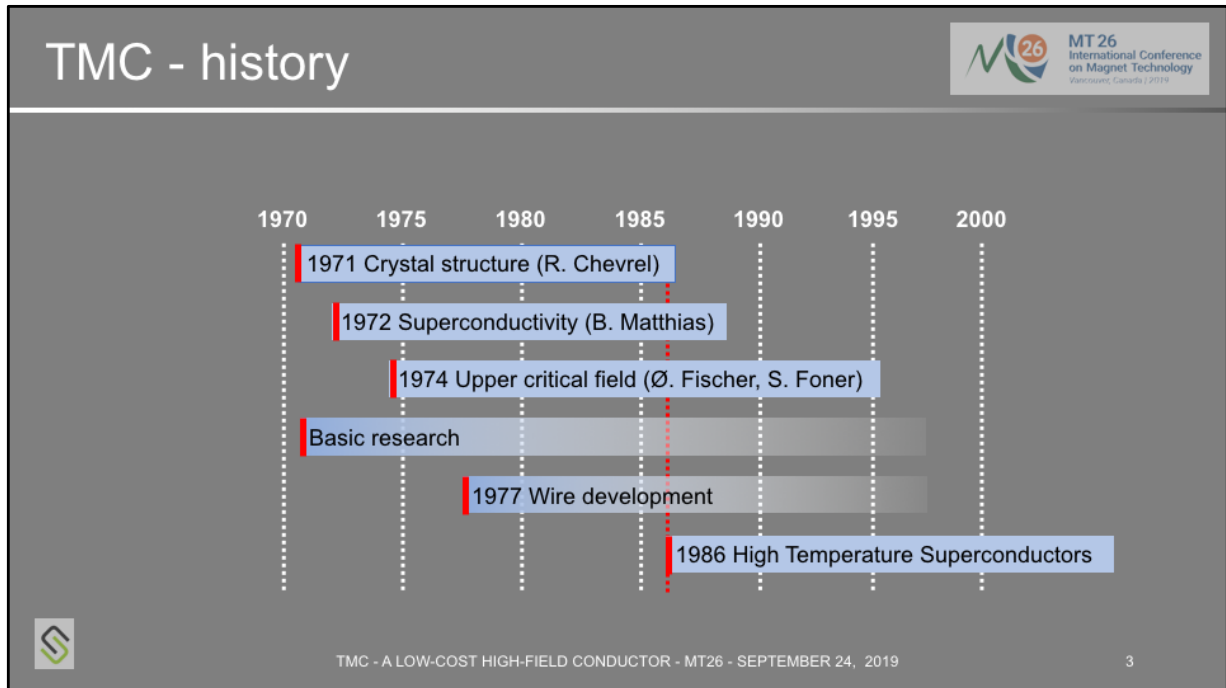
$$B_{c2}(4.2 \text{ K}) \sim 51 \text{ T}$$



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Ternary Molybdenum Chalcogenides, also known as "Chevrel phases", are a class of compounds with the formula MxMo_6X_8 where M is a metal and X is a chalcogenide. The most interesting compound for superconductivity is PbMo_6S_8 with an upper critical field of 51 T @ 4.2 K (58 T @ 1.8 K).

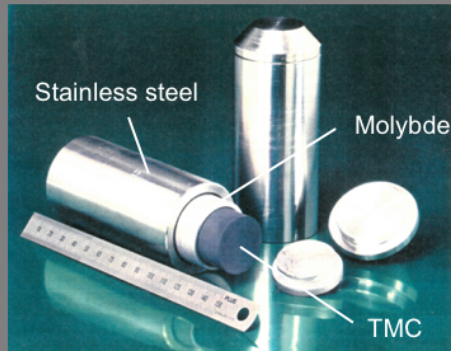


TMC = Ternary Molybdenum Chalcogenides were discovered in 1971 by R. Chevrel, a French chemist. For that reason, TMCs are also known as “Chevrel phases”. Shortly afterwards B. Matthias found that several of them are superconducting. TMCs are the first ternary superconductors, which triggered an important research activity. Interest increased when \emptyset . Fischer (University of Geneva) and S. Foner (MIT, Boston) found extremely high critical fields in some of these compounds. Wire development started in the 1977, first in academia and later also in industry. The author of this presentation was involved since the beginning. R&D activities slowed down with the discovery of High Temperature Superconductors 1986/87 and discontinued around 1997.

1st stage: monofilamentary wire



Extrusion billet: OD 50 mm, length 100 mm (~ 1.5 kg)



Powder in tube process - PIT

Manufactured on industrial fabrication line for Mo wires

~ 1 km with OD = 0.4 mm



R. Grill et al. Proc. Plansee Seminar 1989



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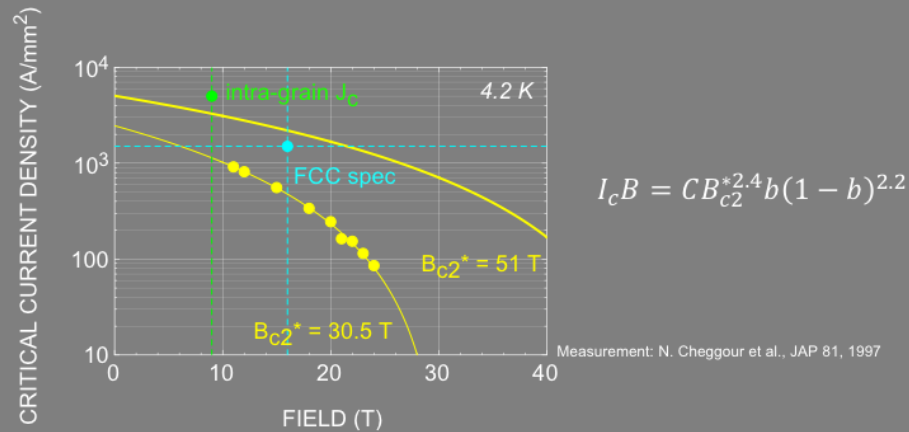
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The most successful technique for the manufacturing of TMC conductors were developed by the PLANSEE company (www.plansee.com). Monofilamentary TMC wires, as a first step to a multifilamentary wire, were manufactured on an industrial production line for molybdenum wires. Unit lengths up to 1 km (OD = 0.4 mm) were achieved. The extrusion billet of about 1.5 kg is shown in this slide. It consists of a cold isostatic pressed (CIP) TMC powder core, inserted in a molybdenum tube which serves as a diffusion barrier and a stainless steel container for the adjustment of thermal compression on the superconductor after cool down.

TMC - critical current density



J_c in the superconductor cross section of a TMC (PMS) wire



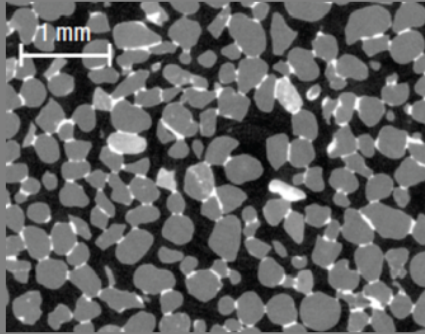
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The latest measurement of the critical current density of a monofilamentary TMC wire were published in 1997 (N. Cheggour et al, JAP 81, 1997). The effective upper critical field was estimated by extrapolating the pinning force to zero (according J. Ekin). The obtained $B_{c2}^*(4.2\text{ K})$ is 30.5 T, a value much lower as measured by specific heat in TMC bulk material. Supposing that a $B_{c2}^*(4.2\text{ K})$ of 51 T can be achieved in a wire, the critical current density is calculated by the above mentioned scaling law. Additional credit for this calculation comes from the measurement of the critical current density inside high quality TMC grains with a small T_c distribution (indicated in green). For comparison CERN's FCC specification (1500 A/mm² at 16 T) is also shown.

Granular superconductor

Wet sand model system illustrated by X-ray tomography



M. Scheel et al., *Nature Materials*, March 2008

Critical current is restricted at grain boundaries:

- Reduced contact area
- Locally reduced T_c and B_{c2}
(uncontrolled grain boundary diffusion)

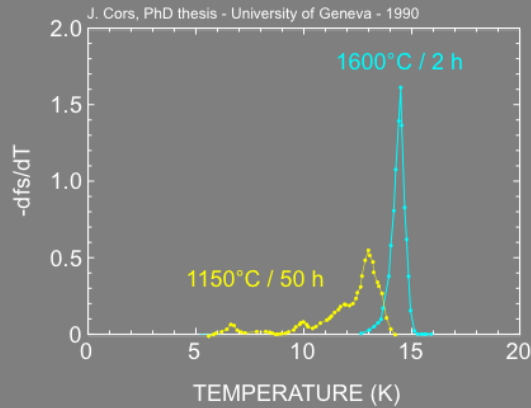
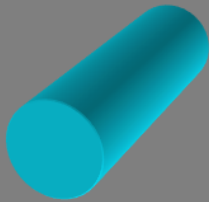


A granular behavior is frequently observed in powder in tube (PIT) manufactured superconductors. First, powder particles (grains) are not fully connected, which causes (obviously) a reduction of the critical current. Secondly, depending of the homogeneity of the TMC powder, undesired grain boundary diffusion occurs. Then critical parameters like T_c and B_{c2} are different inside grains and between grains. Connectivity and grain boundary diffusion are responsible for a reduced critical current density in TMC wires. Note that the shown figure is a model system (wet sand) for the illustration of possible problems due to granularity.

New manufacturing process

Granted patents: US 10128428 (Nov. 2018)
EP 3105799 (Sep. 2019)

100% dense TMC bulk material



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In order to overcome granular behavior of TMC wires, a new manufacturing process is proposed (granted patents are available for licensing). The starting point is a 100% dense TMC bulk material (not powder) with a small distribution of the critical temperature, as it can be obtained by a high temperature synthesis at 1600°C. For comparison the Tc distribution of a TMC powder (low temperature synthesis), as used in a PIT wire, is shown.

New manufacturing process



Granted patents: US 10128428 (Nov. 2018)
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No reaction heat treatment !



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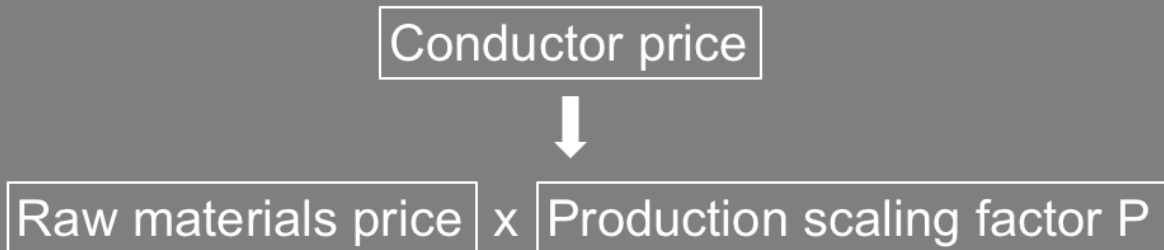
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TMC bulk material can be deformed directly to a wire by extrusion and wire drawing at elevated temperature (like a molybdenum wire). No reaction heat treatment is necessary! Then a TMC conductor can be wound to a magnet almost like a NbTi wire (a minimum bending radius must however be respected).

Conductor price



L. Cooley et al., SUST - 2005



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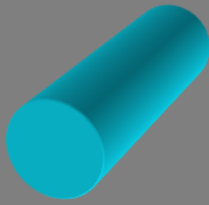
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Following the study of L. Cooley (SUST, 2005), the conductor price can be estimated by the raw materials price times a production scaling factor. Large scale production of NbTi wire for CERN's LHC requires a production scaling factor of 3.3. In the development phase of a superconducting wire the production scaling factor may go up to about 15 (see L. Cooley).

Cost for raw materials - TMC bulk



PbMo₆S₈ (PMS) bulk material (batch of 50 kg)



Constituent	Purity (%)	Price (\$/kg)
Pb granulate	99.9	57
Mo powder	> 99.95	77
S powder	99.5	30
PbMo₆S₈		61



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Improving the purity of Pb and S increases the raw material price, but stay still below 80 \$/kg for PbMo₆S₈.

Conductor layout

The diagram illustrates two conductor layouts: MRI and HEP. The MRI layout shows a circular cross-section with a central core of TMC filaments, surrounded by Mo and a stainless steel sheath. The HEP layout shows a central filament area with a Mo core, TMC filaments, and a stainless steel sheath.

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There are two conductor layouts shown, one for a TMC wire going into a copper profile (wire in channel) as used for MRI applications. In this case a maximum of superconductor can be put in the cross section without taking care of stabilization (matrix/TMC = 0.95). The other layout is for a more challenging design, as required for the FCC at CERN. The stabilizer/superconductor ratio is 1, filament size is 10 micrometer and the number of filaments is 2220.

Conductor price



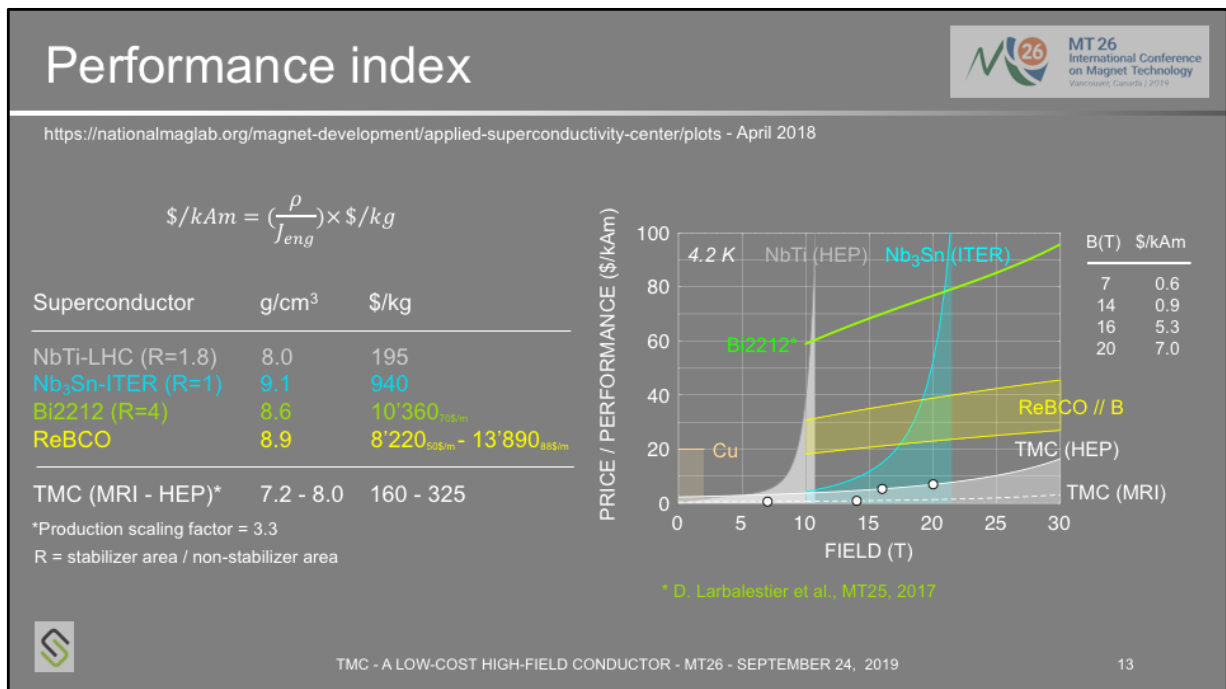
Conductor price = raw materials price x production scaling factor P

Superconductor	Raw materials (\$/kg)	P	Conductor price (\$/kg)
TMC (PMS)	49 - 98 ^a	3.3	160 - 325 ^a
NbTi (LHC dipole)	61 ^b	3.3	201 ^b
N ₃ Sn (ITER poloidal)	120 ^b	7.8	940 ^c

- a) Data for a multifilamentary TMC superconductor (MRI - HEP)
- b) Data from L. Cooley et al. (SUST 2005) + inflation per CPI 2019
- c) Data from Fusion4Energy, Barcelona



Supposing a production scaling factor of 3.3 for large scale manufacturing, the conductor price of a multifilamentary TMC conductor is between 160 \$/kg and 325 \$/kg (depending of the layout). In the development phase, a production scaling factor of 10 seems more appropriate. This means one can count on a TMC conductor price between 490 \$/kg and 980 \$/kg, which is the typical range of Nb₃Sn conductors.



The performance index indicates how much one has to spend in a magnet for one ampere-turn (here in \$/kAm). Supposing that the conductor price per kg does not change with field, the above shown figure summarizes the behavior of different conductors. Because the engineering current density goes down by approaching the upper critical field, the \$/kAm index diverges for NbTi and Nb₃Sn. Then the advantage of a high critical field superconductor like Bi2212, ReBCO and TMC is the weak field dependence of the engineering current density and the performance index is mainly determined by the conductor price. Data for Bi2212 are for a round and isotropic wire. In the case of ReBCO, the situation where the magnetic field is parallel to the tape is shown. The lower line is for a ReBCO tape with a width of 12 mm and the upper line for a width of 4 mm. Assuming an orientation of the magnetic field perpendicular to the tape, the performance index is above 100 \$/kAm at > 10 T. Depending of the application (layout of the conductor), a TMC conductor has the potential to be cost efficient starting already above about 5 T. An enlarged presentation of the price/performance vs. field figure can be found in the enclosed Appendix.

Timescale



Immediate

- Identify industrial wire manufacturer

Three to four years

- TMC bulk material with small T_c distribution

- Multifilamentary wire > 1 km length

- Critical current density as forecasted or better

- TMC wire commercially available



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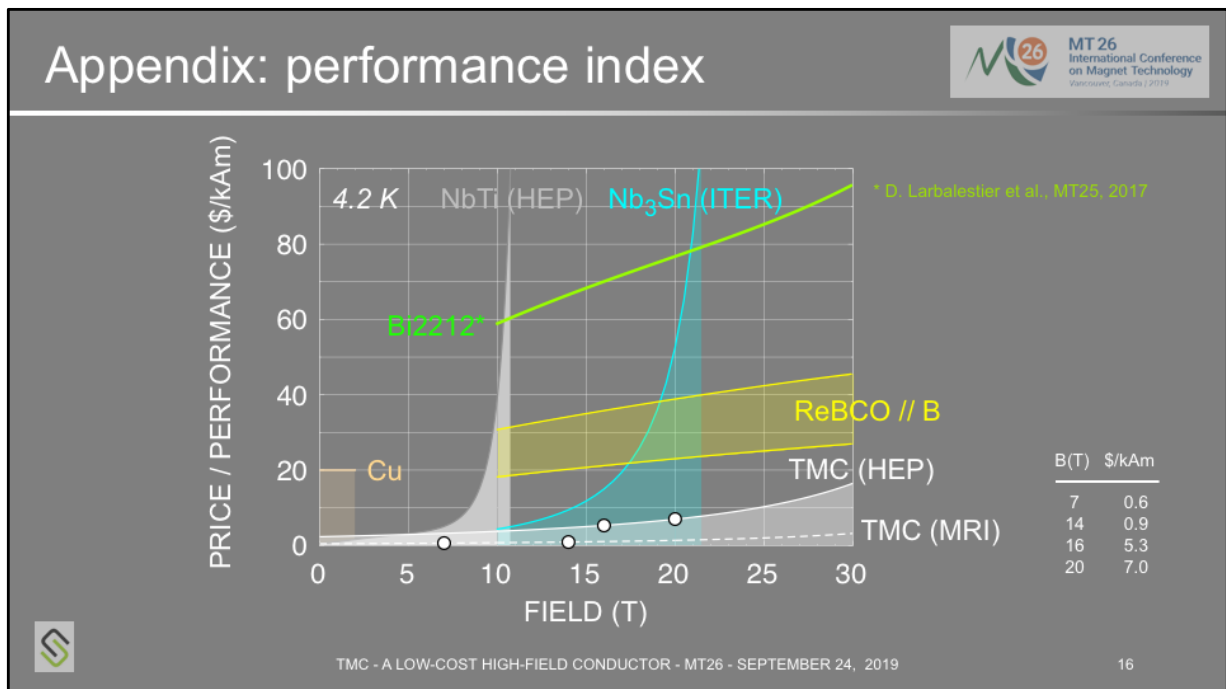
The identification of an industrial wire manufacturer is urgent. Because TMC wire drawing must be carried out at elevated temperatures, industry familiar with the production of refractory metals like Mo and W is preferred. In such a case the required infrastructure and know how for wire drawing at elevated temperatures is available and no important investments are expected. A TMC conductor may be commercialized in rather short time, the guess is three to four years, because about 15 years of R&D in collaboration with industry were already carried out.

Conclusions



- TMC may be considered as “NbTi for high fields”
- Magnet winding like NbTi (limited by bending strain)
- Cost efficient, starting above 5 T
- Patents for new manufacturing process ready for licensing (eventually for purchase)





Enlarged Figure: The performance index indicates how much one has to spend in a magnet for one ampere-turn (here in \$/kAm). Supposing that the conductor price per kg does not change with field, the above shown figure summarizes the behavior of different conductors. Because the engineering current density goes down by approaching the upper critical field, the \$/kAm index diverges for NbTi and Nb₃Sn. Then the advantage of a high critical field superconductor like Bi2212, ReBCO and TMC is the weak field dependence of the engineering current density and the performance index is mainly determined by the conductor price. Data for Bi2212 are for a round and isotropic wire. In the case of ReBCO, the situation where the magnetic field is parallel to the tape is shown. The lower line is for a ReBCO tape with a width of 12 mm and the upper line for a width of 4 mm. Assuming an orientation of the magnetic field perpendicular to the tape, the performance index is above 100 \$/kAm at > 10 T.

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