Trace Element Control in Master Alloys and Impact of Feedstock Purity on a Ta-containing Steel during Electroslag Remelting

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AASC Advanced Alloys Signature Center

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Alloy Fabrication Current Capabilities

Melt Processing Capabilities

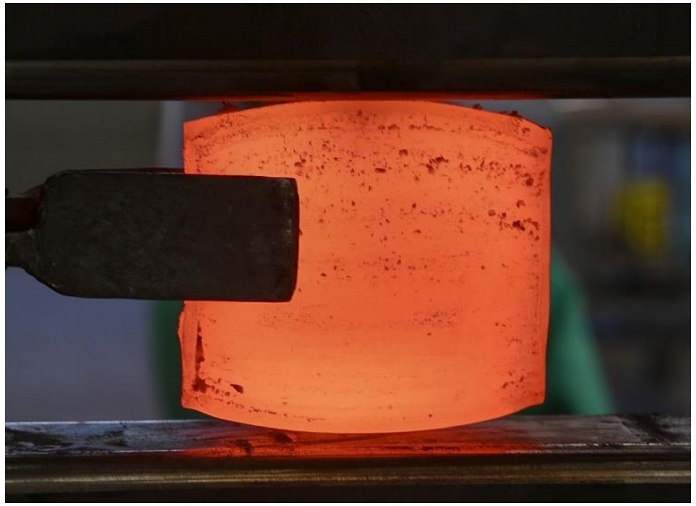
- Air Induction Melting: up to 300 lbs
- VIM: 15, 50 and 500 lbs
- Vacuum Arc Remelt/Electro-Slag Remelt 3-to-8-inch diameter ingots

Thermo-Mechanical Processing Capabilities

- Heat-treatment furnaces:1650^{o}C, inert atmospheres and controlled cooling.
- Press Forge: 500 Ton
- Roll mills: 2 and 4 high configurations.

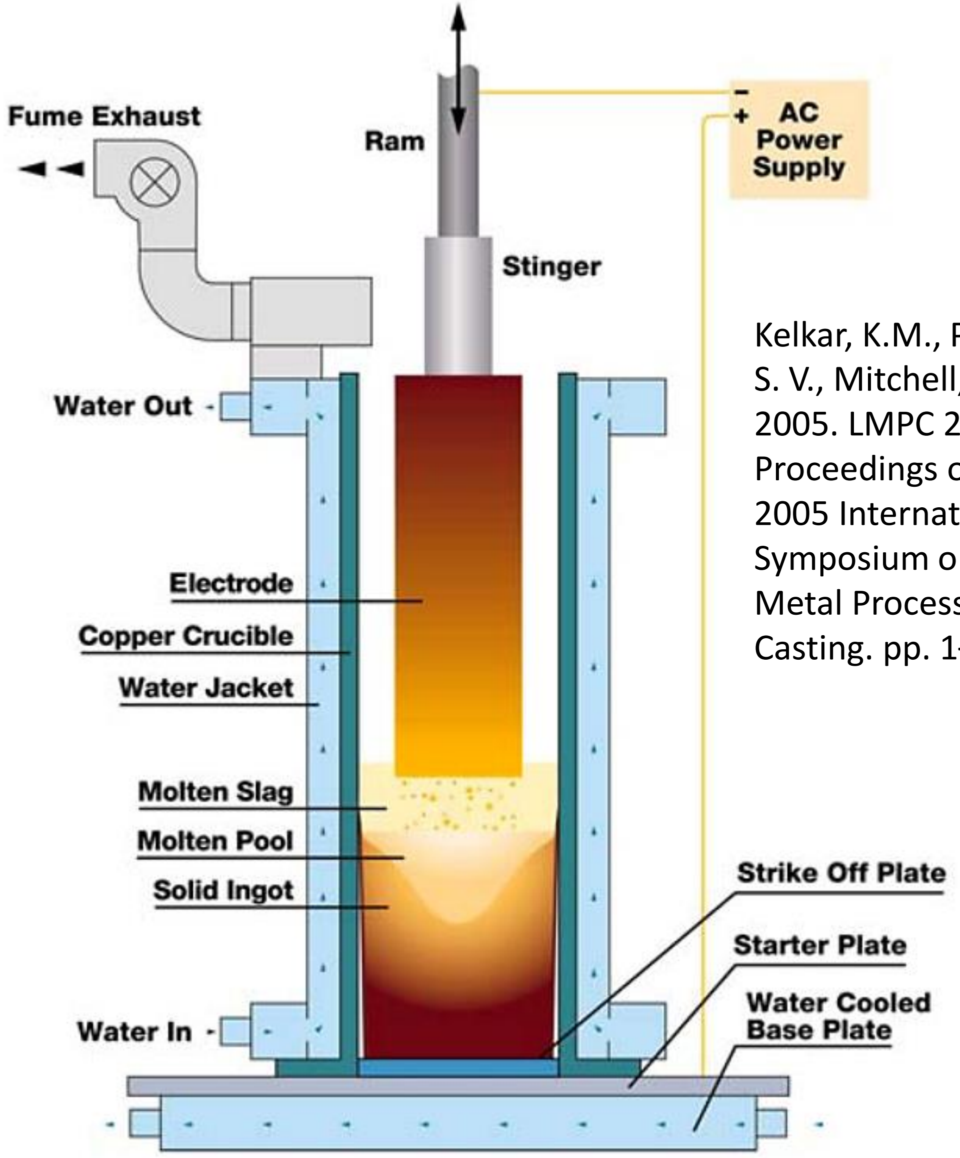
Research Scale Alloy Fabrication

- 8 kg ingots produced using VIM with industry grade feedstock.
- Chemistry slices cut for XRF and combustion analysis.
- Homogenization following a computationally optimized heat treatment.
- Hot working using steps of forging followed by steps of hot rolling to form 10 mm thick plates.
- Heat treatment design.
- Mechanical testing following ASTM standards.



Electroslag Remelting (ESR)

- ESR is a widely used process to produce materials in which cleanliness is of upmost importance.
- A consumable electrode is cast using VIM and placed in a water-cooled crucible that contains a slag.
- Electrical current passes from the electrode through the slag to the bottom of the crucible.
- Liquid metal droplets travel from the bottom of the electrode to the crucible where the ESR ingot forms.
- The droplets are superheated and reactions occur leading to the removal of tramp elements.
- VIM and ESR are essential at controlling the concentration of undesirable elements such as O and S.

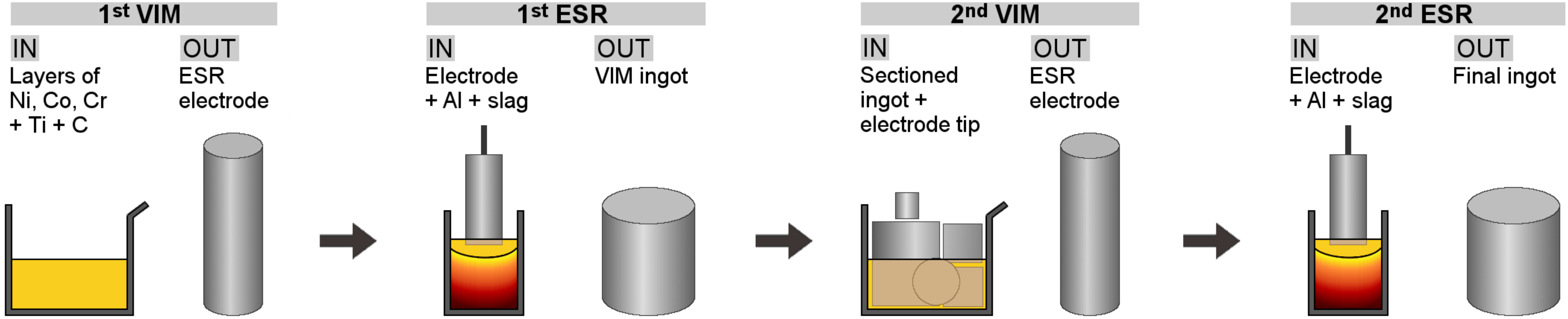


Kelkar, K.M., Patankar, S. V., Mitchell, A., 2005. LMPC 2005: Proceedings of the 2005 International Symposium on Liquid Metal Processing and Casting. pp. 1–8.

Introduction

Topic 1: Trace Element Control in Master Alloys

- Need for greater thermo-mechanical properties of alloys used in power generation applications
- Control the concentrations of O, S, N to reduce the amount of inclusions (TiN, oxides, …)
- Prevent fatigue crack nucleation, interface embrittlement, oxide scale adhesion.
  - Use VIM/ESR
  - Make master alloys: Ni-25Cr, Ni-30Co-30Cr



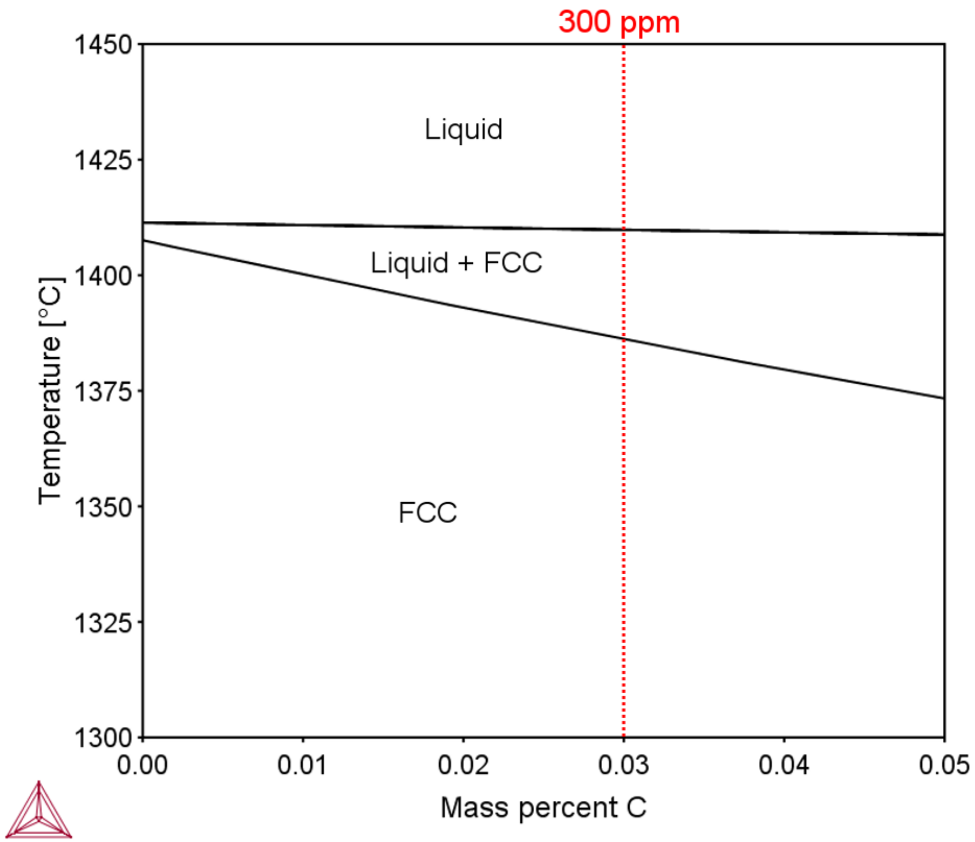
Elemental Additions

Topic 1: Trace Element Control in Master Alloys

Carbon to the VIM melt:

- Melt range of 4 °C in Ni-25Cr
- Increases 6 times to 24 °C with 300 ppm C
- Improves the solidification characteristics
  - Increases the volume of the mushy zone
  - Reduces the enthalpy of solidification

Al to enhance desulphurization during ESR



Slag used in the experiments:

Slag chemistry (wt.%):

CaF_2	CaO	MgO	Al_2O_3	SiO_2	C	S	MnO_2	Fe	TiO_2	P	LOI
38.94	31.50	0.691	28.81	0.16	0.001	0.013	0.006	0.054	0.102	<0.01	0.036

Elemental Additions

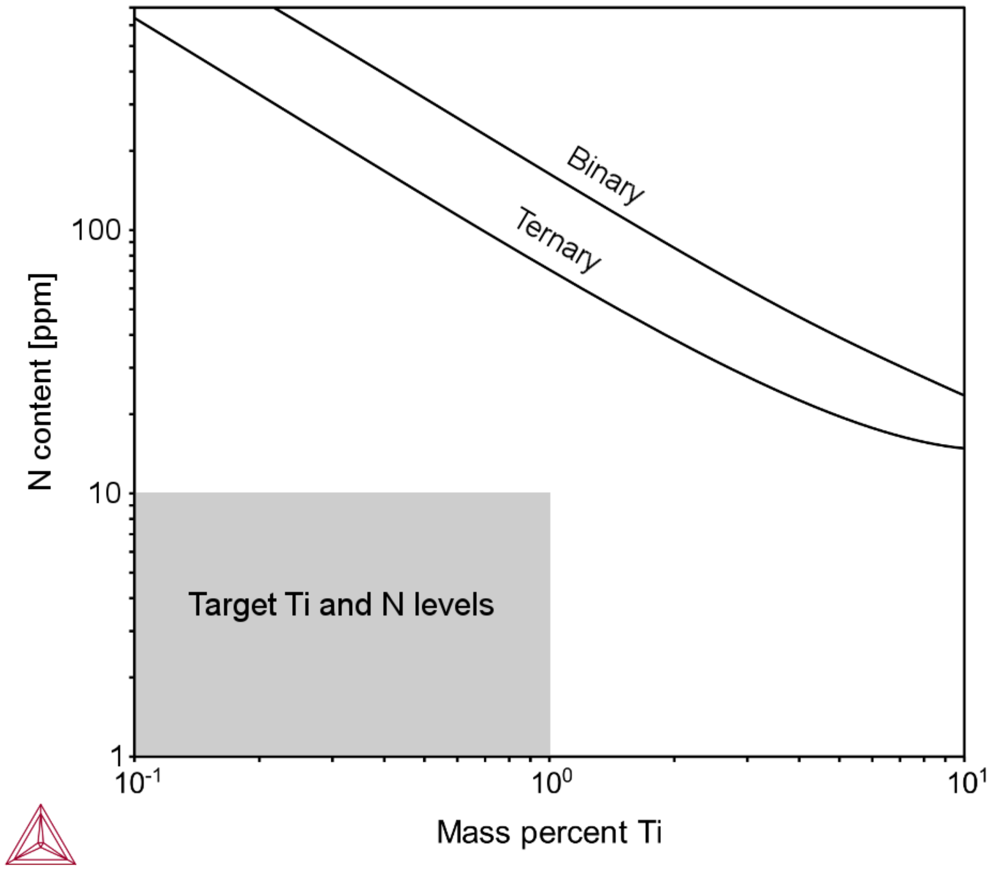
Topic 1: Trace Element Control in Master Alloys

Titanium additions to the VIM melt:

- Cr used contains 5200 ppm O
- Need low O levels following VIM
- Ti is a known deoxidizer:

$$[\mathrm{Ti}]_{\mathrm{metal}} + (\mathrm{O_2})_{\mathrm{g}} \rightarrow [\mathrm{TiO_2}]_{\mathrm{metal}}$$

- Gibbs energies for oxidation reactions of Ti -634 kJmol^{-1} and Cr -455 kJmol^{-1}
- Cr used contains 50 ppm N
- Potential for formation of TiN

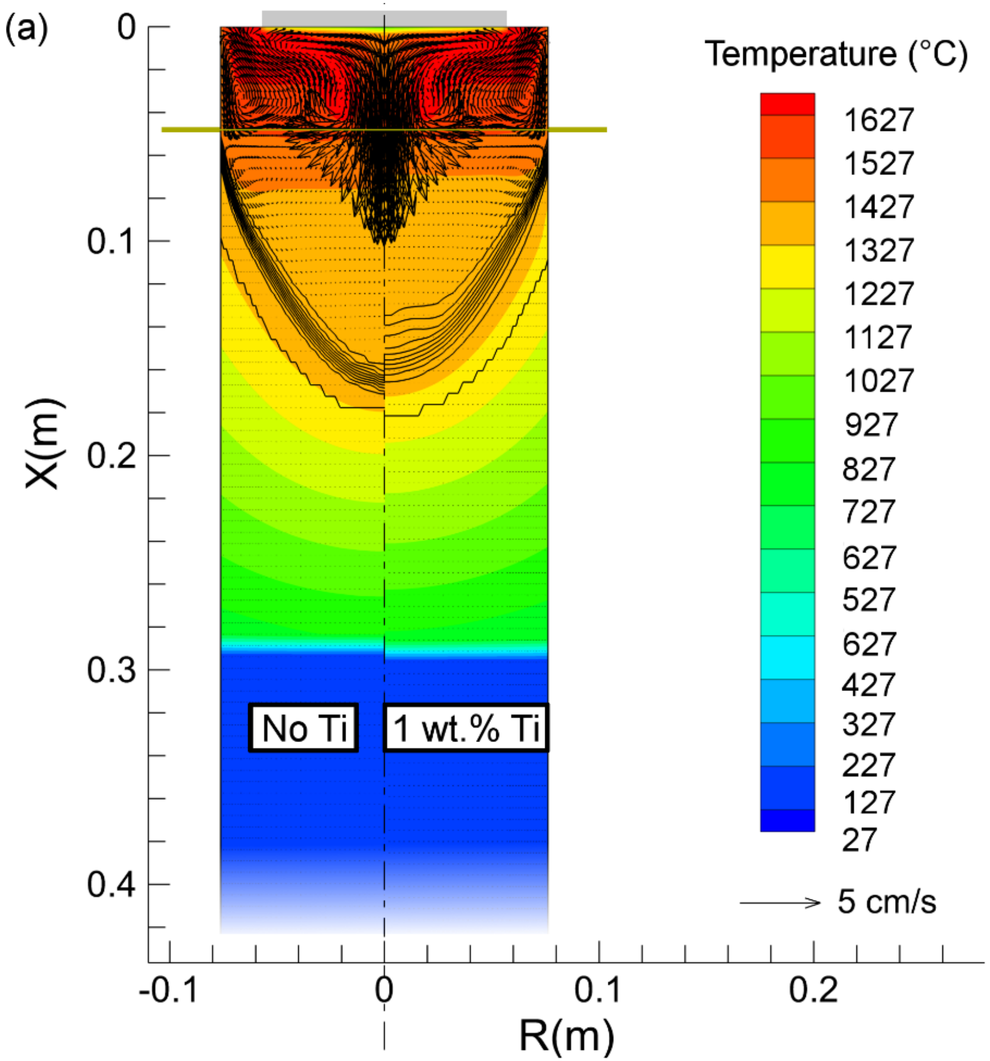


MeltFlow-ESR Simulations

Topic 1: Trace Element Control in Master Alloys

Effect of Ti addition to ESR process

- Simulations using dimensions and melt data from experiments
- Added thermophysical properties from JMatPro and ThermoCalc
- C – 300 ppm / N – 10 ppm
- Steady state of remelting
- Liquid fraction lines are more spread out
- High liquid velocities in the slag, below the electrode
- Two flow cells

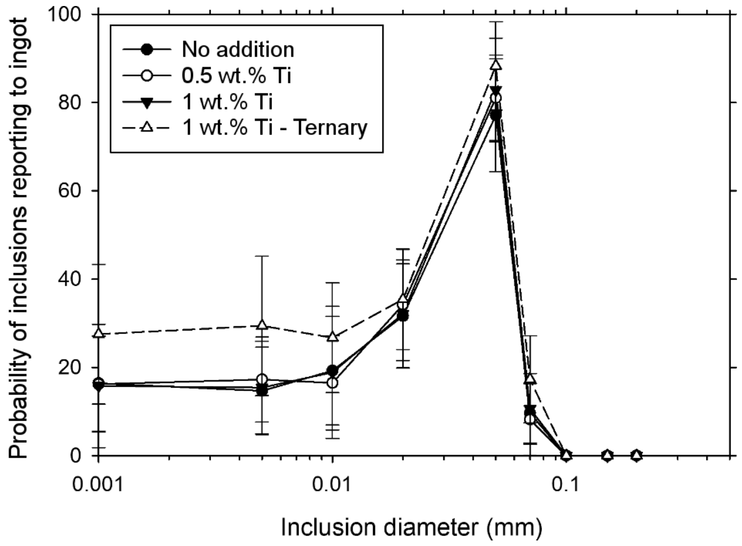


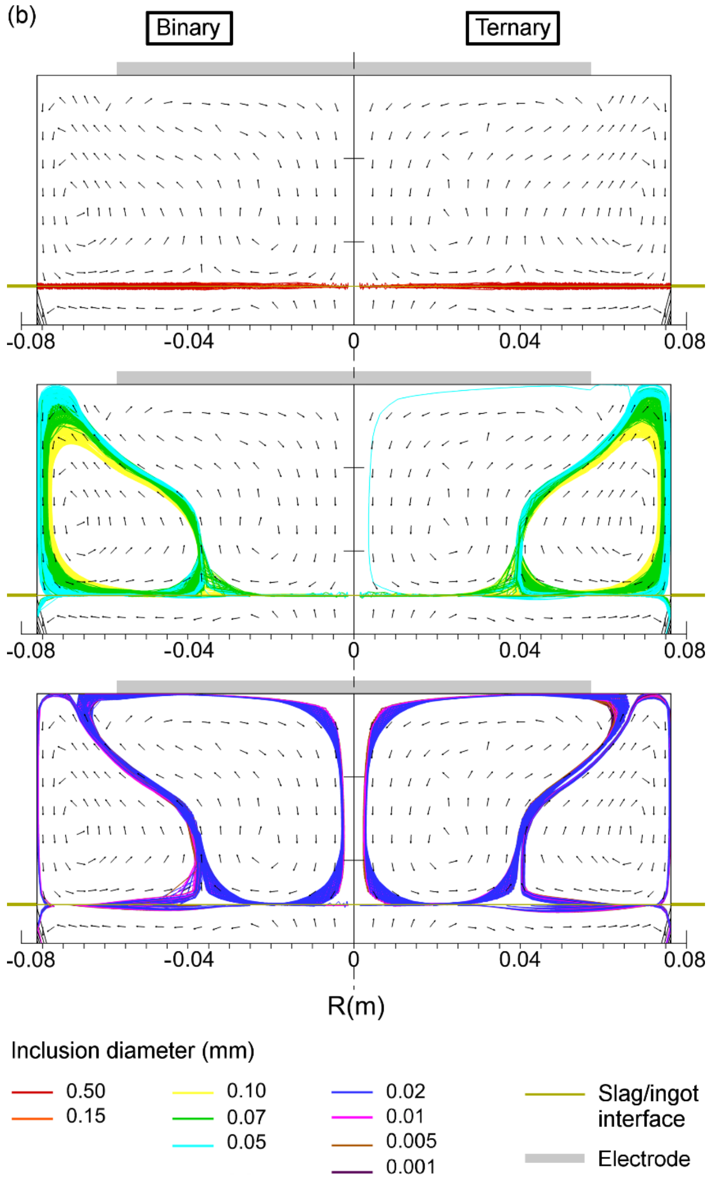
MeltFlow-ESR Simulations

Topic 1: Trace Element Control in Master Alloys

Effect of Ti addition to ESR process

- Inclusion trajectories.
- Larger inclusions remain at the slag/ingot interface.
- Medium-sized particles travel around the outer flow cell.
- High probability of going into the ingot.
- The smaller inclusions preferentially travel in the flow cell beneath the electrode.
- Lower Ti additions should be considered in the ternary master alloy.





Chemistry

Topic 1: Trace Element Control in Master Alloys

Melt		Ni (wt.%)	Cr (wt.%)	Co (wt.%)	Ti (wt.%)	Al (wt.%)	C (ppm)
Ni-25Cr							
1st VIM	IN	Bal.	24.7	-	1.00	-	323
	OUT	Bal.	24.4	<0.001	0.76	0.01	350 ± 7
1st ESR	IN	-	-	-	-	0.07	-
	OUT	Bal.	24.4	<0.001	0.52	0.07	357 ± 10
2nd VIM	IN	-	-	-	-	-	-
	OUT	Bal.	24.4	<0.001	0.53	0.13	349 ± 30
2nd ESR	IN	-	-	-	-	0.08	-
	OUT	Bal.	24.5	<0.001	0.44	0.12	377 ± 48
Ni-30Co-30Cr							
1st VIM	IN	Bal.	29.8	29.8	0.50	-	262
	OUT	Bal.	29.7	30.4	0.24	0.02	289 ± 4
1st ESR	IN	-	-	-	-	0.07	-
	OUT	Bal.	29.7	30.4	0.12	0.04	322 ± 75
2nd VIM	IN	-	-	-	-	-	-
	OUT	Bal.	29.4	30.1	0.17	0.05	303 ± 30
2nd ESR	IN	-	-	-	-	0.07	-
	OUT	Bal.	29.4	30.2	0.10	0.05	290 ± 2

Melt		N (ppm)	O (ppm)	S (ppm)
Ni-25Cr				
1st VIM	IN	13	1318	42
	OUT	8 ± 3	103 ± 86	44 ± 3
1st ESR	OUT	10 ± 3	66 ± 56	19 ± 1
2nd VIM	OUT	5 ± 4	46 ± 22	15 ± 1
2nd ESR	OUT	5	31	6 ± 2
Ni-30Co-30Cr				
1st VIM	IN	16	1596	63
	OUT	2 ± 1	76 ± 32	50 ± 2
1st ESR	OUT	4 ± 2	67 ± 26	20 ± 4
2nd VIM	OUT	9 ± 1	60 ± 1	19 ± 3
2nd ESR	OUT	10 ± 1	65 ± 23	8 ± 1

Chemistry

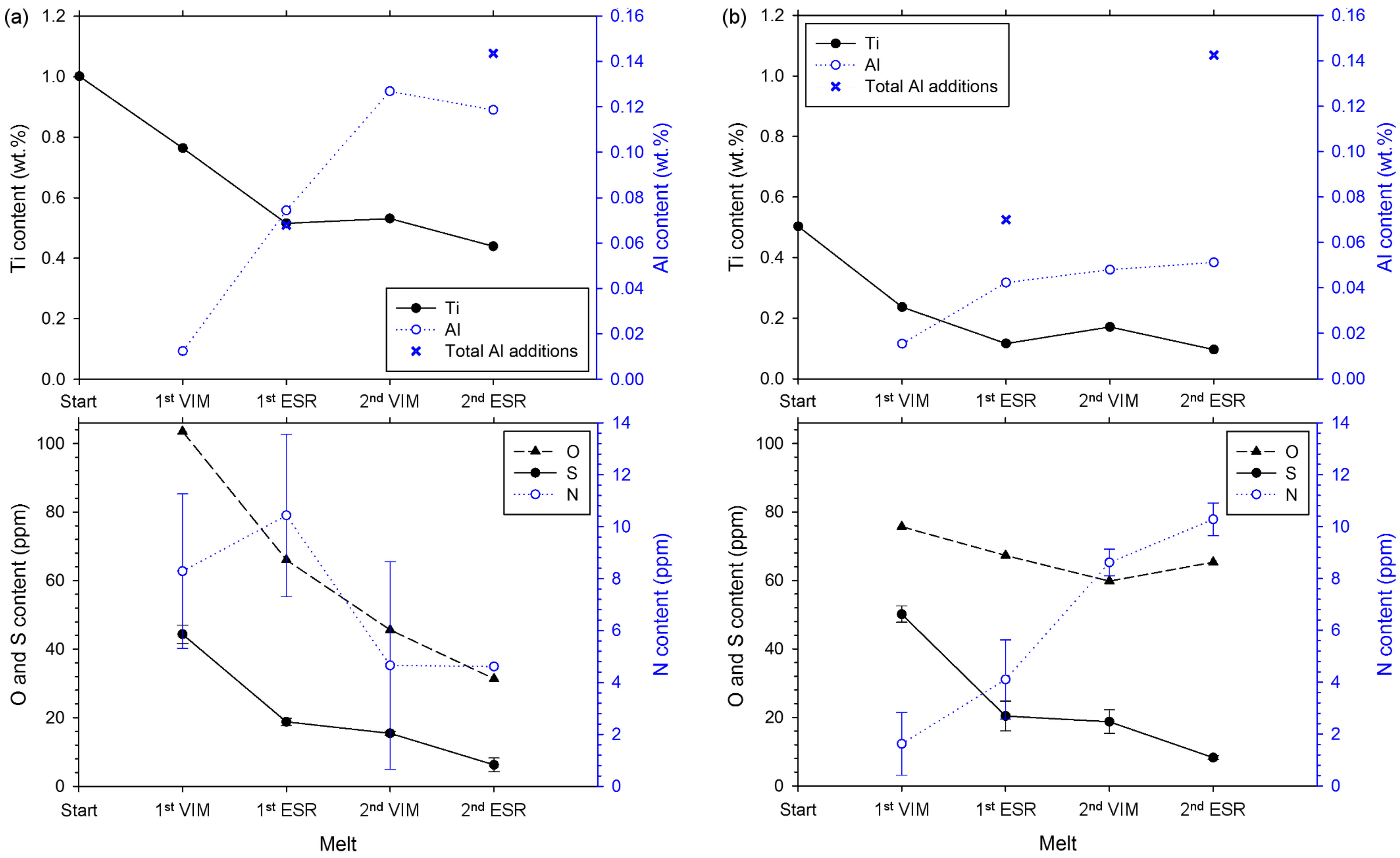
Topic 1: Trace Element Control in Master Alloys

(a)

Ni-25Cr

(b)

Ni-30Co-30Cr



Topic 1: Trace Element Control in Master Alloys

Fig. 1

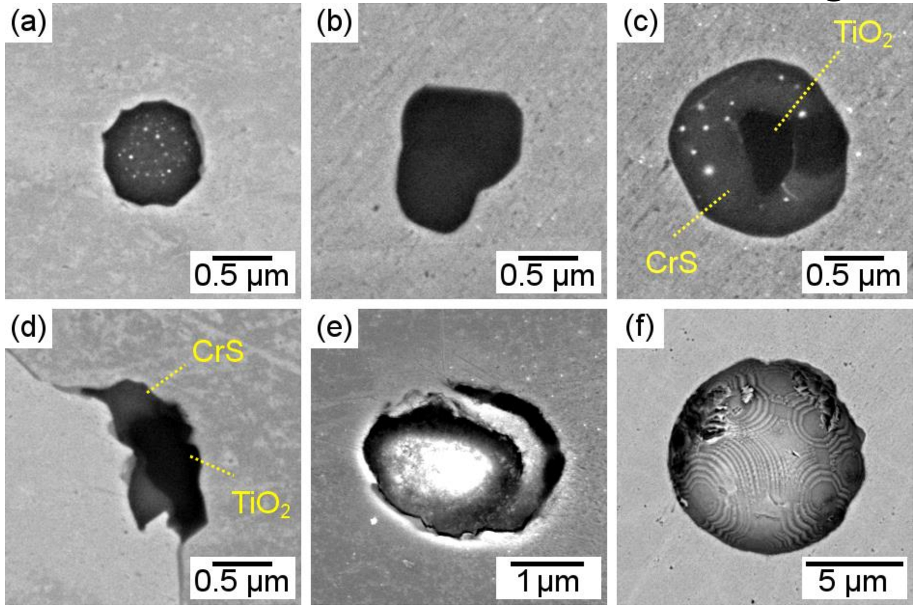


Fig. 2

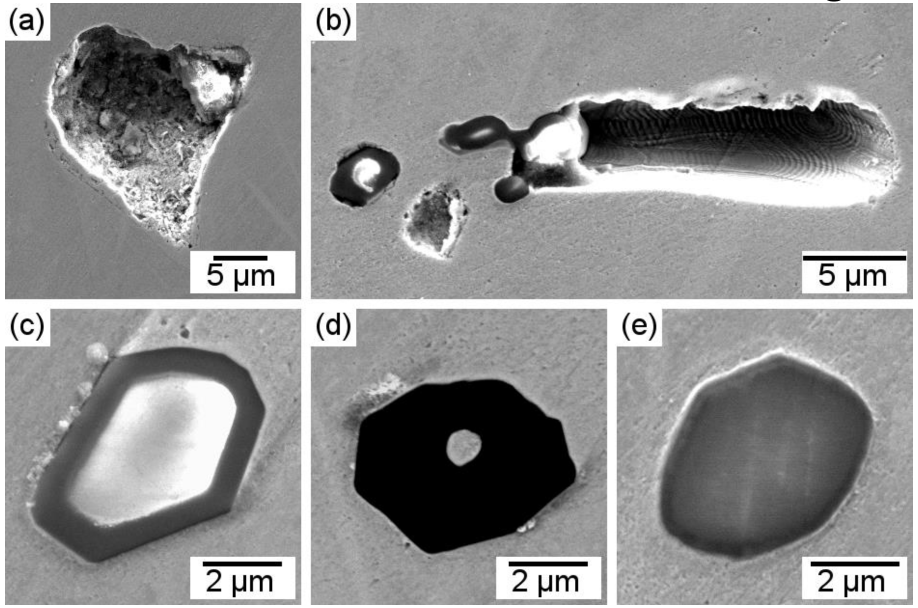


Fig. 3

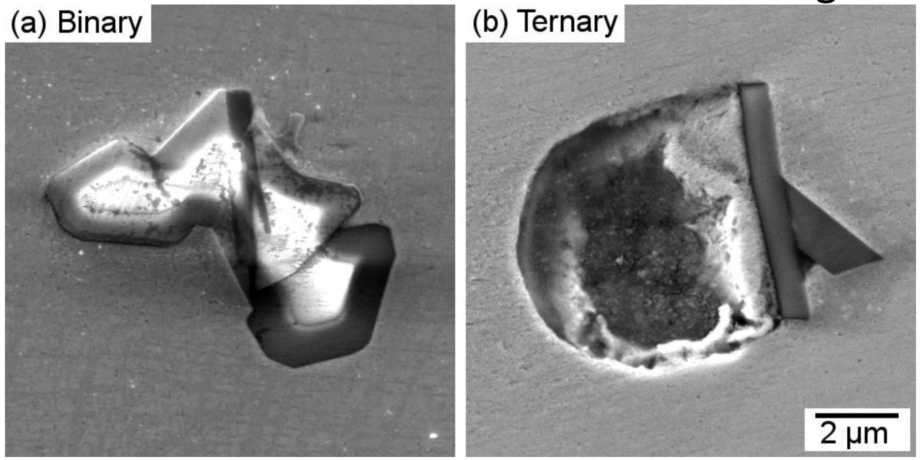


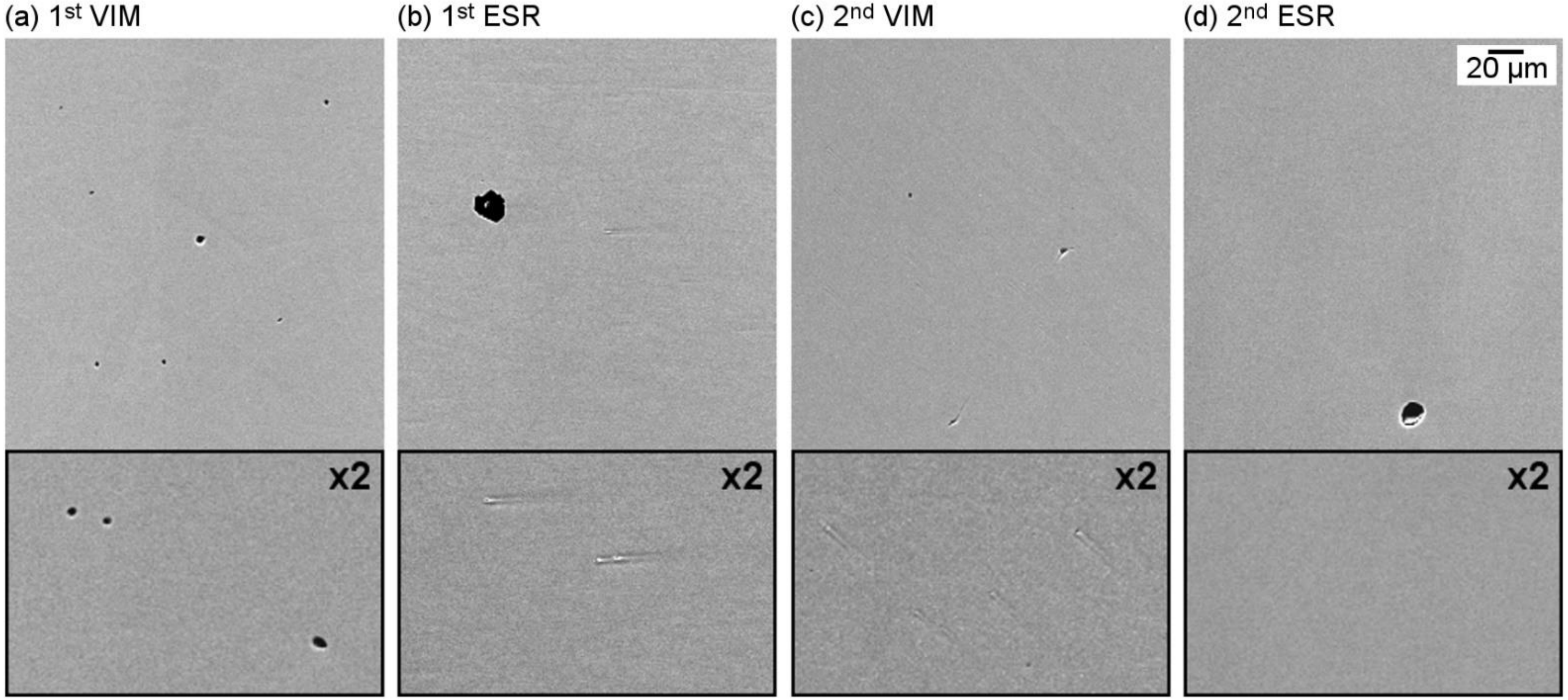
Fig. 1 (a) CrS, (b) TiO_2, (c,d) CrS/TiO_2 core, (e,f) Al-oxide

Fig. 2 Al-oxides

Fig. 3 Al-oxides in the (a) binary and (b) ternary alloy

Chemistry

Topic 1: Trace Element Control in Master Alloys



Inclusions	Partitioning	Diameter (µm)			
		1st VIM	1st ESR	2nd VIM	2nd ESR
TiO_2 / CrS	Cr / Ti	1.6 ± 0.5	3.7 ± 1.3	1.5 ± 0.4	1.7
Al oxide (serrated/void)	Cr	6.8 ± 2.7	12.8 ± 2.3	5.3 ± 1.8	8.8 ± 4.6
Al oxide (facetted)	Cr	-	4.0 ± 1.7	-	2.8 ± 1.4
Slag	Zr, Mg, Al, Cr, O	-	2.3 ± 1.0	2.8	1.8 ± 0.6
TiN	Cr /Slag, O core	-	-	-	1.4

Chemistry

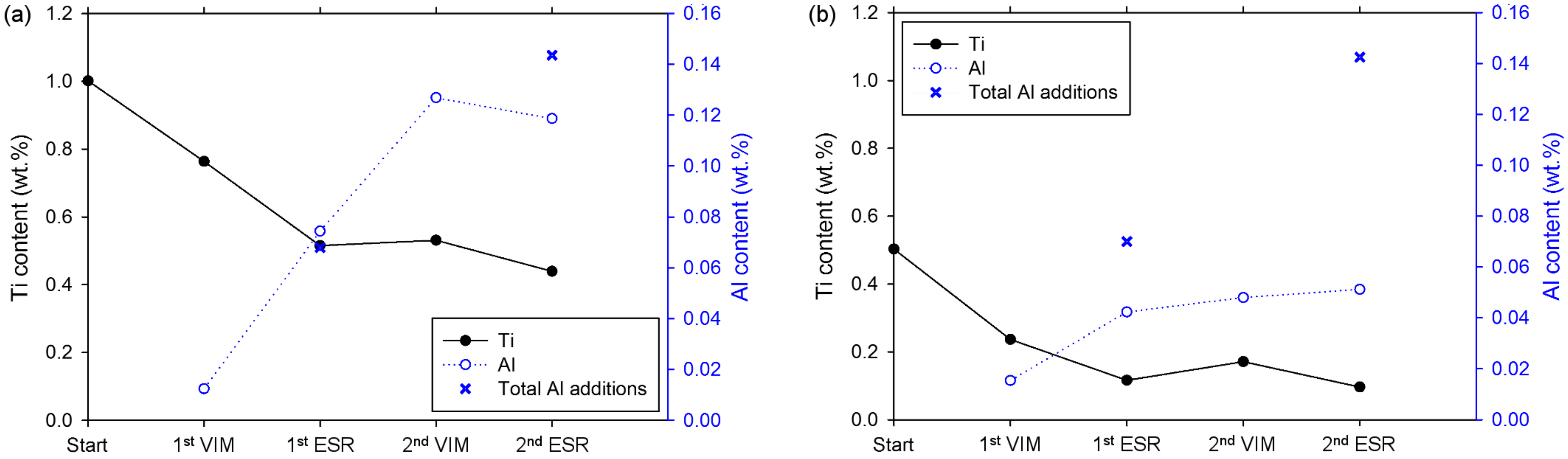
Topic 1: Trace Element Control in Master Alloys

- Alumina crucible + Al in the ESR feeder
- Reaction between Cr and the crucible during VIM:

$$2[Cr]_{metal} + (Al_2O_3)_{crucible} \rightarrow (Cr_2O_3)_{crucible} + [Al]_{metal}$$

- Ti may reduce the alumina in the slag and transfer Al into the metal:

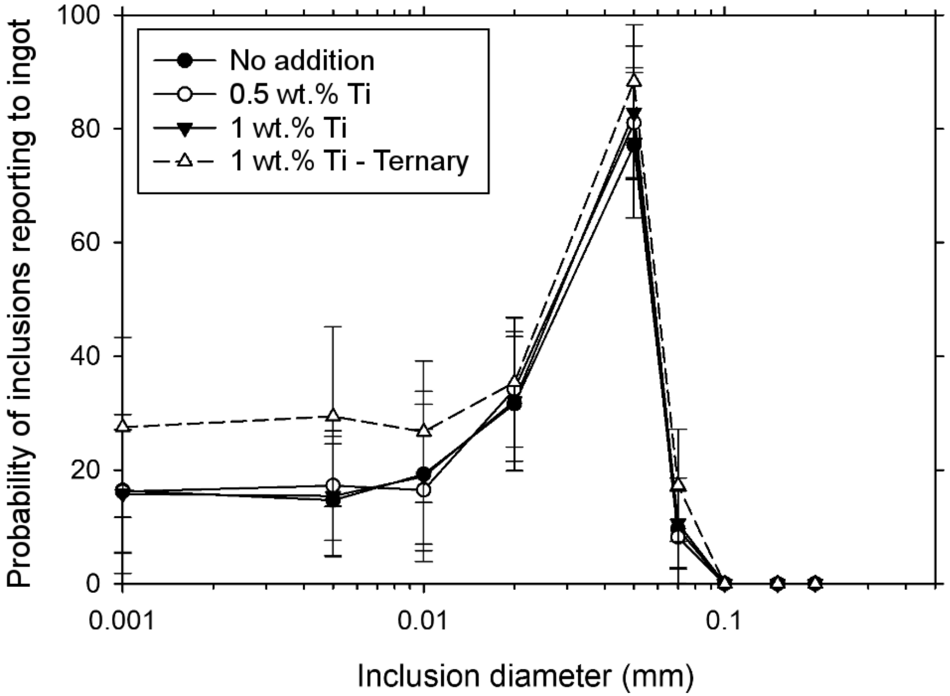
$$3[Ti]_{metal} + 2(Al_2O_3)_{slag} \rightarrow 3(TiO_2)_{slag} + 4[Al]_{metal}$$

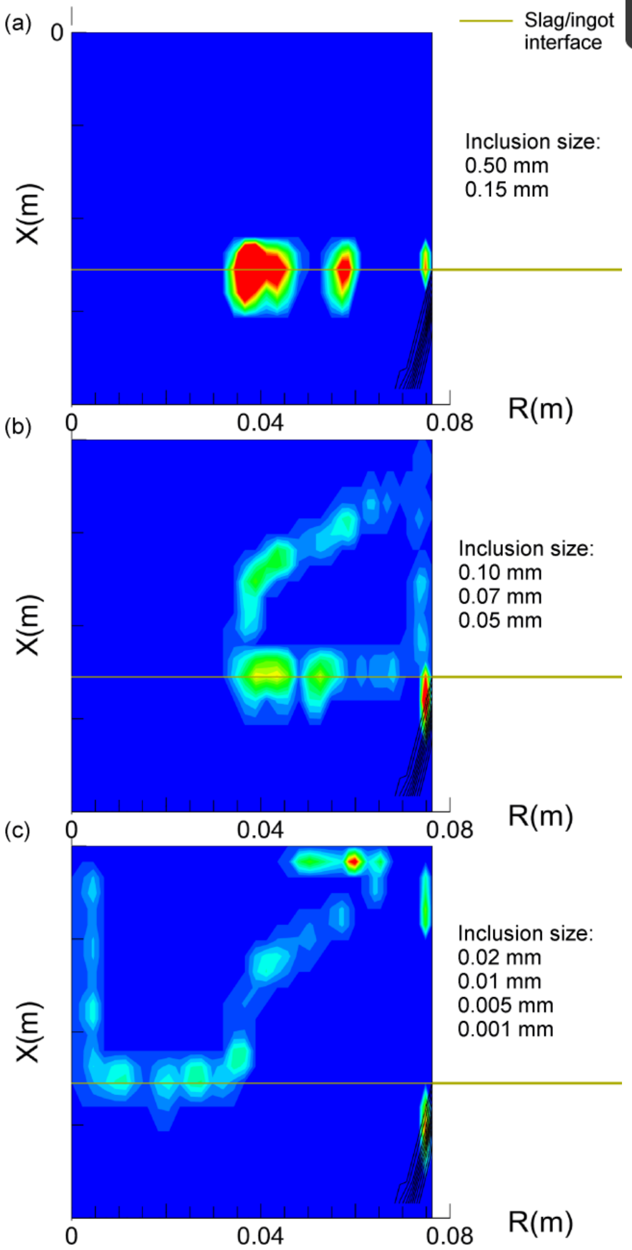


Inclusion Travel

Topic 1: Trace Element Control in Master Alloys

- Small inclusions can travel in the slag, be dissolved in it or be transferred to the ingot.
- Medium inclusions can float, remain in the slag cap but most are predicted to transfer to the ingot.
- Large inclusions remain at the slag/metal interface.





Introduction

Topic 2: Impact of Feedstock Purity on a Ta-containing Steel during Electroslag Remelting

- Novel advanced martensitic steel CPJ7 (contains 15 different elements)
- Highly reactive elements: Si, Nb and Ta
- Ta is used for:
  - Formation of carbides and carbonitrides (MX)
  - Intragranular corrosion resistance
  - Resistance to creep deformation
  - Ta is expensive
- **Use of a research-scale ESR furnace to make 150 lb CPJ7 ingots of higher purity.**

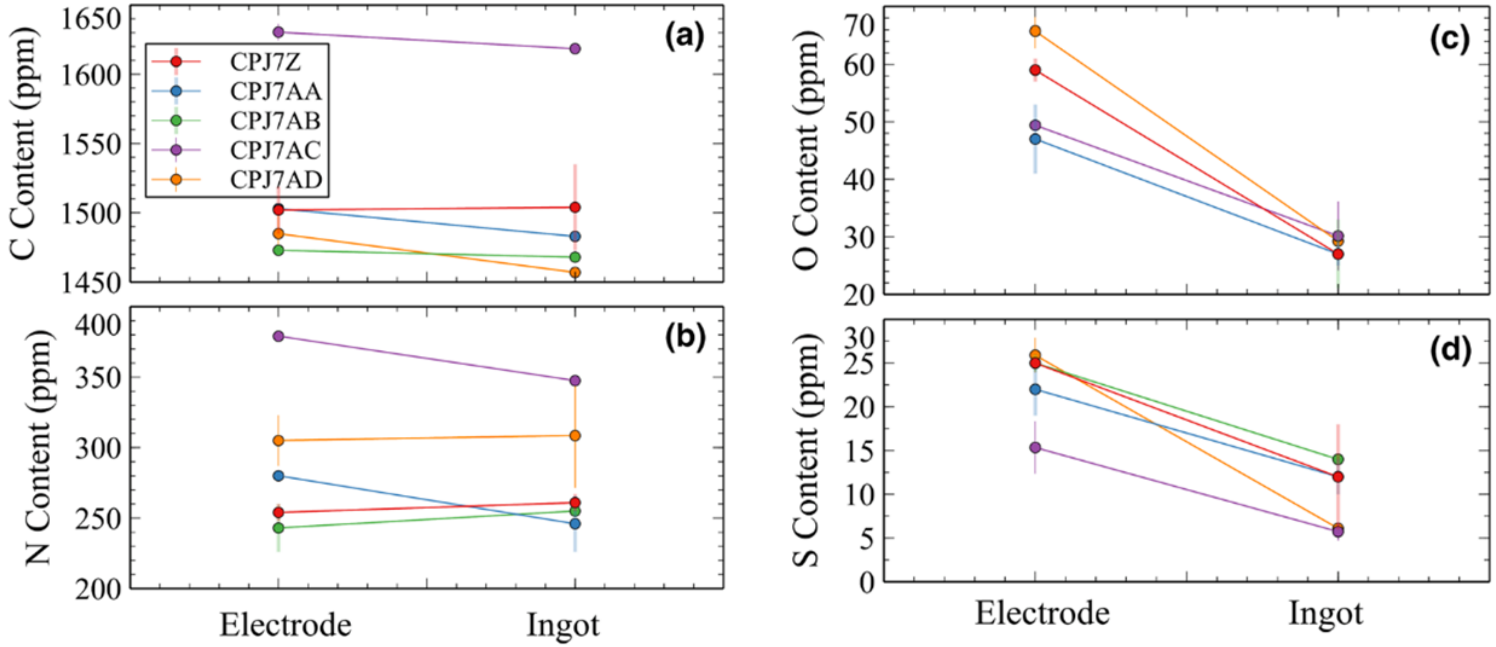
Table I. Composition Range of the CPJ7 Martensitic Steel Investigated with Fe Balanced (Wt Pct)[12]

	Cr	Mo	C	Mn	Si	Ni	V	Nb	N	W	Co	Ta	Cu	B
Min.	9.75	1.0	0.13	0.25	0.08	0.15	0.15	0.05	0.015	0.25	1.35	0.20	0.003	0.0070
Max.	10.25	1.5	0.17	0.50	0.15	0.30	0.25	0.08	0.035	0.75	1.65	0.30	0.30	0.0110

Concentration of Tramp Elements

Topic 2: Impact of Feedstock Purity on a Ta-containing Steel during Electroslag Remelting

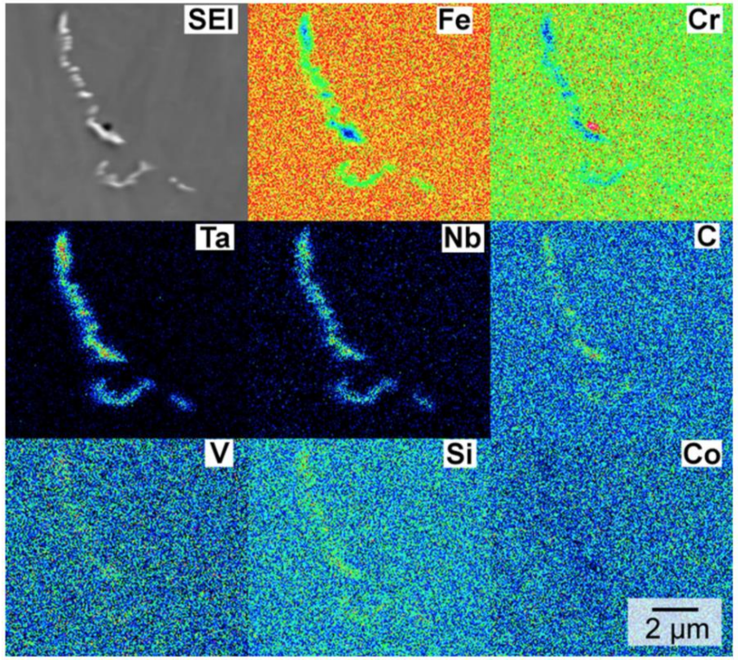
- 5 electrodes were cast using VIM. The C, N, O and S concentrations in the electrodes (following casting) are shown on the left.
- All electrodes were remelted using ESR which resulted in new C, N, O and S concentration in the ingot.
- Significant decrease in O and S from the electrode to the ingot:
  - **~49% decrease in O**
  - **~56% decrease in S**
- Final concentrations in the ingot:
  - **~28 ppm O**
  - **~10 ppm S**
- **<u>However, 25% loss in Ta</u>**

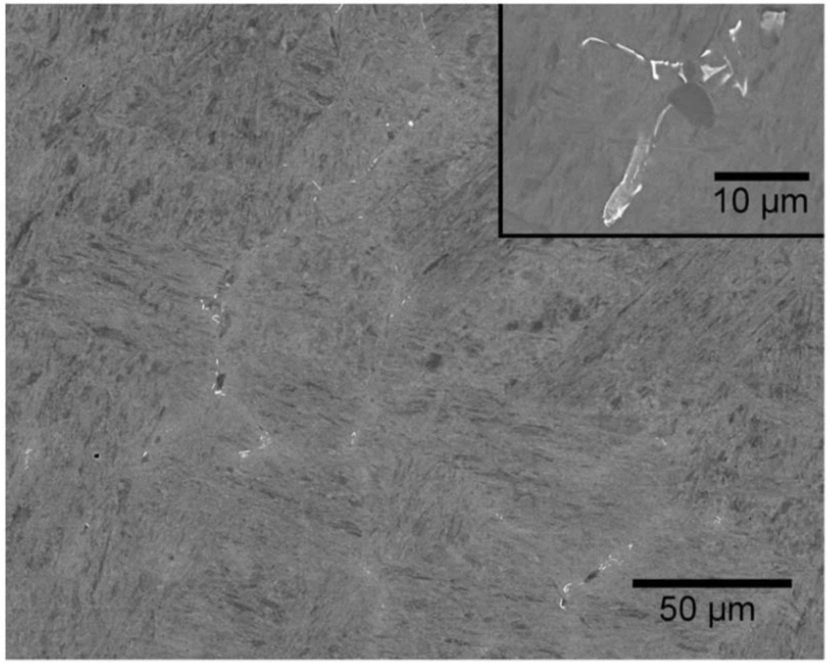


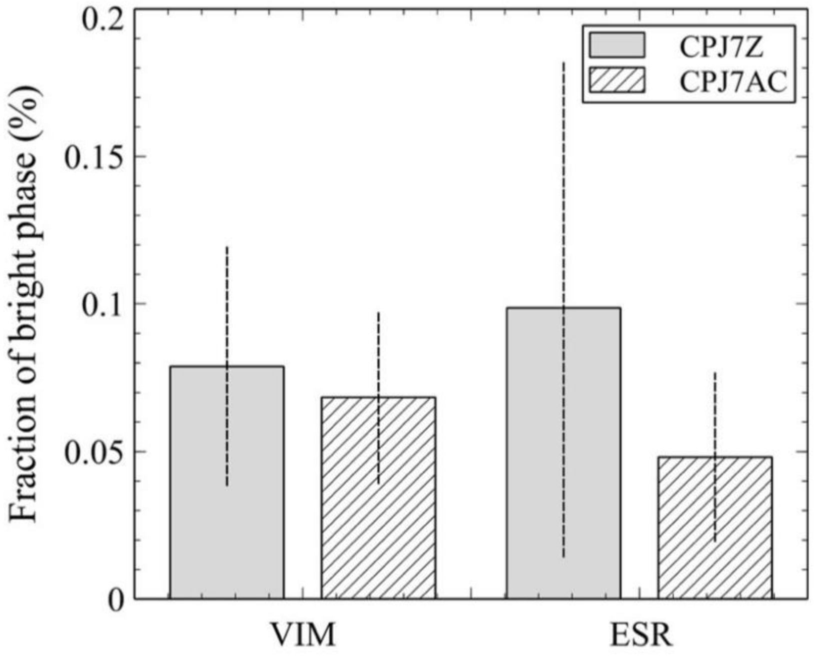
Microstructure Evaluation

Topic 2: Impact of Feedstock Purity on a Ta-containing Steel during Electroslag Remelting

- Observation of the microstructure on the SEM/EPMA revealed two types of phases that contain Ta.
- The first is the interdendritic phase from solidification.
- Microprobe analysis shows concentrations of Ta and Nb.
- No significant variations between electrode and ingots since it is related to solidification.



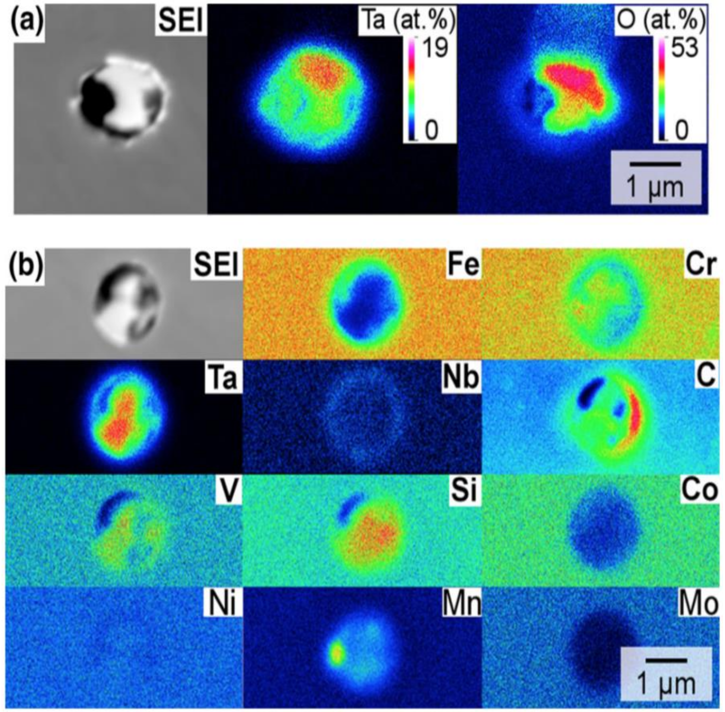


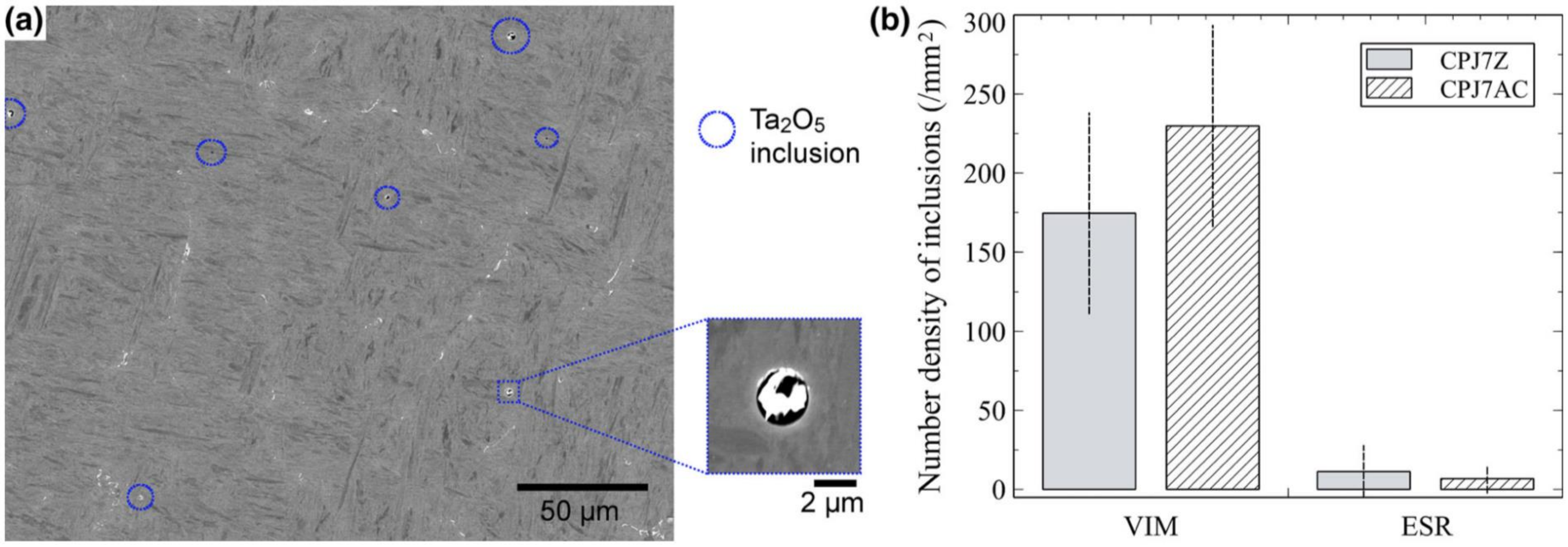


Microstructure Evaluation

Topic 2: Impact of Feedstock Purity on a Ta-containing Steel during Electroslag Remelting

- The second phase is present in the form of inclusions.
- Quantitative EPMA mapping revealed the inclusions to be Ta_2O_5.
- Significant decrease in number density of Ta-oxides during ESR.
  - **95% reduction in number density of Ta-oxide**





Discussion

Topic 2: Impact of Feedstock Purity on a Ta-containing Steel during Electroslag Remelting

- Sources of O:
  - VIM was performed in a 136 kg furnace that was pumped down to 30 μHg pressure prior to starting the melt. Leak rate was 6.5 μHg/min (performed for one minute).
  - The Cr used contained 5000 ppm O. With 10wt.% Cr in the alloy => 500 ppm O in the melt charge.
- VIM was effective at removing most of the O with levels in the electrode between 40 and 70 ppm.
- Some of the O reacted with Ta to form Ta_2O_5.

Table VI. Oxygen Content and Inclusion Density Following VIM of CPJ7 Ingots Under Various Conditions

Furnace	Charge Weight (kg)	O Content in Cr (Ppm)	Pressure at Start (μHg)	Leak Rate (μHg/min)	O Content (Ppm)	Number Density of Inclusions (mm^{-2})
136 kg*	77	~ 5000	29.6 ± 8.7	6.5 ± 1.9	56 ± 8	196 ± 67
9 kg	7	~ 5000	0.042	0.73	74 ± 13	111 ± 41
	7	~ 400	0.028	0.34	105 ± 5	136 ± 41

*Average between the ingots Z, AA, AB, AC, and AD with standard deviations.

Discussion

Topic 2: Impact of Feedstock Purity on a Ta-containing Steel during Electroslag Remelting

- Two small VIM melts (7 kg ingots) were performed to investigate the influence of pressure/leak rate.
- The furnace employed possesses a leak rate of 0.3 to 0.7 μHg/min for a 0.03-0.04 μHg starting pressure.
- Using 5000 O grade Cr:
  - 74 ppm O in ingot (close to large castings)
  - Lower number density of Ta-oxides. 111 mm^{-2} compared to 196 mm^{-2}.

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- Two small VIM melts (7 kg ingots) were performed to investigate the influence of pressure/leak rate.
- The furnace employed possesses a leak rate of 0.3 to 0.7 μHg/min for a 0.03-0.04 μHg starting pressure.
- Using 400 O grade Cr:
  - 105 ppm O in ingot (higher than in the large castings, some location dependency)
  - Lower number density of Ta-oxides. 136 mm^{-2} compared to 196 mm^{-2}.
  - Slightly higher than in the first small VIM melt.

Table VI. Oxygen Content and Inclusion Density Following VIM of CPJ7 Ingots Under Various Conditions

Furnace	Charge Weight (kg)	O Content in Cr (Ppm)	Pressure at Start (μHg)	Leak Rate (μHg/min)	O Content (Ppm)	Number Density of Inclusions (mm^{-2})
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Summary/Conclusion

Topic 1

- Melting characteristics were improved for master alloys using C and Ti additions.
- Ti additions reduced the oxygen content during VIM through the formation of Ti-oxides. The inclusions were then removed during ESR.
- Aluminum was used to deoxidize the slag; however, Al pickup was observed in the solidified ingots with large Al-oxides.

Topic 2

- Ta content in CPJ7 decreased by 25% during ESR.
- This was attributed to the formation of Ta-oxide inclusions and subsequent 95% reduction in their number density during ESR.
- Ta is highly reactive and prone to the formation of Ta_2O_5.
- Ta-oxides formation was influenced by the leak rate and pressure at start.

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