Final Conference

Potential innovation pathways in the recovery of refractory metals from secondary resources

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Nb and **Ta**: Stéphane BOURG & Didier HARTMANN (CEA)

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TANTALUM – COMPARISON OF TWO MARKET REPORTS (1/2)

- The Ta market is very opaque, worldwide as well as in Europe
  - ➢ very difficult to obtain reliable figures about the actual consumption of tantalum in the EU
  - ➢ the largest European companies do not publish any details about the countries shares of their supply and their production
- Two reports have been ordered in November 2016 (preparation and concertation with G. Lefebvre, BRGM)

General features of the Ta market reports

Report	**Roskill**	**IndexBox Marketing**
Diffusion	Special order for REFRAM project	Official 2016 edition
Years covered	2015	2015-2020
Experts' location	UK	UK
Number of pages	11	69
Number of tables	2	22
Number of figures	3	39
Author	Patrick Stratton	no named author identified
Price (€)	3,520 (3000 GBP) 2 days of expert labour	1,490

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TANTALUM - COMPARISON OF TWO MARKET REPORTS (2/2)

- Some Roskill figures:
  - EU imports are estimated in 2015 between 648 t and 800 t (gross weight)
  - The recycling of scraps and other secondary materials meets about 25% of tantalum demand but could be higher because Ta is not recovered from the superalloys involved in turbine blades

    → Ta loading is increasing
- Some IndexBox figures (Ta and articles thereof are concerned, but **waste and scraps are excluded**):
  - The 2015 Ta market volume reaches 250 t, with a production inside the EU 28 of 295 t, 222 t of (extra-EU) imports and 267 t of exports
  - waste and scraps, which are the most important part of EU Ta imports could reach > 400 t of Ta
  - 222 t of EU imports given by IndexBox would correspond to only "slag, ashes and residues" + concentrates from ores

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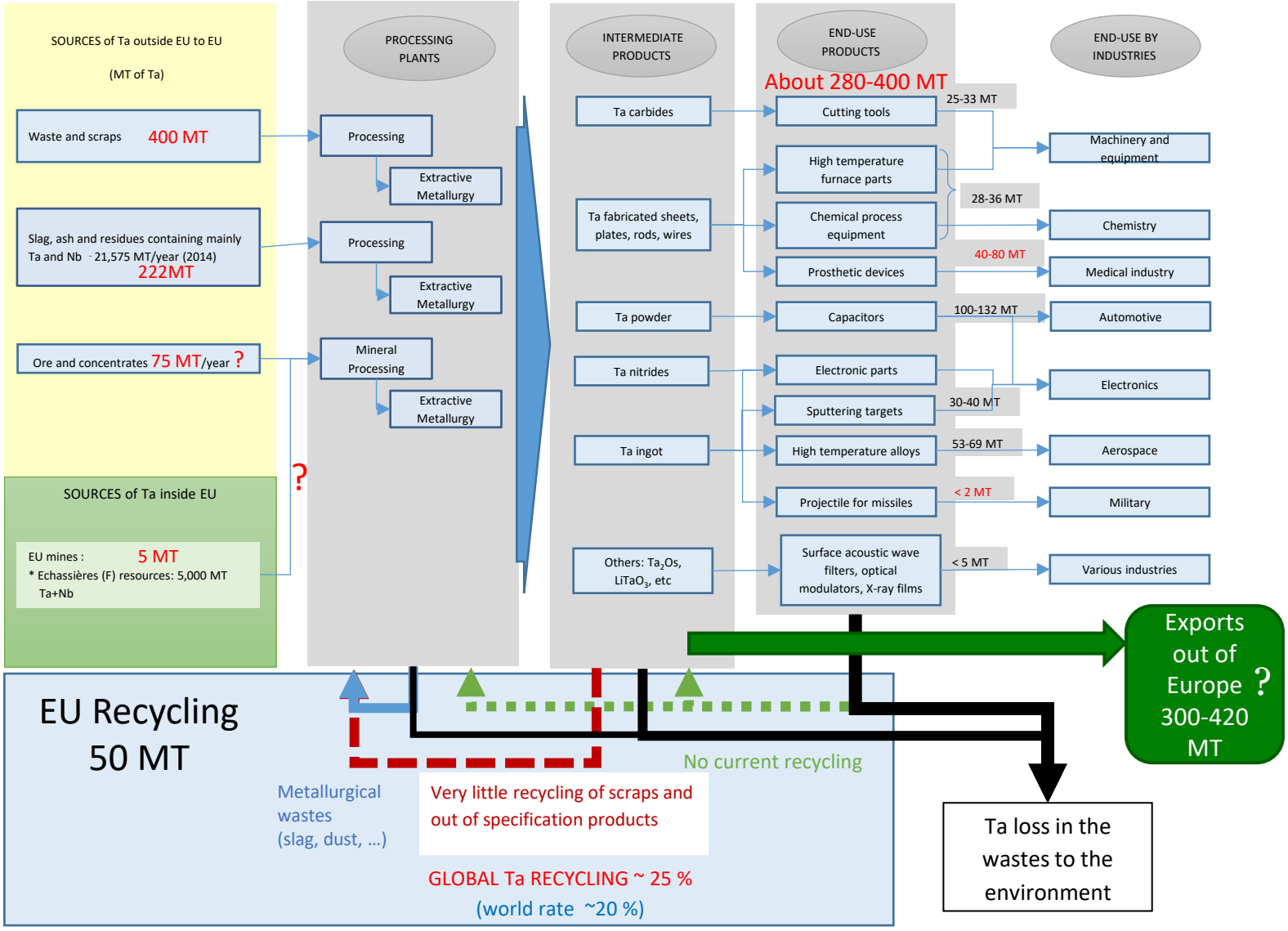
Current value chain of tantalum (based on 700 MT/year)

MT = metric tonne



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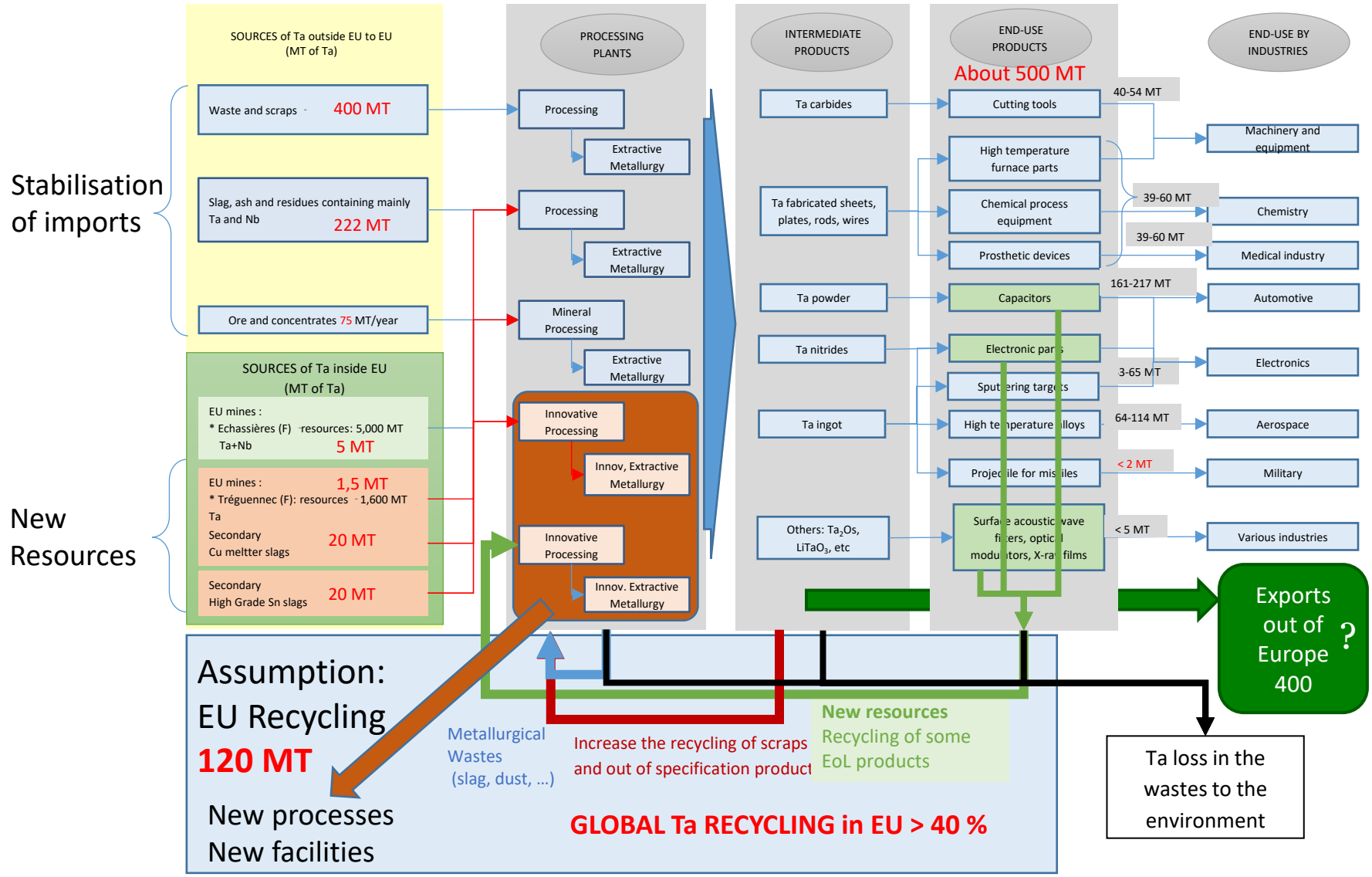
Future value chain of tantalum (based on 500 MT/year of Ta in EU made products)



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Innovation potential in the recovery of Nb and Ta

based on references found by
Eugen Andreiadis
(CEA)
Marta Macias Aragonés
(IDENER)

presented at REFRAM's Second Workshop, September 27-29 2016

with some new additions

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Focus on secondary resources in Europe

1. Recovery from slags
   - Tin slags
   - Copper smelting slags

2. Nb low grade by-products

3. Recovery of Ta from alloy scrap

4. Recovery from tungsten carbide sludge

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How far secondary sources are already treated?

- Synthetic concentrates (SynCon)
  - reprocessed secondary materials containing Ta
  - prepared from the processing of scraps, residues, sludges and the pyrometallurgical treatment of Sn slags into a product containing 70-90% Ta
  - HC Starck maintains large scale capabilities to produce synthetic concentrates.
- Scraps and recycling
  - reprocessing of capacitors (majority)
  - cutting tools (balance) [Zogbi D.M. 2008]
- Overall Ta recycling rate ~ 20 %
  - **Roskill has estimated 25 % for the EU** → 295*0.25 = 74 tonnes Ta recycled/yr

    (rough estimation because depends on timelife of products)

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1. Recovery from slags

- High-grade tin slags (>10% Nb+Ta)
  - Usually processed directly by hydrometallurgy
  - Carbochlorination at 500°C allows complete extraction and recovery of pure Ta and Nb compounds (Gaballah 1997)
    - → each process has advantages but hydrometallurgy could be favoured because of many impurities to deal with
    - → **could be developed in Europe with no further R&D efforts**

- Copper smelting slag
  - Processing using froth flotation with alkyl hydroxamates as collectors (selective chelation to Ta or Nb-containing minerals) [Roy 2015]
  - → why are these slags not recycled by Cu metallurgists (UMICORE, AURUBIS)?
  - → are these slags amenable to froth flotation with a sufficient yield?
    - If so, **a limited R&D programme could be proposed, including recovery of the different valuable metals**

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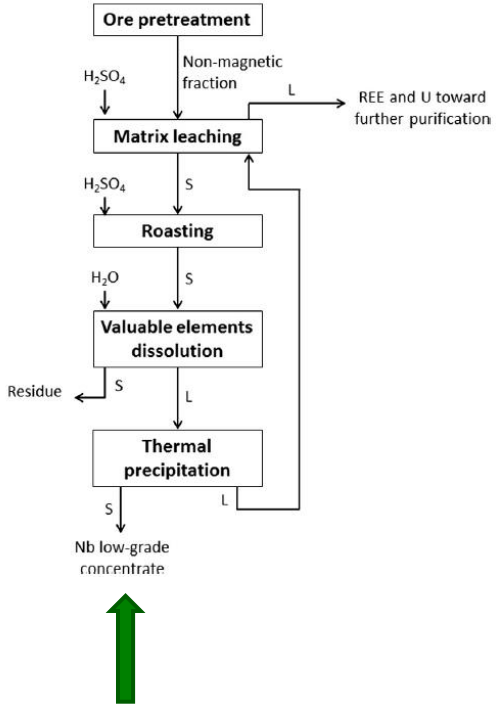
2. Recovery of Nb as a by-product

→Example of the Mabounie (Gabon): production of a low-grade Nb concentrate (Nb= 10-15 %, Ta=0,25 %, Fe=6-10 %, Ti=8-12 %)

- Fluoride-free process using caustic conversion (Deblonde, 2016 - ERAMET)
  - Formation of water-soluble sodium hexaniobate and hexatantalate
  - Recovery yield 70% Nb (<1% Fe and Ti)
- Global Nb and Ta recovery yields 65% during continuous pilot test

→ Demonstration of Nb and Ta recoveries without using HF

→ **Probably other secondary mining resources to be valorised**



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3. Recovery of Ta from alloy scrap

	Cr	Co	Mo	Re	W	Al	Ti	Ta	Nb	Hf	Autres
CMSX4[1]	5.7	11.0	0.42	3.0	5.2	5.2	0.74	5.6	-	0.1	-
CMSX10[1]	2.0	3.0	0.4	6.0	5.0	5.7	0.2	8.0	0.1	0.03	-
René N5	7.0	8.0	2.0	3.0	5.0	6.2	-	7.0	-	0.2	-
René N6	4.2	12.5	1.4	5.0	6.0	5.75	-	7.2	-	0.15	
RR3000	2.3	3.3	0.4	6.3	5.5	5.8	0.2	8.4	-	0.03	
UCSX1	2.3	6.0	1.5	6.3	7.0	5.8	0.2	8.4	-	0.03	2.0Ru
UCSX8	2.3	6.0	3.0	6.3	6.0	5.8	0.2	8.4	-	0.03	6.0Ru
TMS75	3.0	12.0	2.0	5.0	6.0	-	-	6.0	-	0.1	-
TMS138	3.0	12.0	3.0	5.0	6.0	-	-	6.0	-	0.1	2.0Ru
TMS162	2.9	5.8	3.9	4.9	5.8	5.8	-	5.6	-	0.1	6.0Ru

Ni-based superalloys [Bhadeshia 2010, quoted by Roskill]

- Most of the superalloys are recycled for their Ni and Re content
- Currently Ta from alloy scrap is recycled to low-value mill products
- New process based on iodization of Ta scrap (Lessard, 2015)
  - Formation of volatile TaI_5 (sublimes at 543 °C)
  - Subsequent H_2 plasma reduction to Ta metal powder
  - Recycling of resulting HI to molecular iodine and H_2

❖ Process designed for the production of electronic grade Ta nanopowders
→ clearly innovative but what about its cost at industrial scale?

❖ For other applications, shouldn't we better consider a pyrometallurgical process?

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4. Recovery from tungsten carbide sludge

- Important secondary resource for recycling Nb and Ta

  average composition: [Nb] = 5.6 % [Ta] = 7.2 %

- No innovative processes found
  - ❖ hydrometallurgy: conventional processes using H2SO4-HF or alkaline leaching?
  - ❖ pyrometallurgy:

    FFC Cambridge Process (Frey, Farthing & Chen, 1997):

    oxides are cathodically reduced to metals or alloys in molten salts

    $MO_x + x\,Ca \rightarrow M + x\,CaO$

- Probably a way to recycle several valuable elements at the same time: W, Nb, Ta

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Innovative solvent extraction processes

- Innovative improvements expected:
  - Less or no HF used for digestion and SX metal separations
  - → use of impregnation and maturing by H_2SO_4, like for some refractory ores
  - More robust extractants with higher stability and lower water solubility
    → best results obtained with phosphinic acid (PA) or D2EHPA as extractants
  - Increased recycling of reagents to reduce liquid and solid waste

Innovative pyrometallurgical processes

- ✓ Direct Electrolytic Reduction of Solid Ta2O5 to Ta with solid-oxide-oxygen-ion conducting membrane (SOM) Process [Chen 2013, 2016 - *China*]
  → electrolysis in molten CaCl2 or MgF2-CaF2 at higher potential than FCC Cambridge process
- ✓ Tantalum Powder Preparation from Ta2O5 by Calciothermic Reduction [Ha 2012, *South Korea*]
  → molar ratio Ca/Ta2O5 > 10 (2*stoichiometry), 900 °C leads to Ta with 1 % O2

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Just a glimpse of new applications

- Market of Ta in hip and knee prosthesis:
- 0.16 % of the population
- In EU : 800,000 hip procedures are carried out every year, costing some € 1.5 billion
- The main advantage of Ta over Ti is the regeneration of the bones around the metal: much better integration and thus resistance

  → it seems that Ta will substitute Ti in prosthesis
- Need of a nanostructured material for trabecular metal (American company: Zimmer)

❖ A survey of present needs has been made by Ana Diez de la Rosa (ADE), using data from Spain, Sweden and England.

→ Need for Ta powders at a reasonable price in order that everyone who will need an implant can afford it in his (her) old days…

Definitive implants with a tantalum cone

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CONCLUSION

Technical part

- Lack of primary resources of Ta/Nb in the EU; mining projects will be difficult to develop
- Many secondary resources are not enough exploited for the moment and could be improved

  → Sn and Cu slags, Ni-based superalloys, WC sludges (recovery of different metal values at the same time)
- A lot of R&D has been done on these materials

Strategy

- What can we do to foster recycling of Ta/Nb in Europe?
  - ➢ pilot tests to confirm the feasability of new processes
  - ➢ technical-economic studies to determine the break-even point
  - ➢ EU or/and states could better support recycling in order to reduce imports (in some cases from conflict regions)

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