Optimized metals separation for remanufacturing of product-centric recycled and reclaimed scrap

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About the Presenter

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  - B.Ed., Chemical Engineering, RVCE, India
  - Undergraduate senior year project on N-doped reduced graphene oxide/Mn_3O_4 composite as electrode materials for supercapacitors at IISc, India
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- Funding source: Army Research Laboratory
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Motivation

- **Problem / Opportunity:**
  - Many of today's products are made of multiple materials, making recycling/reclamation difficult
  - Various kinds of coatings are applied on metal substrates for protection against service conditions and enhanced performance. Higher material properties of coatings makes its removal a challenge
  - **Motivation for coating removal-** Refurbishment, recycling o secondary materials, inspection and sustainable developmen
- Approach:
  - Review coating separation techniques for most efficient method
  - High temperature oxidation for tantalum metal or alloy separation from steel substrate
- Project Objective: Efficient removal of coating with minimal damage to substrate

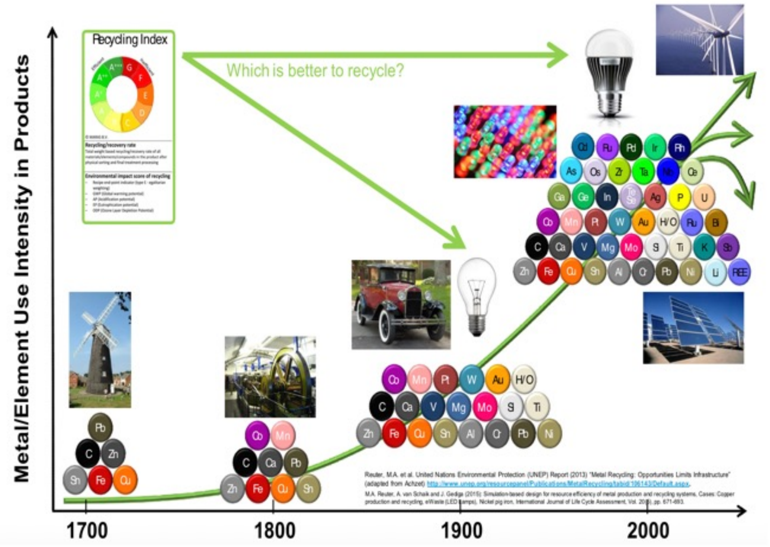


Figure 1: The ever-increasing use of complex mixtures of metals in products

Project Information

- **Success Defined as:**
  - Ability to efficiently separate coating from substrate with minimal damage to the substrate
- **Potential Impact of Success:**
  - Value added recycling of scrap; positive economic and environmental impact
  - Refurbishment and reuse of metal substrate after separation from coatings leads to reduce in consumption of primary metals
- **What is the current state of the art?**
  - Cr is replaced by Ta in gun barrels as it is more susceptible to heat resistance. There is not much literature on Ta-based coating separation technique from steel substrate. Traditionally, Ta is recycled or recovered by hydrometallurgy and oxidation methods
  - The recovery% - 90-95, by a combination of hydrometallurgy and oxidation from electronic capacitors

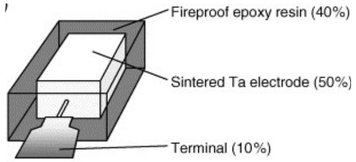
Project Information

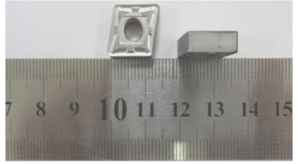
- **What is the current state of the art?**
  - Nichrome coated steel:
  - ➢ Traditionally, first precipitate nickel using chemicals like sulfides and carbonates followed by separation from water as sludge; difficult and waste by-product producing method since plating contains stabilizers, inhibitors, etc.
  - ➢ Other methods- Ion exchange and batch electrochemical treatment
  - ➢ Recovery% > 90, by hydrometallurgy, but this is incase of superalloy scrap

  - Sn coated steel:
  - ➢ Detinning processes such as hydrometallurgy, dry metallurgical methods, electrolytic processes and processes that use dry chlorine
  - ➢ Most of the tin recycled is from industrial waste stream. Current detinning processes are mostly steel upgrading processes

Types of coating

COATING	DEPOSITION METHOD	REMOVAL METHOD
Organic coatings (Paint, polymer, ormosil)	PVD, CVD, sol-gel, thermal spray gun	Physical, chemical, thermal
Inorganic oxides (Al_2O_3, Cr_2O_3)	PVD, sol-gel, thermal spray gun	Thermal, chemical
Refractory coatings (Ta, TaW)	Cold spray, Cladding, thermal spray	Thermal, Cryogenic, Chemical
Metal and alloys (Fe, Steel, Ni, Al and alloys)	Cold spray, Cladding, thermal spray gun	Chemical, Electrochemical Cryogenic, Physical or their combinations





Traditional coating removal methods

REMOVAL METHODS	FACTORS ASSOCIATED WITH COATING AND SUBSTRATE	REMARKS
Mechanical (Machining tool with cutting edge)	High thickness, low adhesion, poor efficiency	-Less applicable on complex geometry -Additional steps may be required
Chemical (Stripping or leaching; strippers vary by pH)	Small thickness coating has higher efficiency, removes tough coatings	-Waste and byproducts formed -can damage substrate by forming localized degradation
Electrochemical (Electrolytes vary by pH)	Applicable on variable thickness, high efficiency, less impact on substrate	-High consumption of power -High efficiency -Less viable on large scale
Thermal (Laser, heat lamps, cryogenic, CO_2 pulsed laser beam)	Applicable on variable thickness, selective removal possible, high efficiency	-High consumption of power -Low damage to substrate -Requires robotic application
Physical (Impact method using pressurized gas or liquid; High pressure waterjet, plastic media, abrasive media)	Applicable to variable thickness, high adhesion can cause damage on substrate, applicable on variable hardness	-Robotic application may be required -Many abrasive media with different hardness can be chosen

Tantalum coated steel

- **Tantalum cold sprayed 4130 steel**
- **Tantalum cold sprayed A36 steel**
- **Tantalum alloy clad steel**

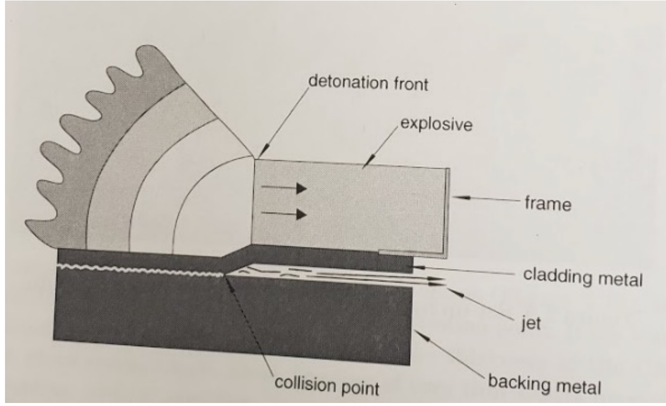


Figure 3: Schematic of explosion bonding process

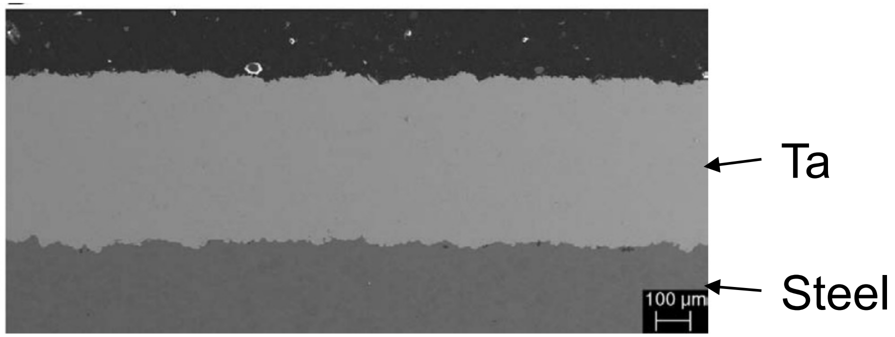


Figure 2: SEM image of Cold sprayed Ta on steel

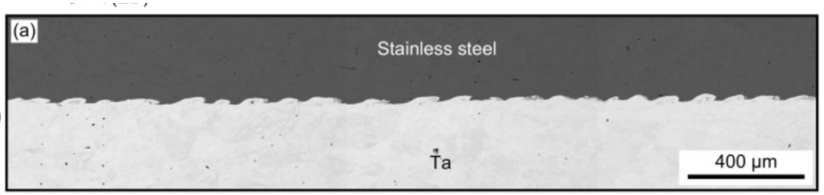


Figure 4: SEM image of Ta explosion welded on steel

Source: Koivuluoto, Heli, et al, "Cold-sprayed copper and tantalum coatings — Detailed FESEM and TEM analysis", *Surface and Coatings Technology*, 204 (2010):2353-2361

Source: Paul, H., et al. "Microstructure and phase constitution in the bonding zone of explosively welded tantalum and stainless steel sheets." *Materials & Design* 153 (2018): 177-189.

Tantalum coated steel

- Only attacked by acids HF, fuming H_2SO_4 and strong bases. Thus, chemical separation is not a preferred separation method
- Ta readily absorbs oxygen and oxidizes above 500℃, and forms Ta_2O_5 phase
- $Ta\text{-}O_{S\text{-}Sol}$ = (TaO_z) = $\beta\text{-}Ta_2O_5$ (Parabolic (I))
- $Ta\text{-}O_{S\text{-}Sol}$ = (TaO) = $\beta\text{-}Ta_2O_5$ (Parabolic (II))

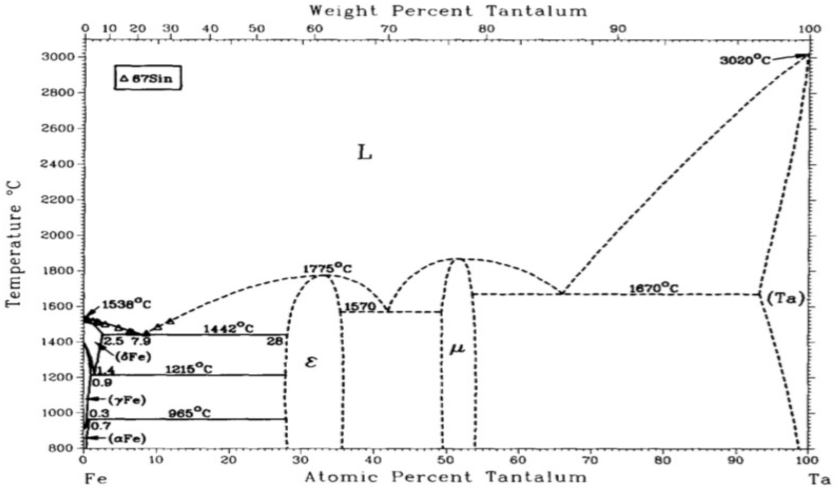


Figure 8: Phase diagram of Ta and Fe, showing brittle intermetallic phase formation of Ta and Fe at high temperatures

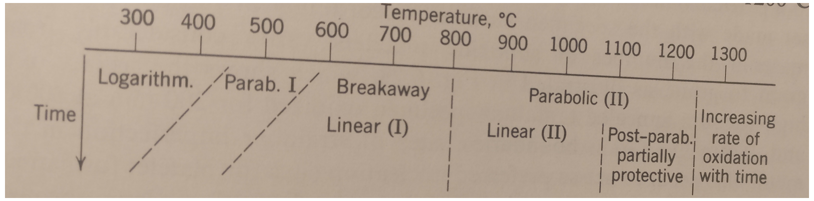


Figure 9: Schematic summary of the rate equations observed in oxidation of tantalum at 300-1300C

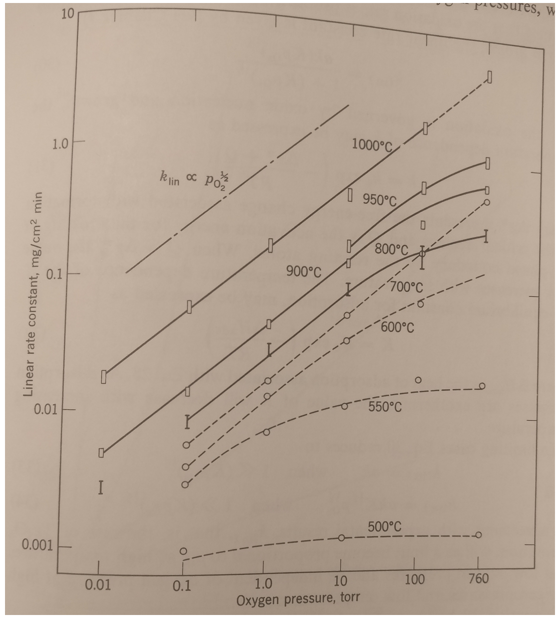


Figure 10: Linear oxidation of Ta as a function of temperature and oxygen pressure

Tantalum coated on steel

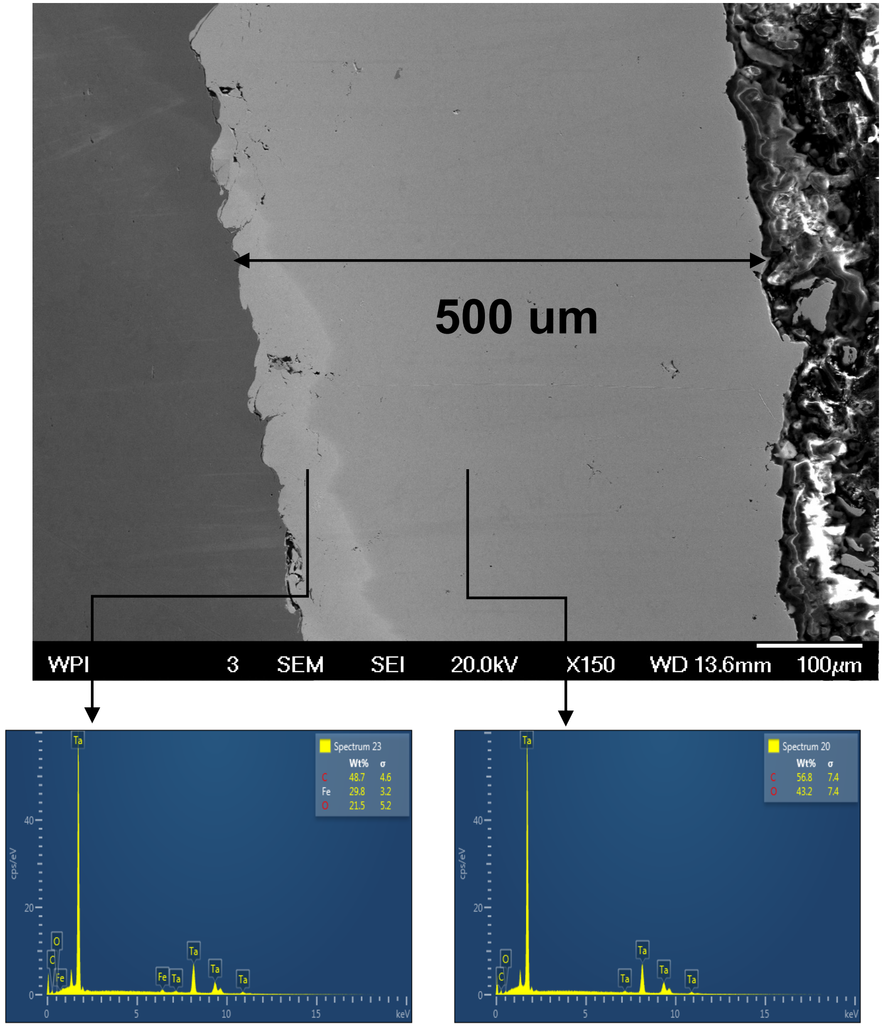
Oxidation tests were carried out on:

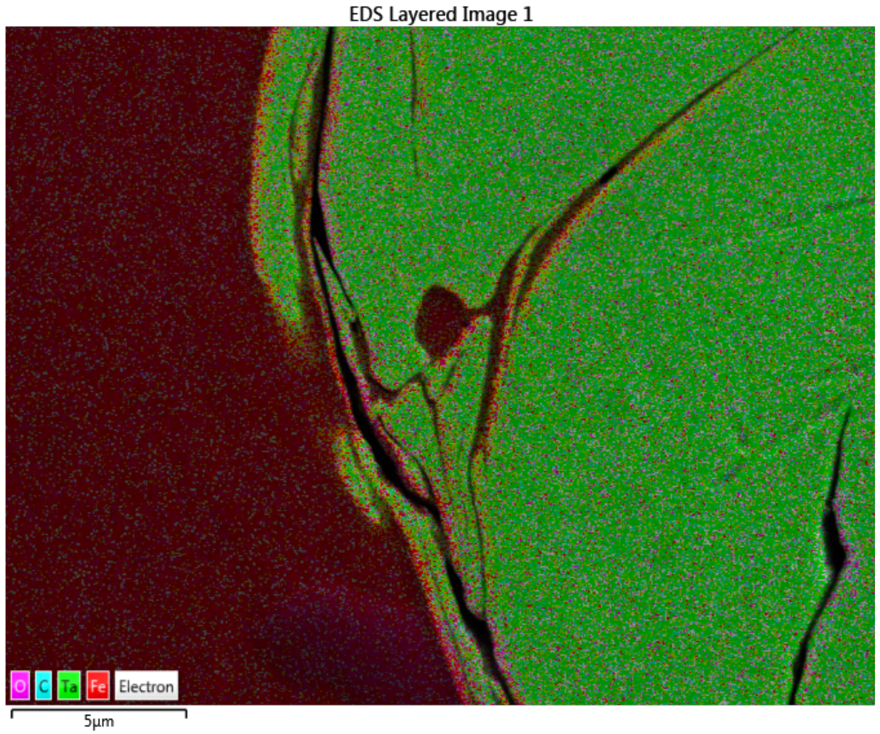
Sample 1. Tantalum cold-sprayed 4130 steel

Sample 2. Tantalum cold-sprayed A36 steel

Sample 1: Ta cold-sprayed 4130 steel

Sample information- Ta cold-sprayed 4130 steel



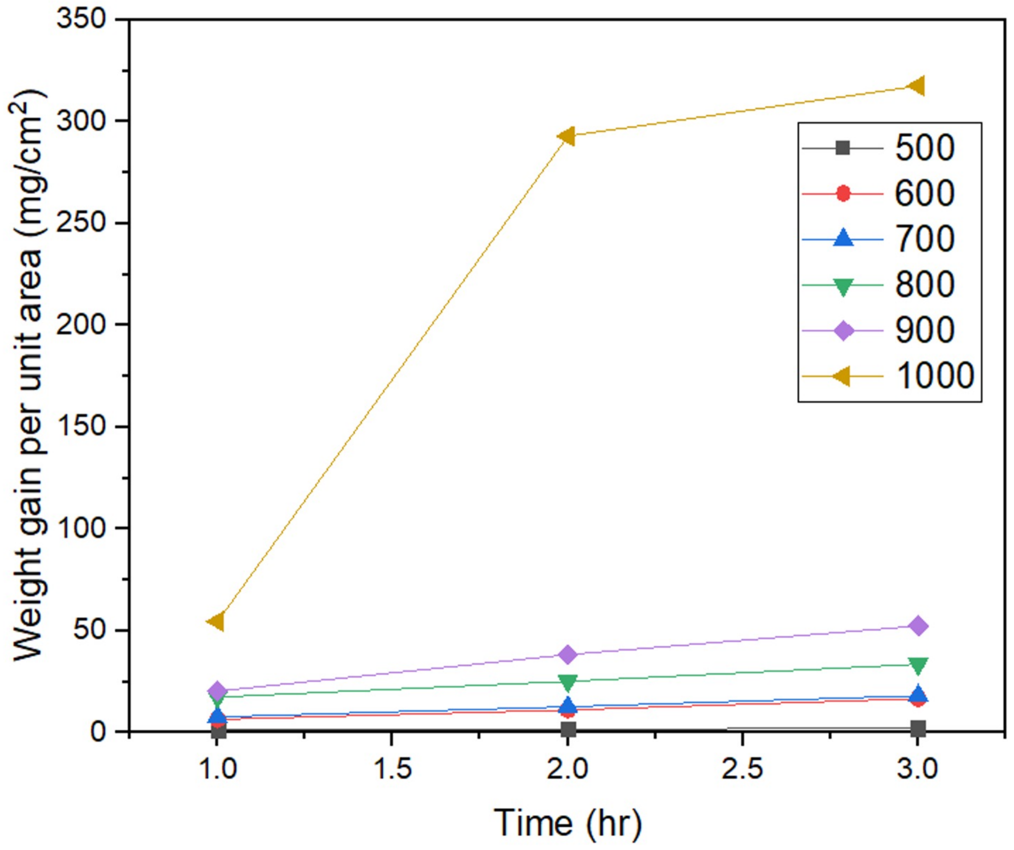


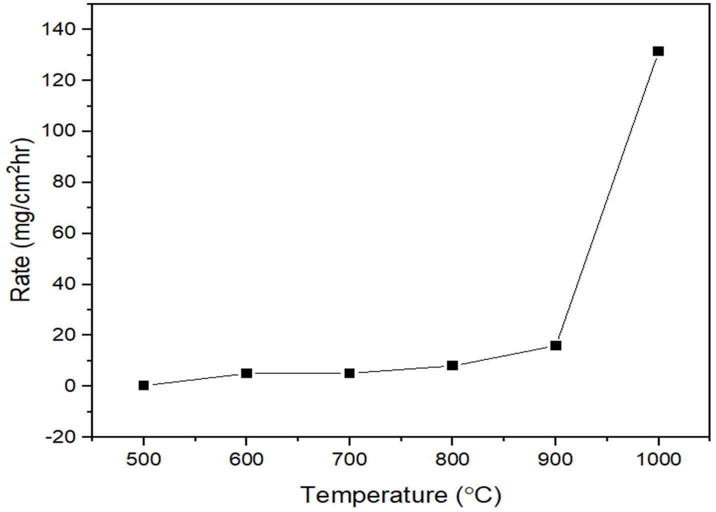
Experimental design- Ta cold-sprayed 4130 steel

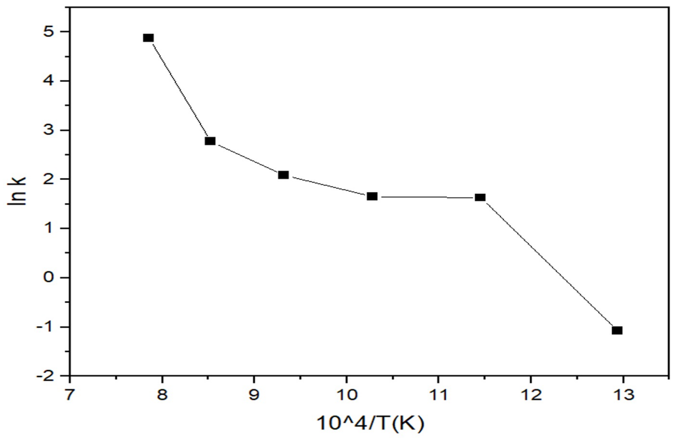
- Oxidation tests were conducted in a muffle furnace in air
- Temperature is varied between 500-1000C, time is constant at 3hr

Experiment	Temperature (C)
1	500
2	600
3	700
4	800
5	900
6	1000

Results- Ta cold-sprayed 4130 steel

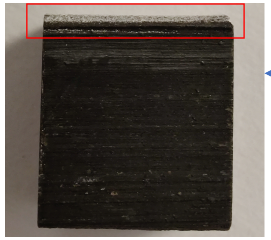


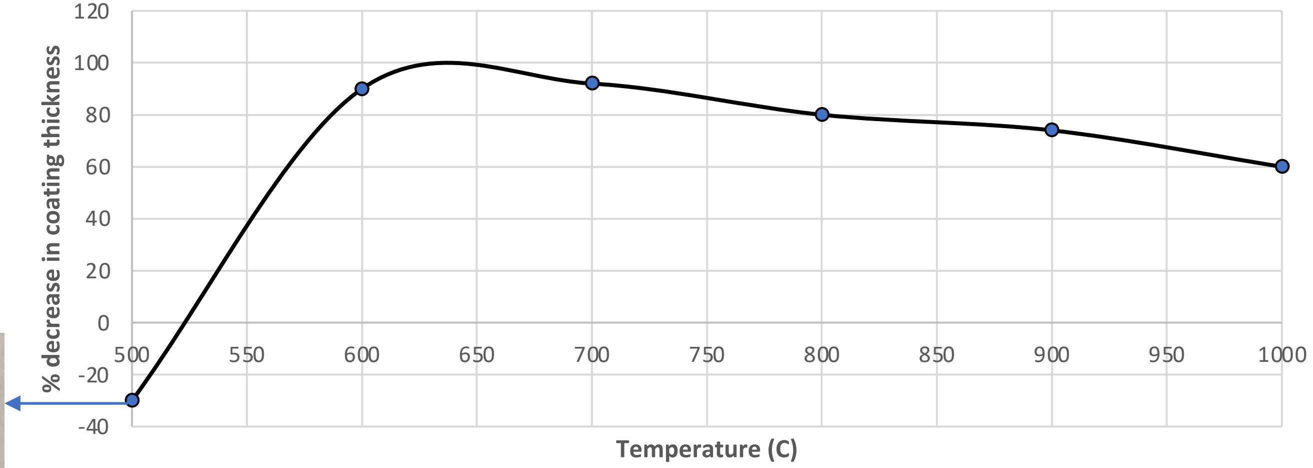


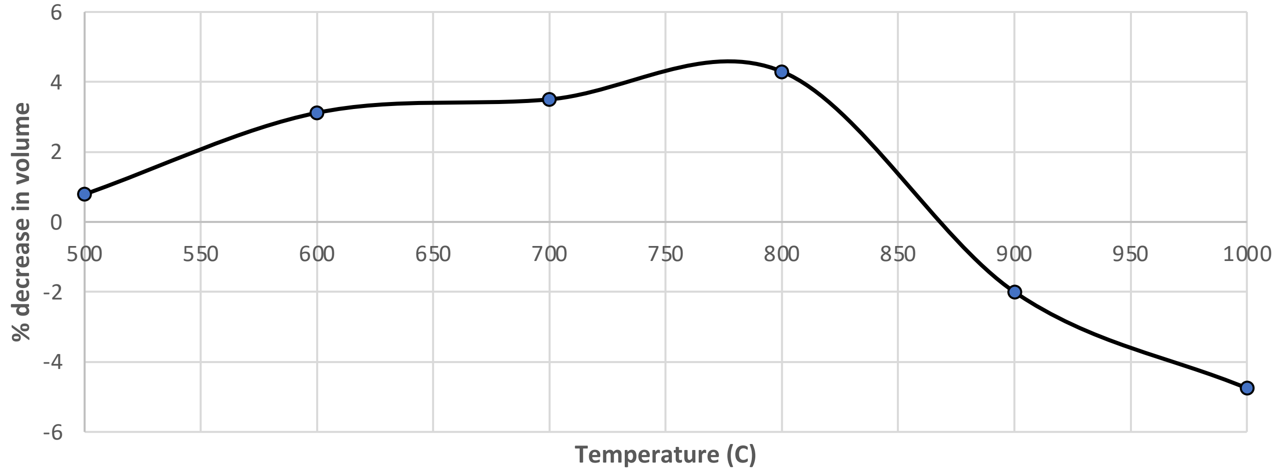


Activation energy = 78.52 kJ/mol

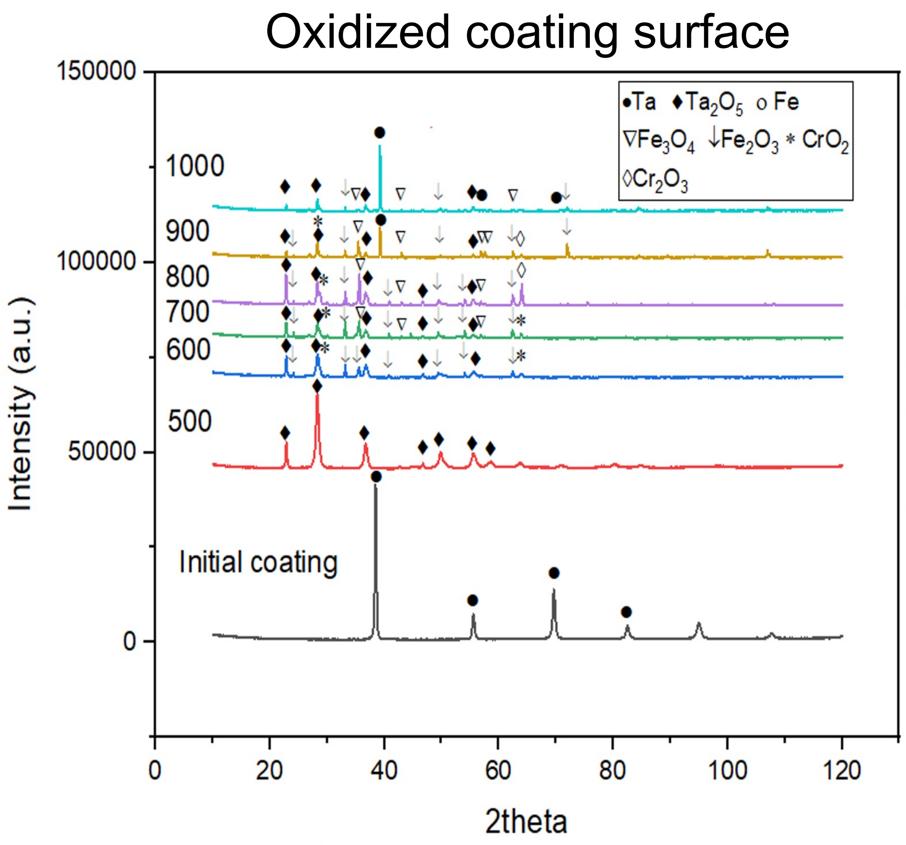
Results- Ta cold-sprayed 4130 steel

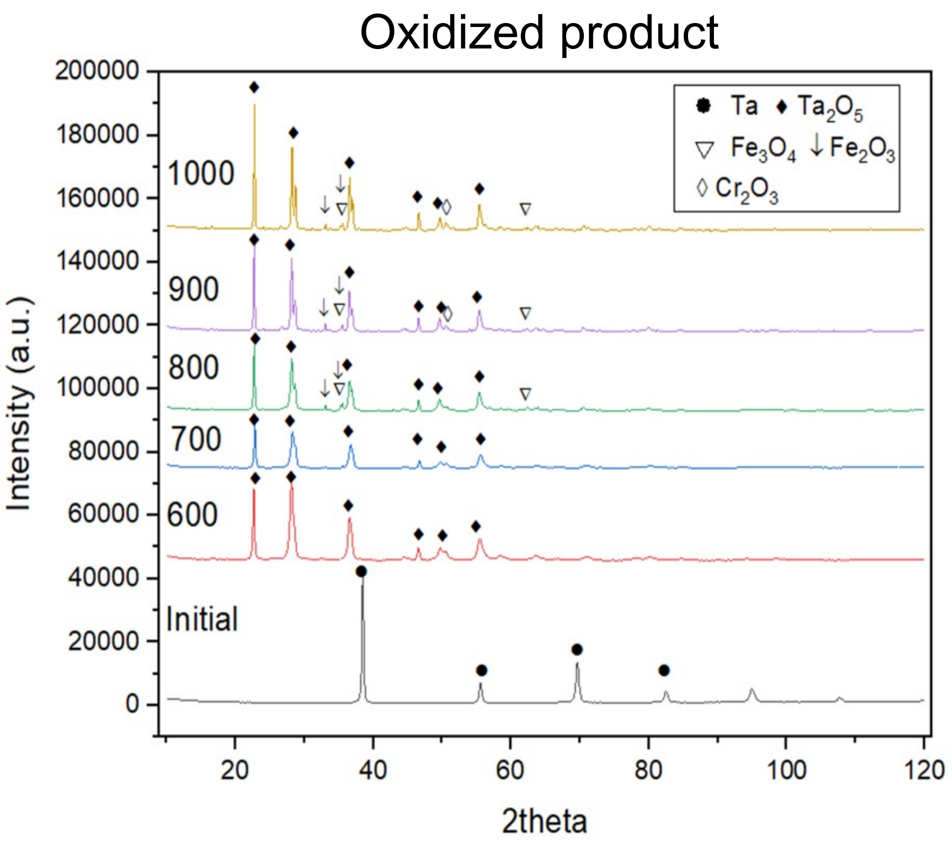




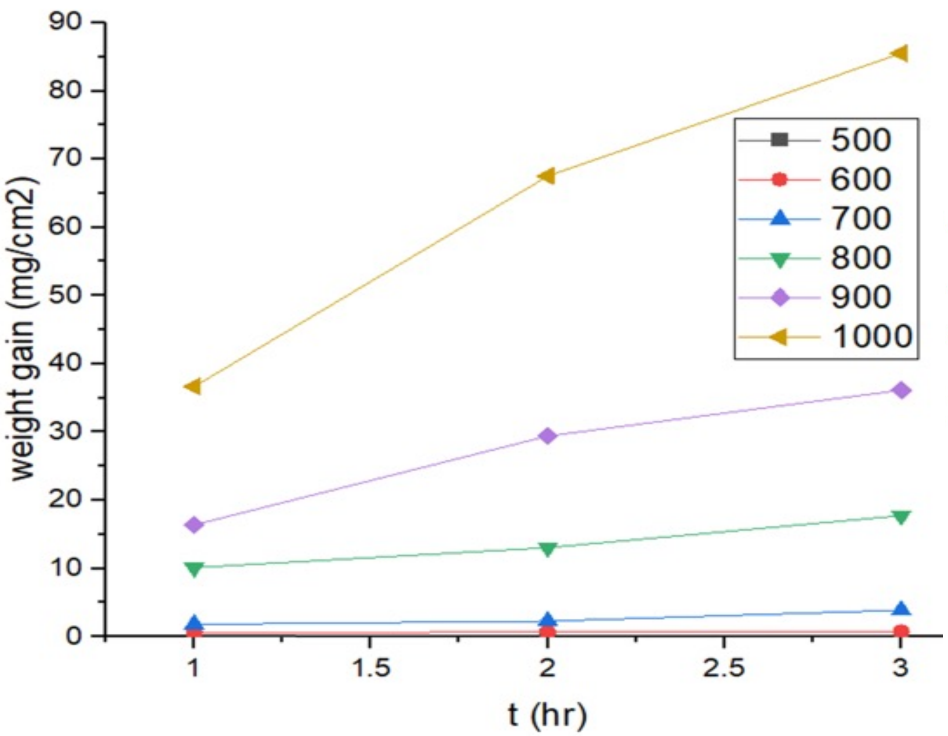


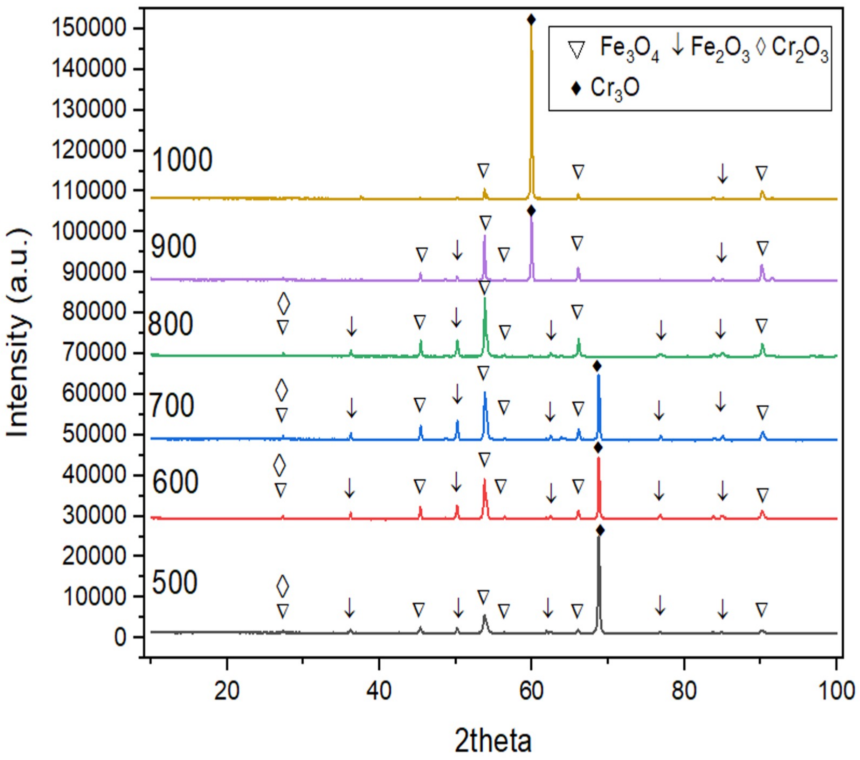
XRD- Ta cold-sprayed 4130 steel





Oxidation of 4130 steel substrate





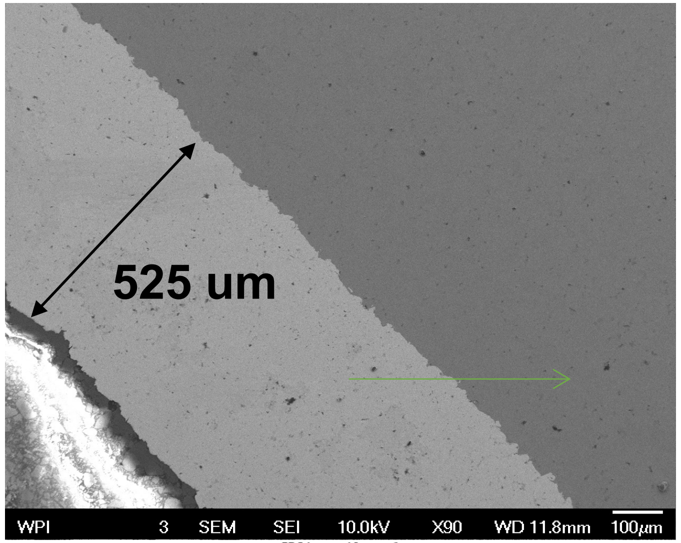
Sample	Activation energy (kJ/mol)
Ta cold-sprayed 4130	78.52
4130 steel	101.31

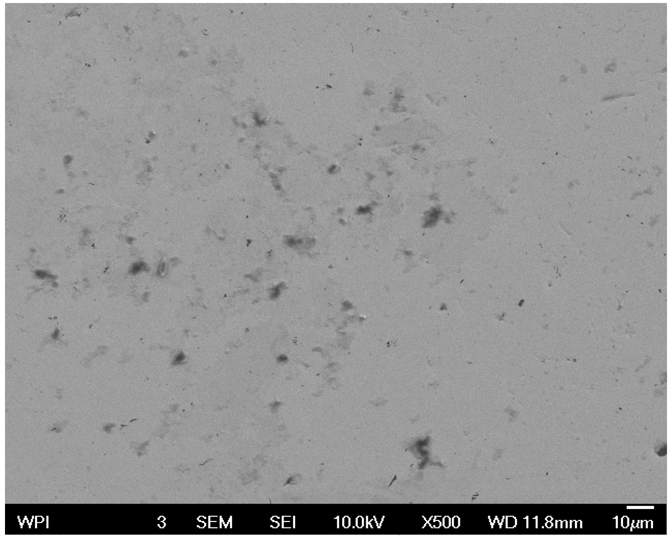
Conclusion

- With increasing temperature, Ta_2O_5 recovery increases in the product, as observed from XRD. It is also observed that ~90% of coating thickness is reduced for temperatures 600C and 700C.
- With increasing temperature from 800C to 1000C, Ta_2O_5 recovery increased but so did oxidation of steel substrate.
- Thus, from 500-700C, relatively lower substrate oxidation and higher Ta_2O_5 recovery is observed.

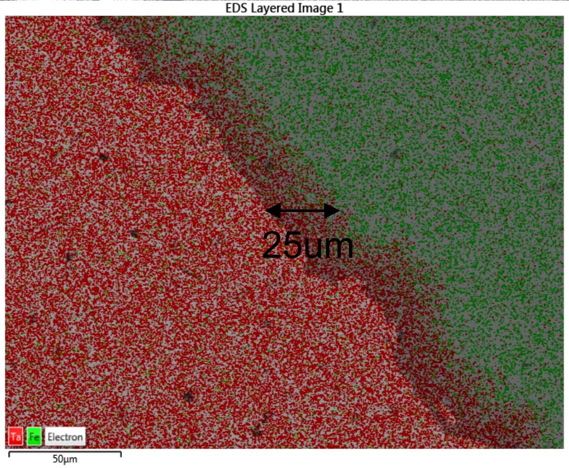
Sample 2: Ta cold-sprayed A36 steel

Sample information- Tantalum cold-sprayed A36 steel





EDS Layered Image 1



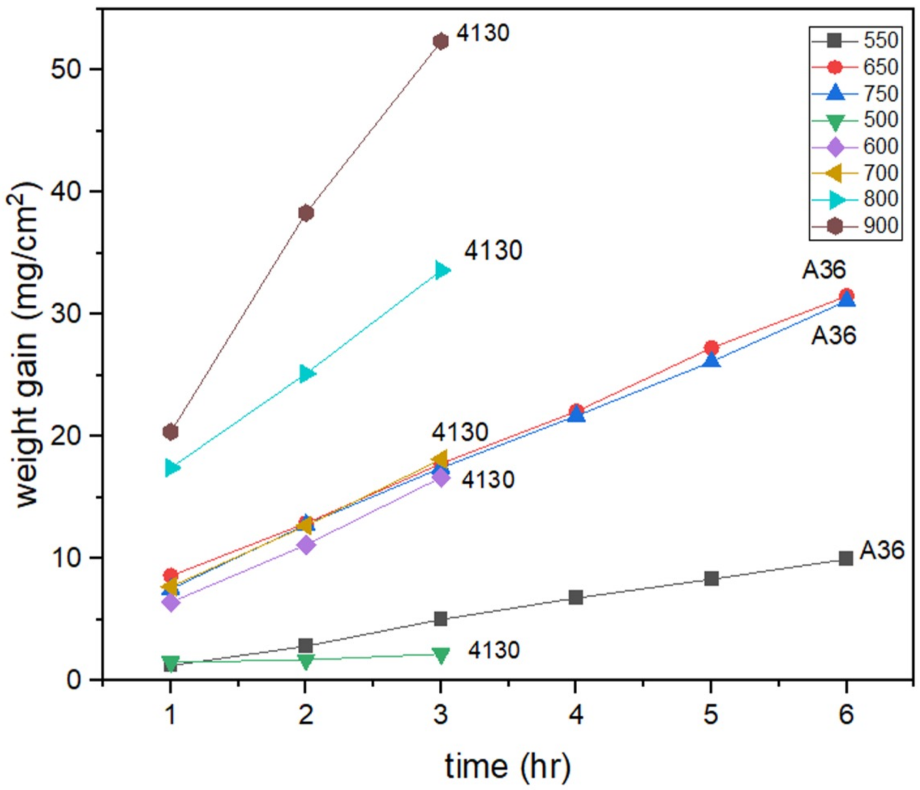
Element	Content
Carbon, C	0.25 - 0.290 %
Copper, Cu	0.20 %
Iron, Fe	98.0 %
Manganese, Mn	1.03 %
Phosphorous, P	0.040 %
Silicon, Si	0.280 %
Sulfur, S	0.050 %

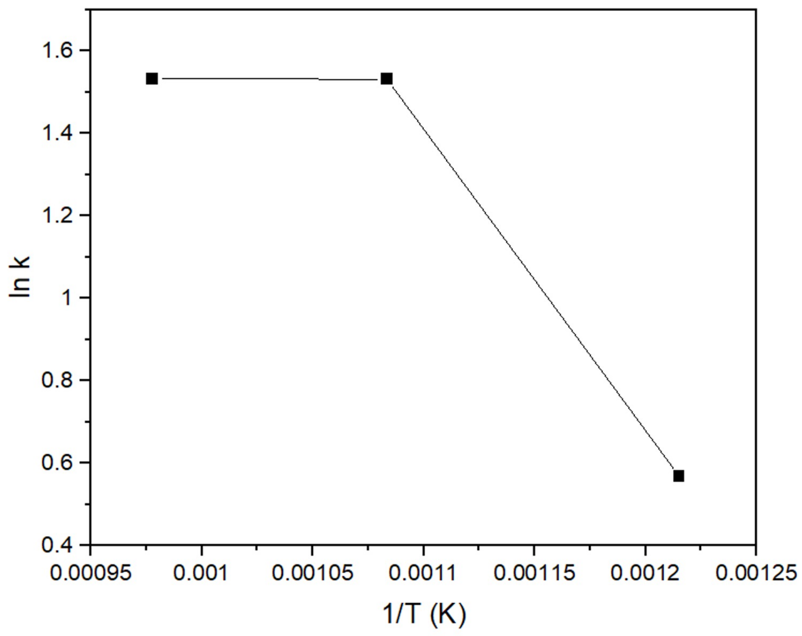
Experimental design- Tantalum cold-sprayed A36 steel

Variable: Temperature (550, 650, 750C), time (4, 5, 6hrs)

Experiment #	Temperature (C)	Time (hr)
1	550	4
2	550	5
3	550	6
4	650	4
5	650	5
6	650	6
7	750	4
8	750	5
9	750	6

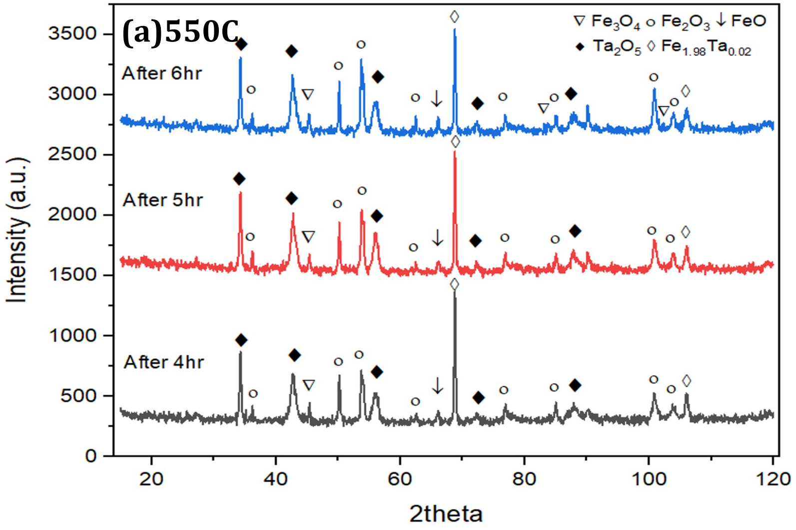
Results- Tantalum cold-sprayed A36 steel

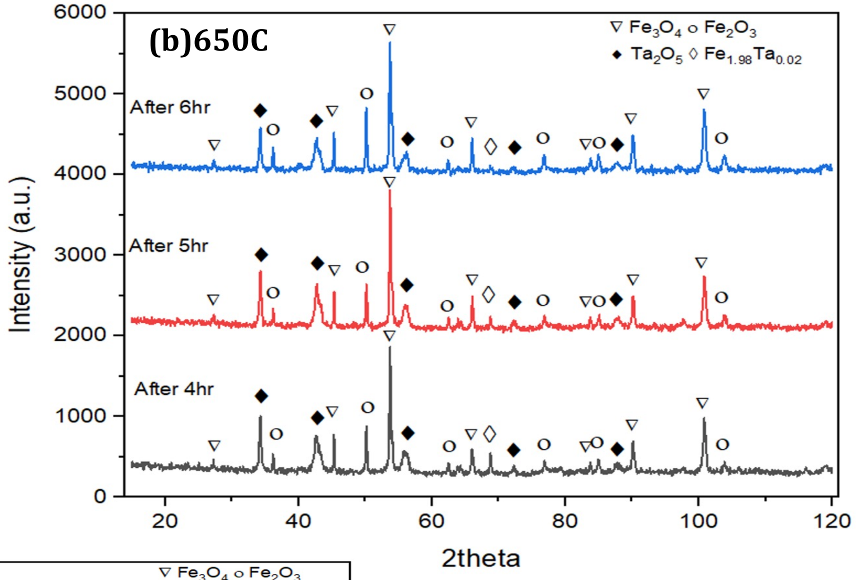


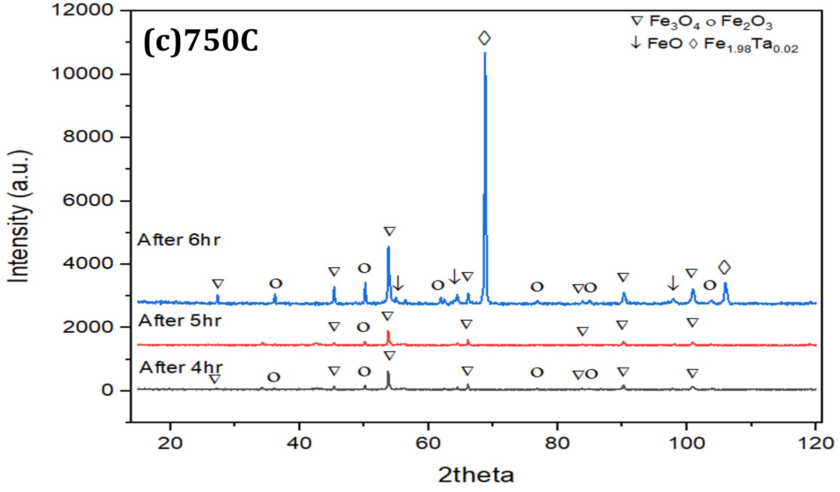


Sample	Temperature (C)	Activation energy (kJ/mol)
Ta cold-sprayed 4130	500-800	68.67
Ta cold-sprayed A36 steel	550-750	34.9

XRD analysis of oxidized coating surface

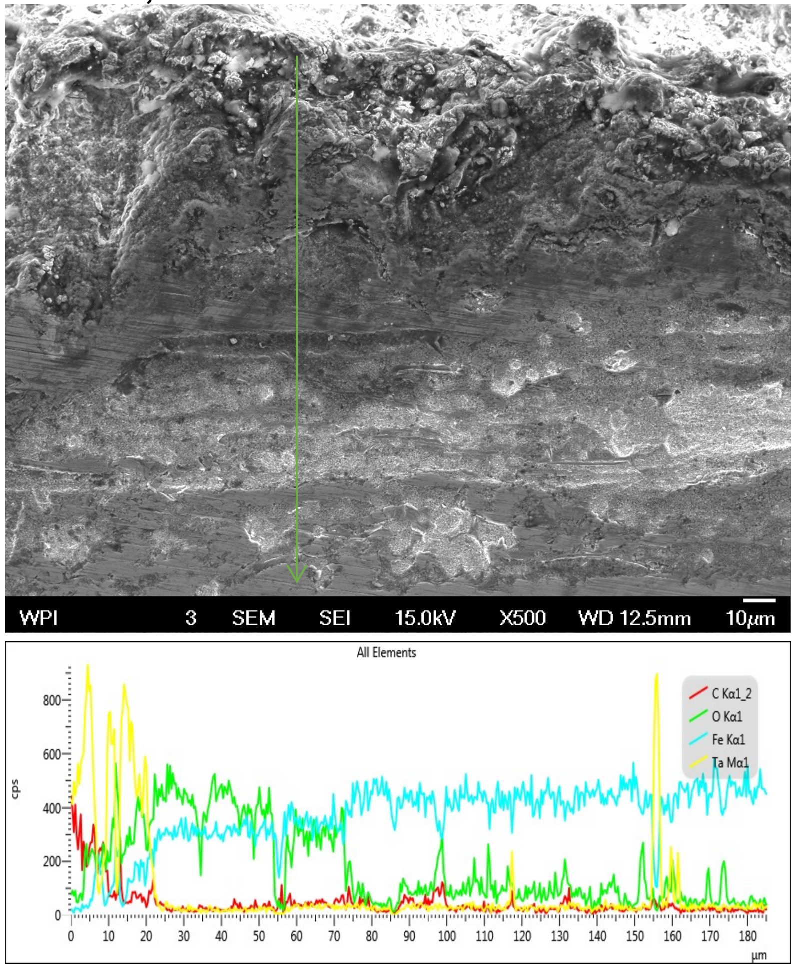




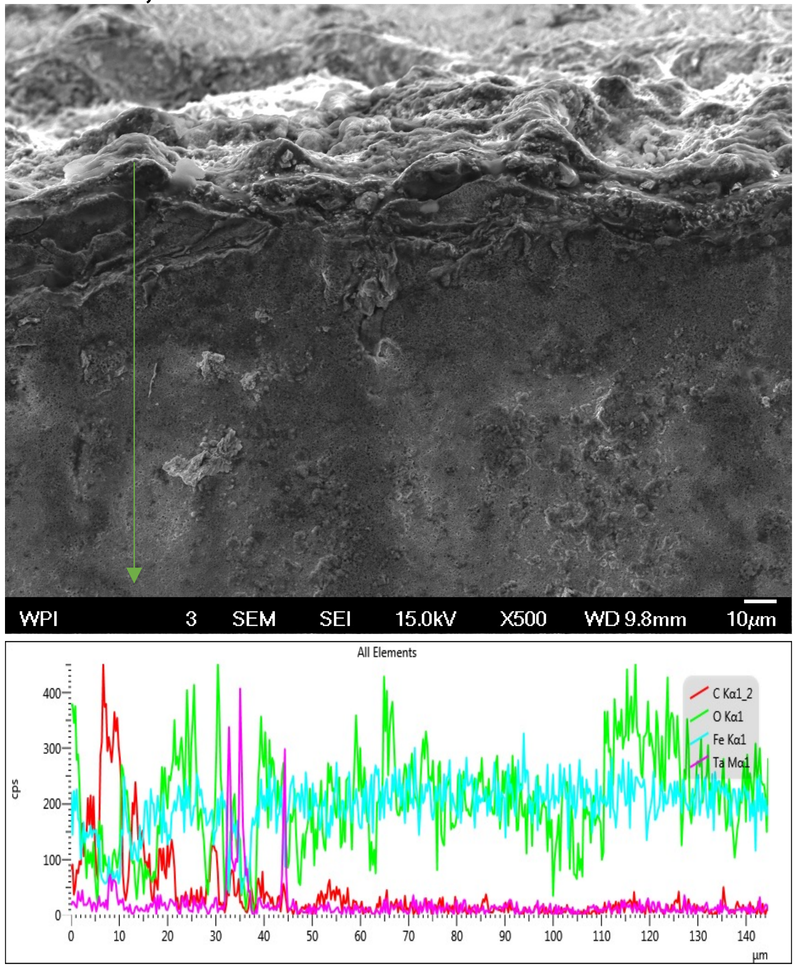


SEM at the interface

550C, 4hr

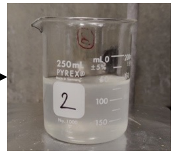


650C, 4hr



Determining % Purity

No.	Flux	Acid	Result
1	-	HNO_3 + HF	Sample settled at the bottom of the beaker
2	-	15M HNO_3 + H_2O + 40% HF	Colloidal solution and some sample settles at the bottom
3	-	H_2SO_4 heated to 50C + HF	Sample settles at the bottom
4	3 LiT: 2 LiM	25% HNO_3 (4M)	Sample settles at the bottom
5	LiT	25% H_3PO_4 (4.3M)	Colloidal solution (more clear)
6	LiT (1:40)	6.14M H_3PO_4 + HF	Colloidal solution (more clear)
7	3 LiT: 2 LiM	6.14M H_3PO_4 + HF	Colloidal solution (less clear)



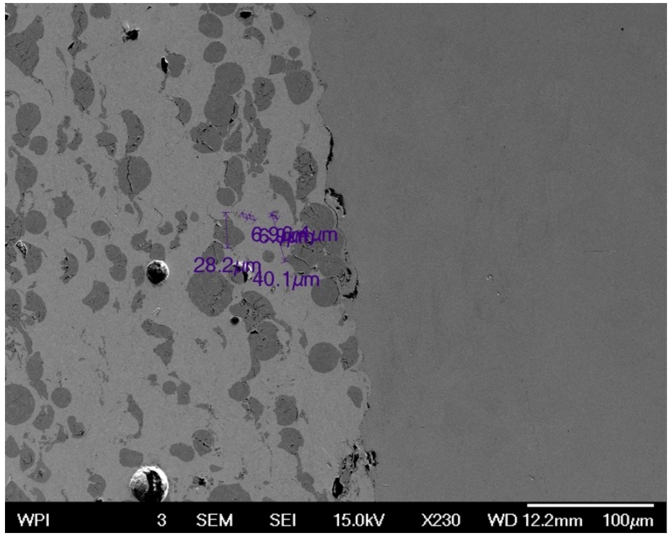
- Conclusion: Fusion shows the best result, and will be explored further to determine the purity %

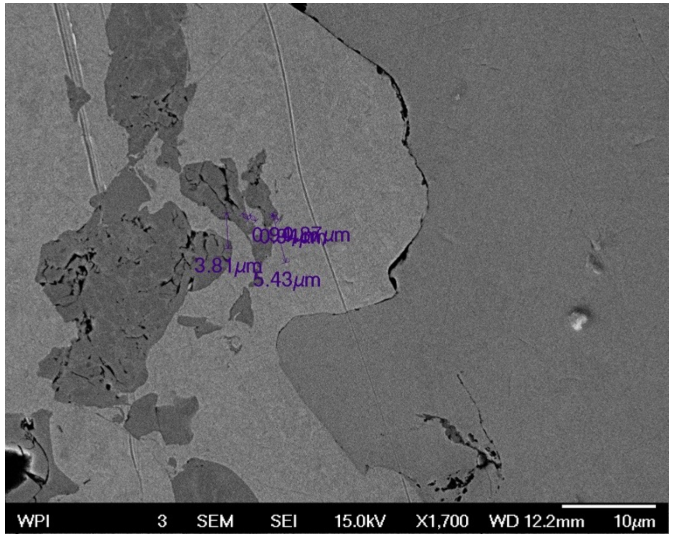
Future Work

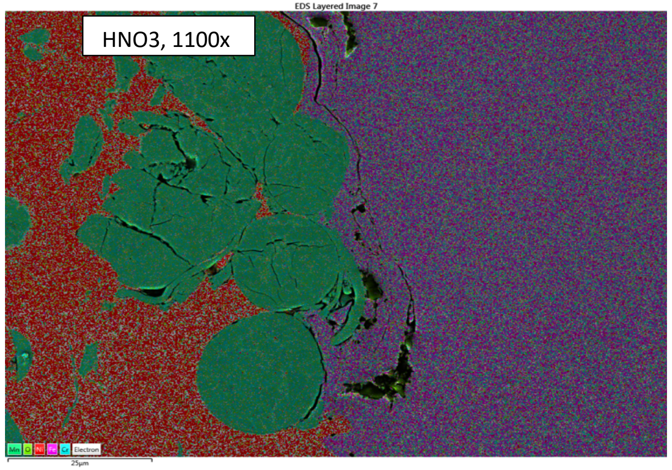
- Oxidation kinetics of pure Ta, A36 steel and 4130 steel between 500-1000C using TGA
- Oxidation kinetics of A36 steel substrate
- Determining the % recovery and % purity of oxidation products by using a suitable flux to analyze with ICP-OES
- Determining migration rate of major elements (Fe, Ta) during oxidation

CrC-NiCr cold-sprayed 316 stainless steel

- Coating thickness = 2.5mm
- Coating composition = 80% Ni, 20% Cr; measured by ICP-OES
- No interdiffusion interface

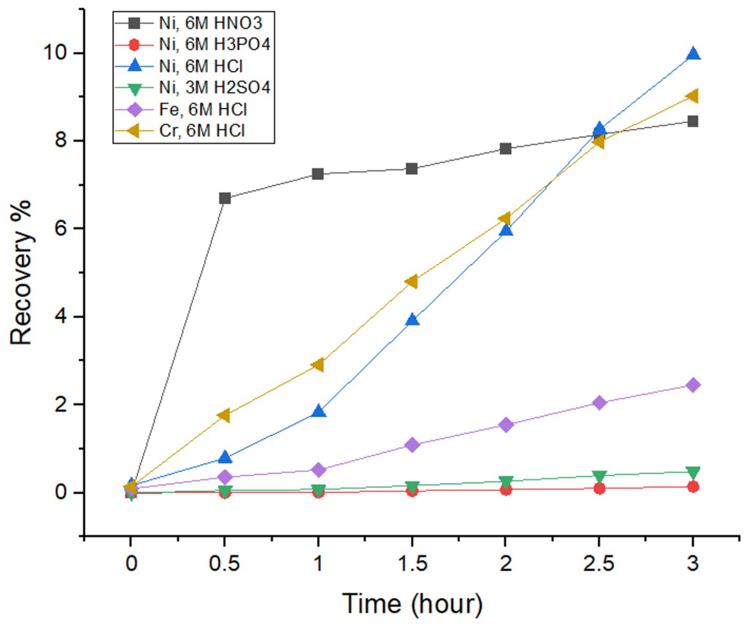


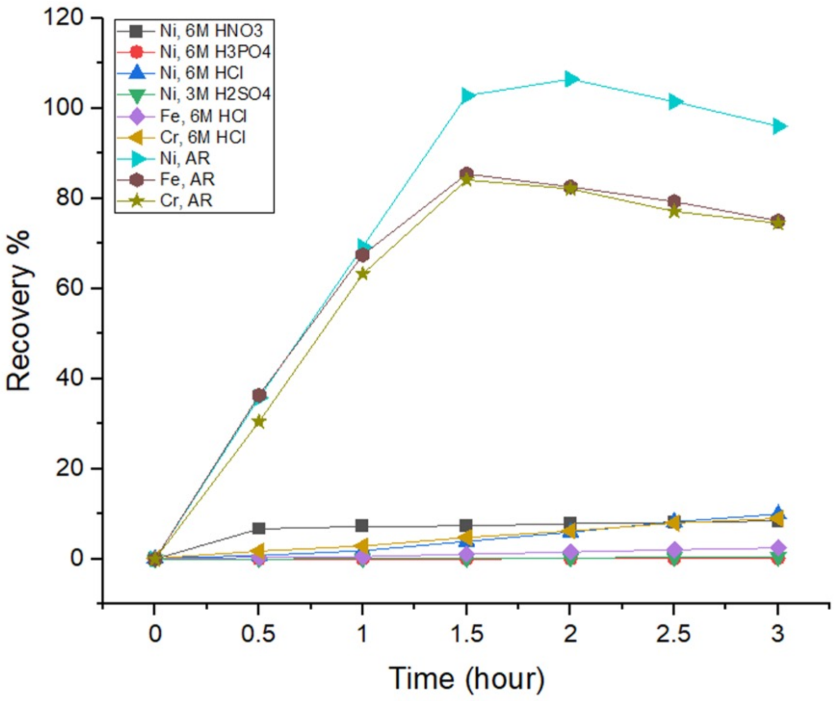




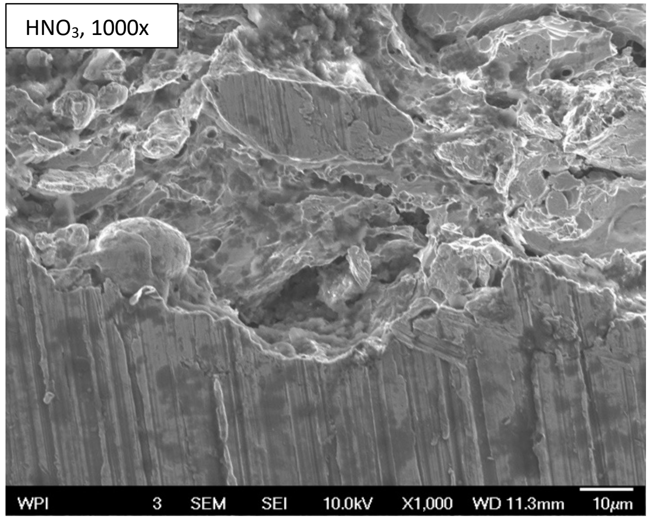
Acid leaching

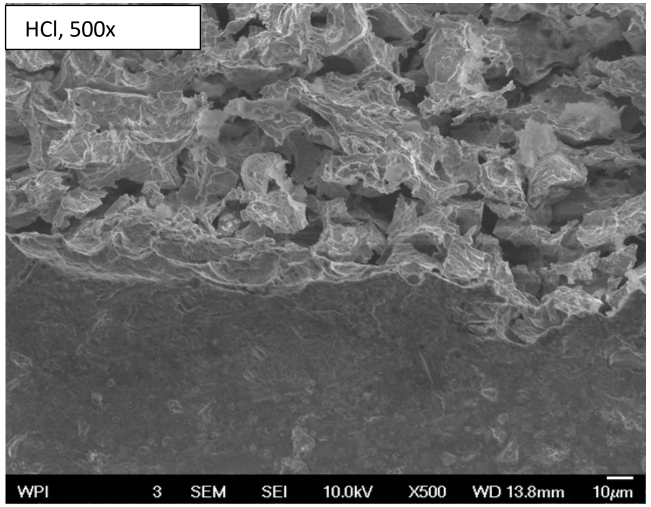
Effect of type of acid:
Variable: Acid type
Constant: time = 3hrs, temperature = 50C, concentration = 6M except 3M in case of H_2SO_4

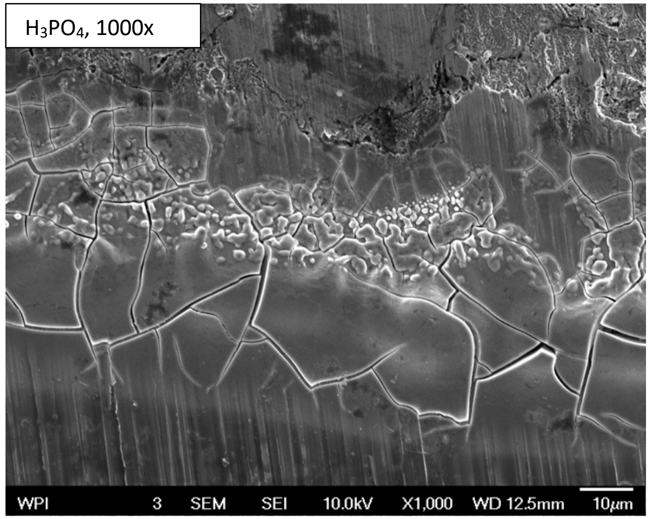




SEM analysis at interface between coating and substrate







- At the Interface:

Initial

Element	Wt%
Ni	27.4
Fe	31.7
Cr	29

After H_3PO_4 leaching

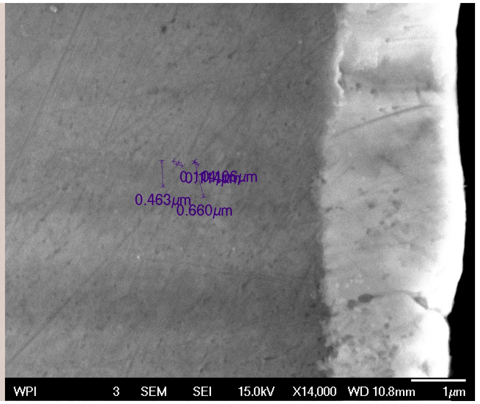
Element	Wt%
Ni	32.5
Fe	17.9

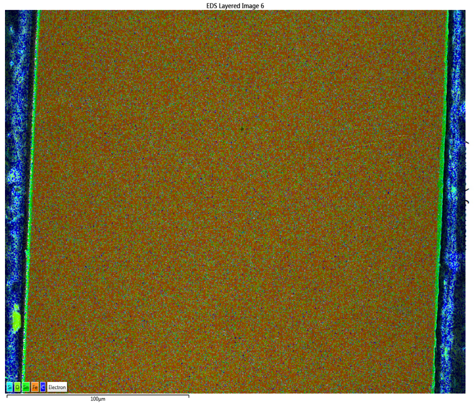
Future work:

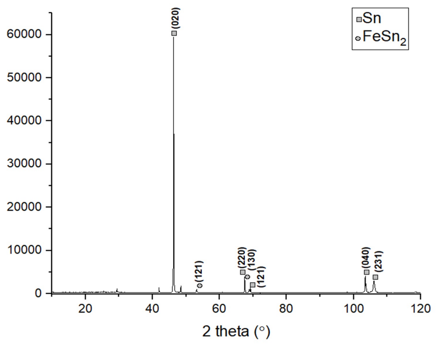
- Electrodeposition of CrC-NiCr coating on a suitable cathode
- Remelting and adjusting of composition to reproduce steel

Sample information: Tin coated steel

- Samples procured from SMS Group
- Dip coated
- Coating thickness = 1.5um, measured by SEM-EDX







Future work:

- Electrolytic stripping of Sn from steel substrate
- Alkaline detinning followed by electrowinning

THANK YOU