Research Fund for Coal and Steel project
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STeELS-EM Project

Characterization of precipitates in hot strips and final products

Dissemination Day
November 25th 2024

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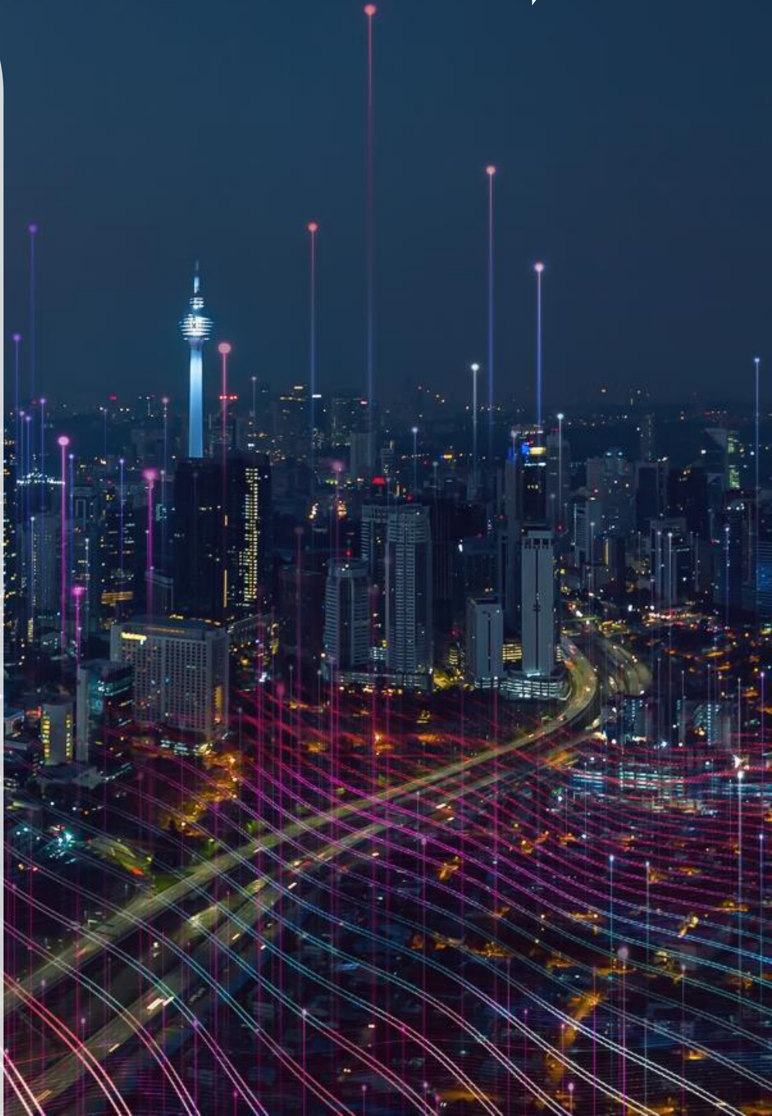


Alloying strategy

- According to the preliminary thermodynamic calculations, Titanium has been found to be the most promising alloying element for reducing the effect of precipitation on magnetic properties in comparison with Nb and V.
- This is due to the very low solubility of its carbides (TiC), nitrides (TiN) and carbosulphides ($Ti_4C_2S_2$).
- The aim of the alloying strategy was to maximize the precipitation of coarse particles at high temperature (slab reheating stage), thus reducing the fraction of small precipitates which form at lower temperatures during hot rolling and coiling.
- Two levels of Ti have been considered during the Project: **0.2%** and in a second phase **0.5%**.
- The precipitation state of the new materials has been compared with that of a standard Ti-free Fe-Si steels of the same grade.
- Mean size and chemical analysis of smaller particles (affecting recrystallization and grain growth kinetics) have been determined by TEM by extracting precipitates on a carbon film replica on selected samples of as-hot rolled and cold rolled and recrystallized steels.

Advantages and disadvantages of Ti-alloying

Advantages

- Titanium in solid solution increases the strength of the steel and this can be exploited in some specific applications where mechanical properties are relevant.
- Titanium could increase the resistivity of the steel, thus contributing to a reduction in magnetic losses.

Disadvantages

- Titanium strongly reduces the amount of carbon in solid solution in ferrite: this promotes the development of <111>//ND fibre texture during recrystallization after cold rolling which is unfavourable for achieving a good magnetization.

Overview of the precipitation state As detected by TEM-EDS

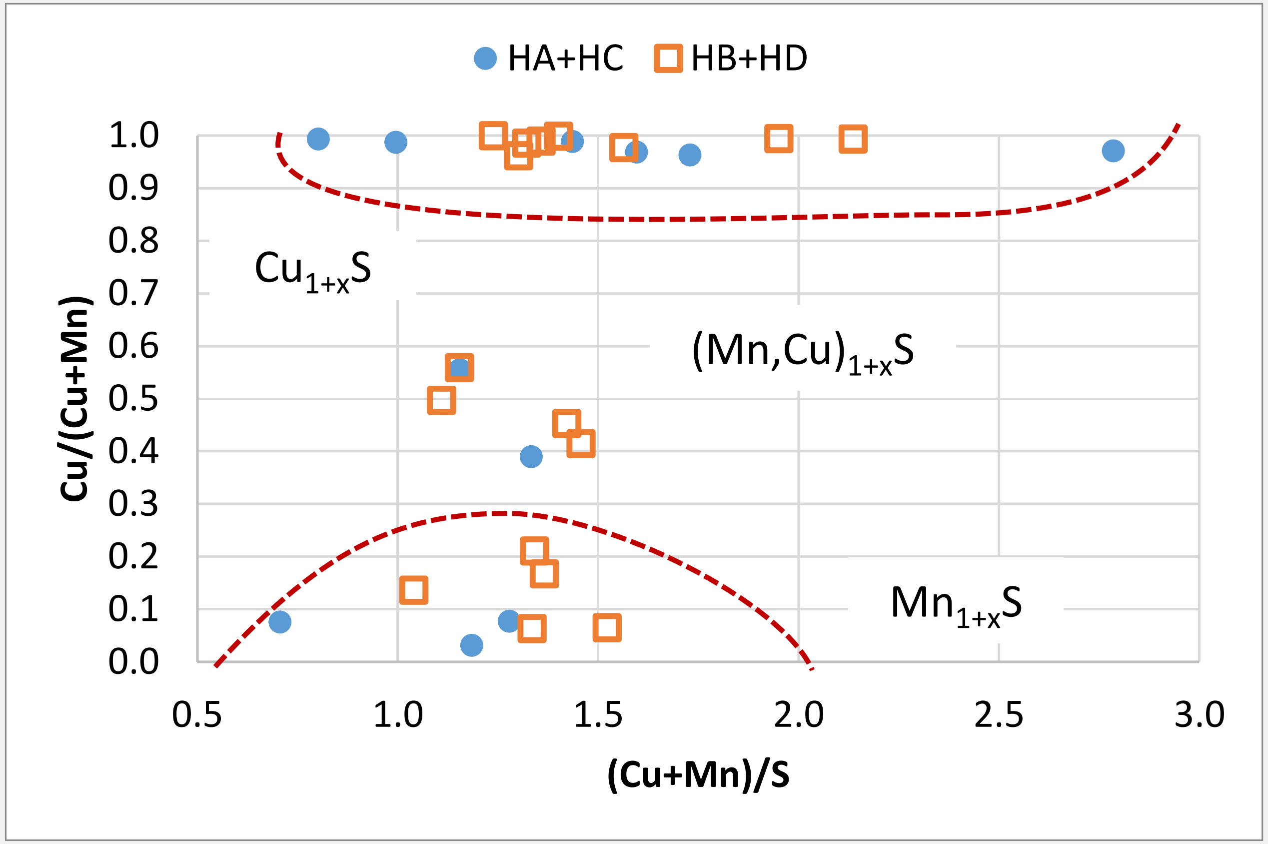
- **Ti-free Fe-Si steels**
  - Aluminium nitride AlN
  - Manganese sulphide (Mn, Cu)S
  - Copper sulphide Cu_2S
  - Cementite Fe_3C

- **Ti-added Fe-Si steels**
  - Titanium carbonitrides Ti(C, N)
  - Titanium carbosulphide $Ti_4C_2S_2$
  - Phosphides $(Ti, Fe)_3(P, Si)$
  - Intermetallics Fe_2TiSi

Sulphides (hot strip)

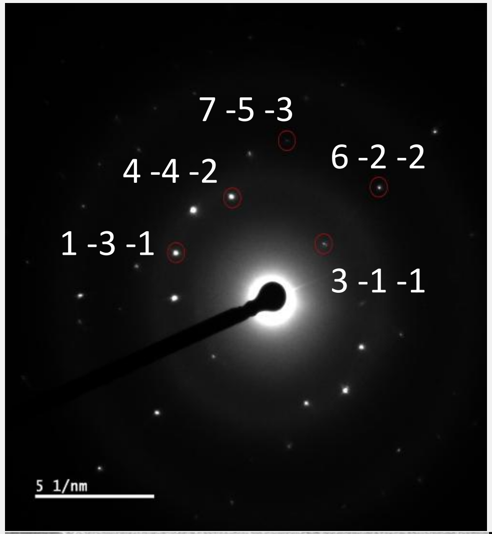
- Small **sulphides containing Mn and Cu** have been found in **Ti-free steels** only.
  They are characterised by a defective stoichiometry that can be considered to derive from the mixing of two ideally pure phases **MnS** and **Cu_2S**.
- **$Mn_{1+x}S$** particles range from 120 to about 70 nm.
- **$Cu_{1+x}S$** particles are in the range 25-30 nm.

- There are no reliable thermodynamic data on copper sulphides. Its solubility seems comparable to that of MnS. These particles are expected to be quite stable during the subsequent annealing treatments of the industrial production cycle for these steels.

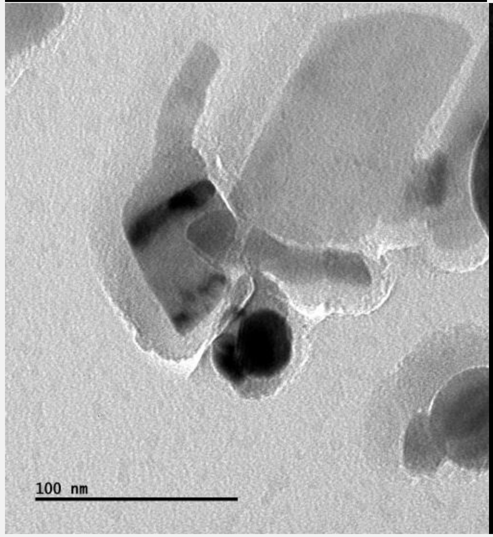


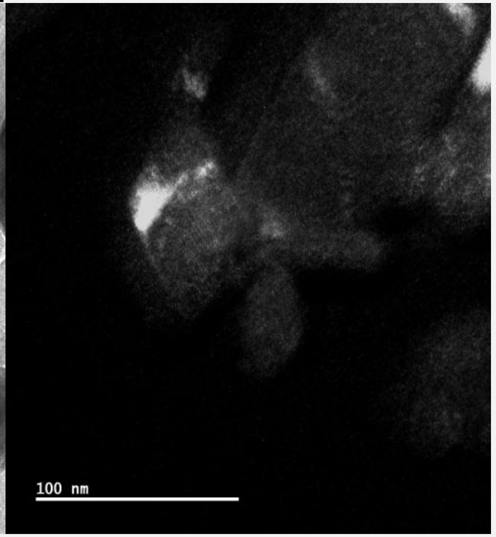
Phosphides (hot strips)

- Small precipitates identified as **M_3P in association with Fe, Ti and Si** have been found in **high-Ti steels only**.
- To identify the structure the atomic ratio (Ti+Fe)/(Si+P) has been considered which resulted 2.75±0.26, leading to **M_3P**.
- Electron diffraction confirmed the tetragonal crystal structure with lattice parameters a=0.905 nm and c=0.439 nm.
- A representative stoichiometry is **$(Ti_{0.5}, Fe_{0.5})_3(P_{0.5}, Si_{0.5})$**.
- The mean size of the particles ranges from about 30 up to 80 nm.
- There are no reliable solubility data for such a mixed composition. Literature works on pure iron phosphide Fe_3P suggest a quite high solubility.
- For a phosphorus content of 0.015% the solvus temperature is estimated to range from about 270°C up to about 440°C and the particles are expected to fully dissolve during the annealing treatments.



d = 90 nm
M_3P, tetragonal
a = 0.905 nm
c = 0.439 nm





Estimate of the precipitate fractions in hot strips (reference and 0.2% Ti steels)

- Volume fractions in hot strips have been estimated based on a mass balance assuming that the amount of the understoichiometric element controls the extent of precipitation.
- Estimates can be affected by a high error due to the poor statistics intrinsic in TEM investigations.

Controlling element	*S*	*S*	*N*	*Ti*	*P*	*C+N*
Precipitate	**MnS**	**Cu_2S**	**AlN**	**Ti(C,N)**	**$(Fe,Ti)_3P$**	**Ti(C,N)**
Hi-Si ref.	1.01E-4*	1.25E-4*	3.21E-4**	1.87E-5		
Lo-Si ref.	1.01E-4*	1.25E-4*	2.53E-4**	1.87E-5		
Hi-Si 0.2% Ti					7.50E-4	3.27E-4***
Lo-Si 0.2% Ti					8.18E-4	4.10E-4***

- The estimated volume fraction of fine Ti(C,N) particles in 0.2% Ti steels is about 4 times that of the either MnS or Cu_2S in the reference material.

* *Volume fractions refer to each phase considered as the only one present*

** *Volume fraction for high-T precipitation of AlN calculated by thermodynamics at 1250°C.*

*** *Precipitate fraction of small Ti(CN) particles corrected by subtracting the fraction of high-T coarse TiN calculated from the thermodynamic equilibrium at 1250°C (2.60E-4).*

Average particle size

- Average size of small particles detected by TEM

Precipitate	MnS	Cu_2S	AlN	Ti(C,N) *Limiting: Ti*	$(Fe,Ti)_3P$	Ti(C,N) *Limiting: C+N*
Hi-Si ref.	30	30	>200*	31		
Lo-Si ref.	25	25	>200*	15		
Hi-Si 0.2% Ti					60	71
Lo-Si 0.2% Ti					76	80
Notes			*High-T pptn only*	*Calc. solvus 840°C*	*Solvus 270-440°C*	*High-T pptn of large TiN not determined*

* *Estimated size for high-T precipitation of AlN.*

Inhibition to grain growth

- Only the fraction of fine particles is considered
- An estimate of the contribution that each phase provides to the overall inhibition to grain growth has been calculated using the following relationship:

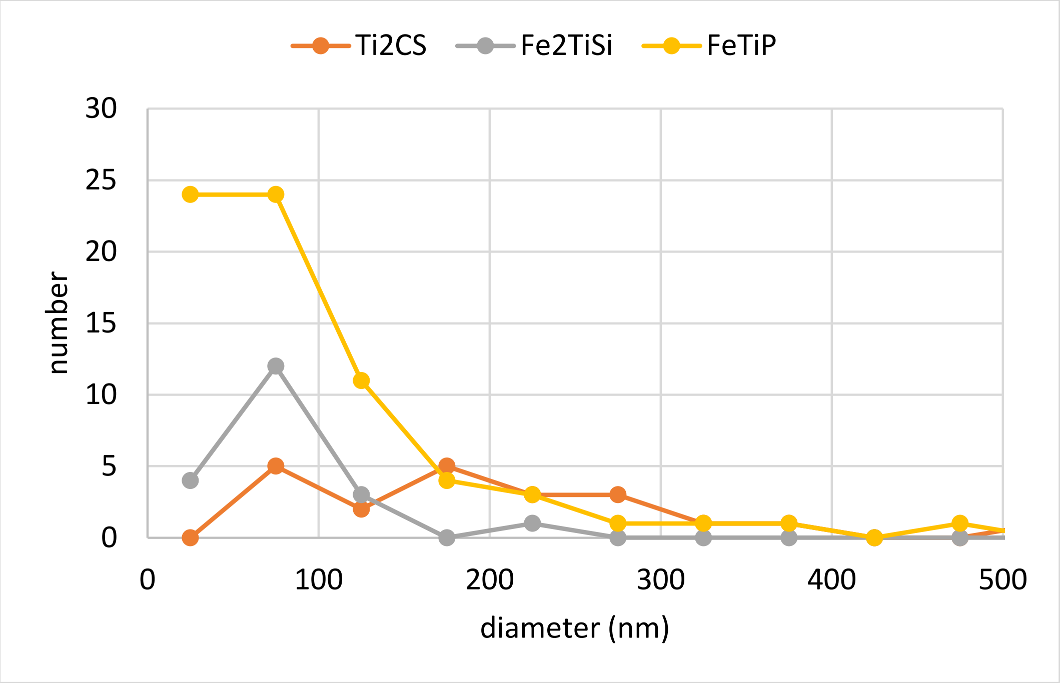
$$I_Z = \frac{3}{2} \cdot \frac{f_V}{< r >}$$

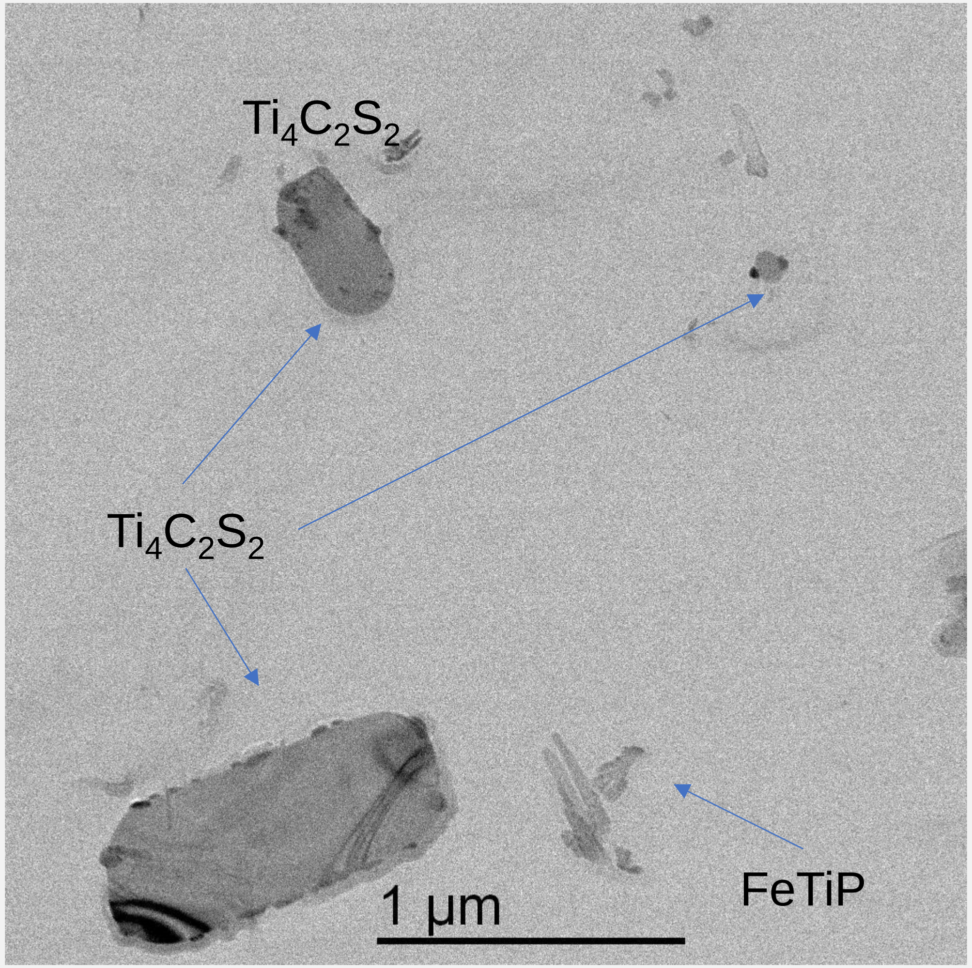
Steel	$MnS + Cu_2S$		$Ti(C,N)$	$Ti(C,N) + (Fe,Ti)_3P$
Hi-Si and Lo-Si ref.	≈ 100 cm^{-1}			
Hi-Si and Lo-Si 0.2% Ti			≈ 140 cm^{-1}	≈ 540 cm^{-1}

- In the hypothesis that phosphides dissolve during annealing, the Ti added steels are expected to have a higher level of inhibition and this can represent an issue.

Hot strip Lo-Si (1% Si, 0.5% Al 0.5% Ti)

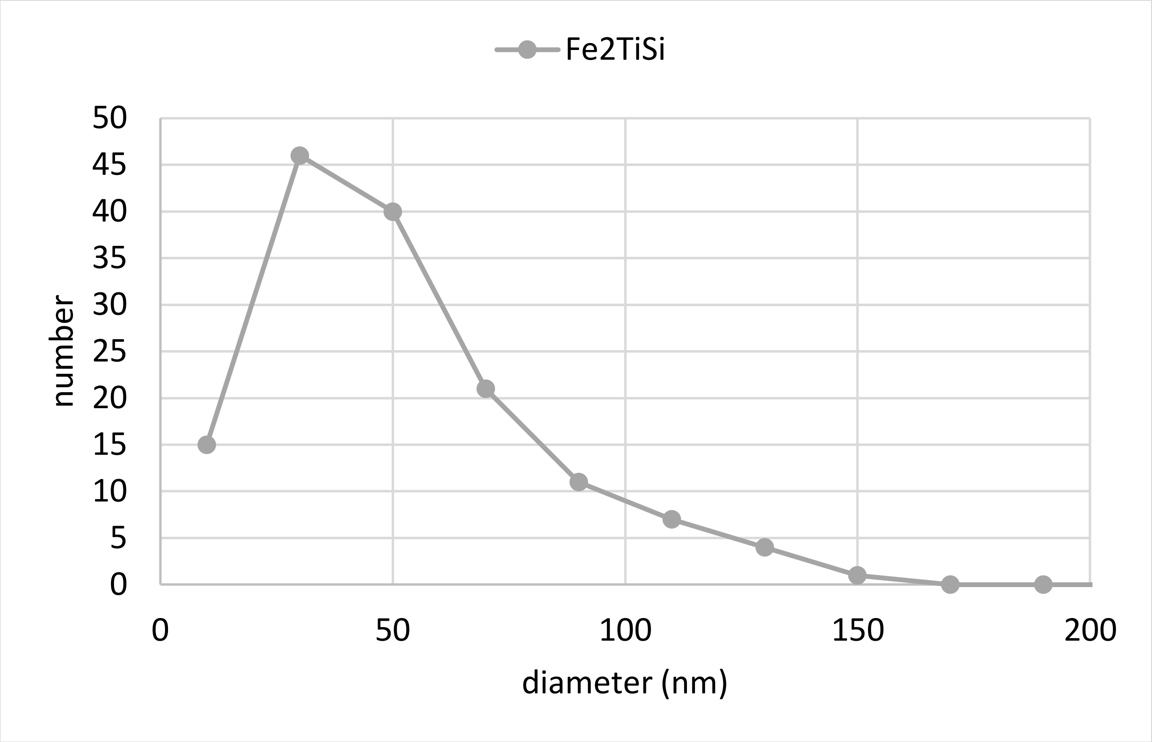
- Fe_2TiSi : <d> = 80 nm
- $Ti_4C_2S_2$: <d> = 550 nm
- Ti(C,N) : <d> = 640 nm
- $(FeTi)_3P$: <d> = 100 nm

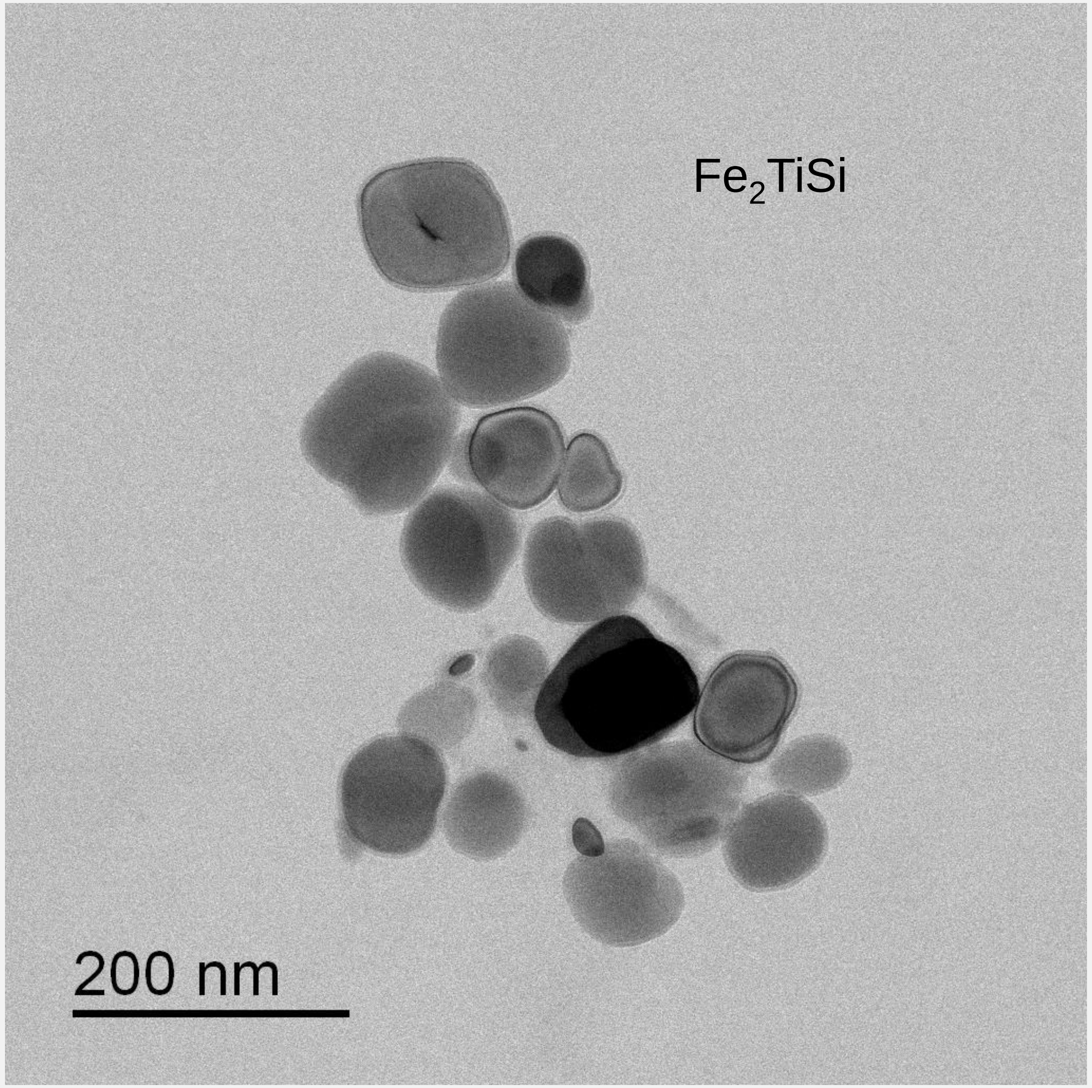




Hot strip Hi-Si (3% Si, 1% Al 0.5% Ti)

- Fe_2TiSi is the only phase detected by TEM
- Its mean size is 50 nm



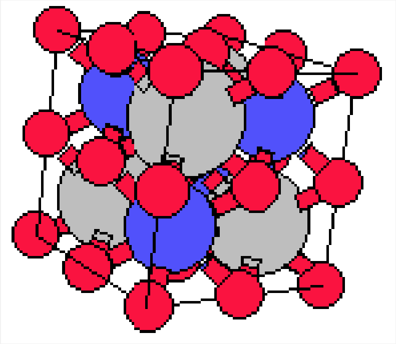


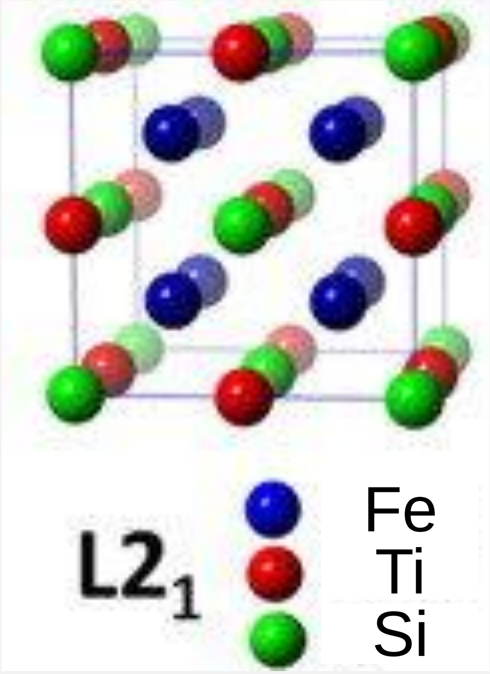
The intermetallic phase Fe_2TiSi

- The intermetallic compound Fe_2TiSi is a metastable phase which forms at temperatures below 800°C [Jack & Honeycombe, Acta. Metall. 20 (1972) 787-796]
- It has a $L2_1$ ordered crystal structure belonging to the space group Fm-3m with lattice parameter a=0.5709 nm
- It is coherent with the ferrite matrix up to a size of about 150 nm
- It undergoes coarsening at temperatures in the range 600-800°C controlled by Ti diffusion
- Its volume fraction should be zero at T>800°C

- ➔ ***it is expected that its dissolution during the recrystallization annealing does not produce a significant grain boundary pinning***

- If hot band annealing is not performed, these coherent particles in the hot rolled strips might play a role in the first cold deformation stage by affecting the work hardening rate



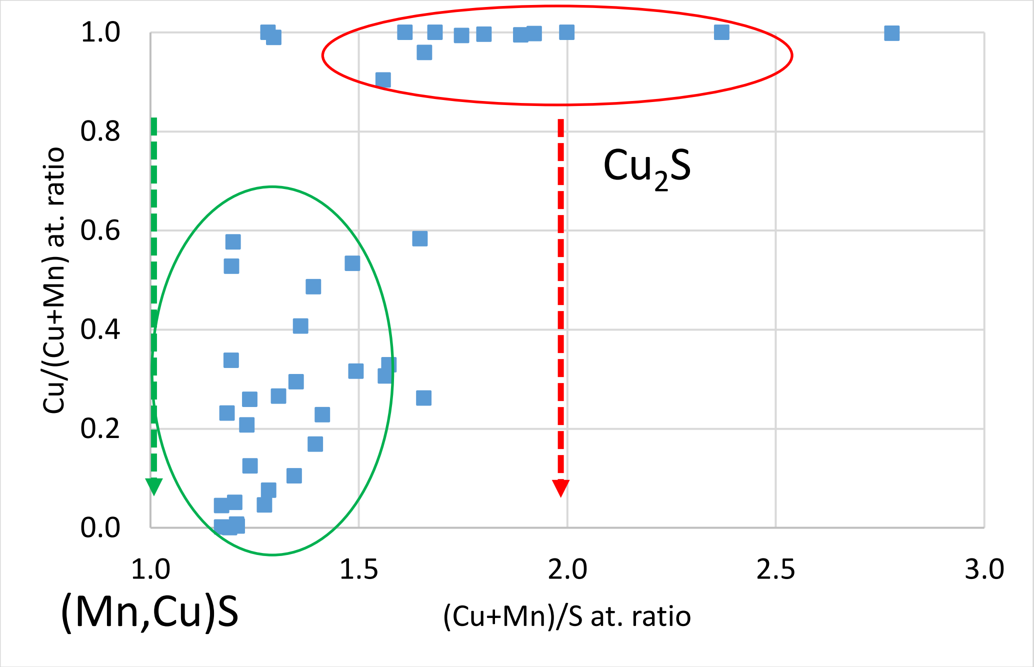


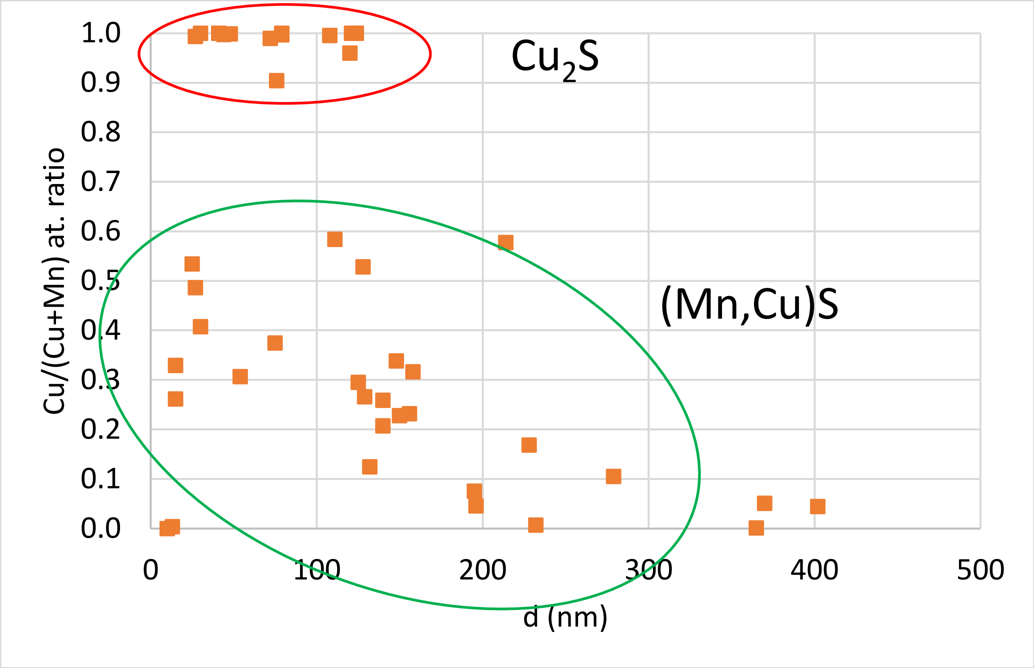
Cold rolled and annealed strips

- Hot rolled strips are cold rolled and heat treated in order to obtain a fully recrystallized microstructure.
- Two cold rolling + annealing treatments are necessary to reach a final thickness of 0.5 mm.
- During the treatments at high temperature (above 900°C) precipitates evolve undergoing dissolution or coarsening depending on their solubility.
- Second phase particles, especially if they are small and have high volume fraction, interact with recrystallization and grain growth processes by slowing down the kinetics.

- The characterization of the precipitate population at this stage is very important.
- Also important are the processing conditions and in particular the slab reheating temperature and the hot band annealing treatment which affect the amount and the size of precipitates.

Hi-Si Reference, cold rolled & annealed SRT=1050°C + Hot Band Annealing

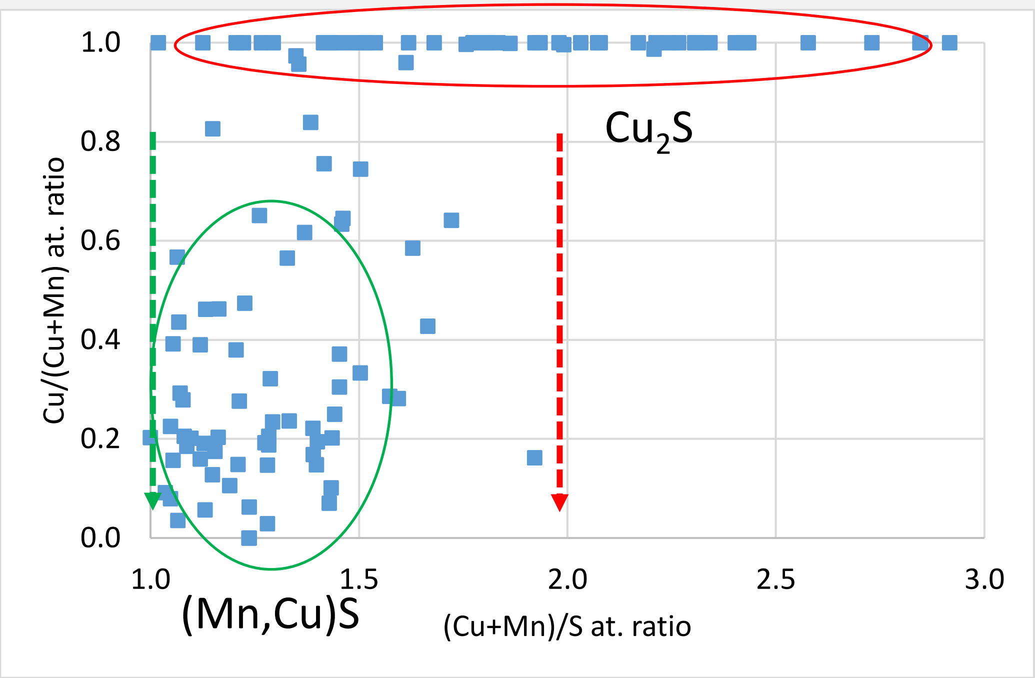


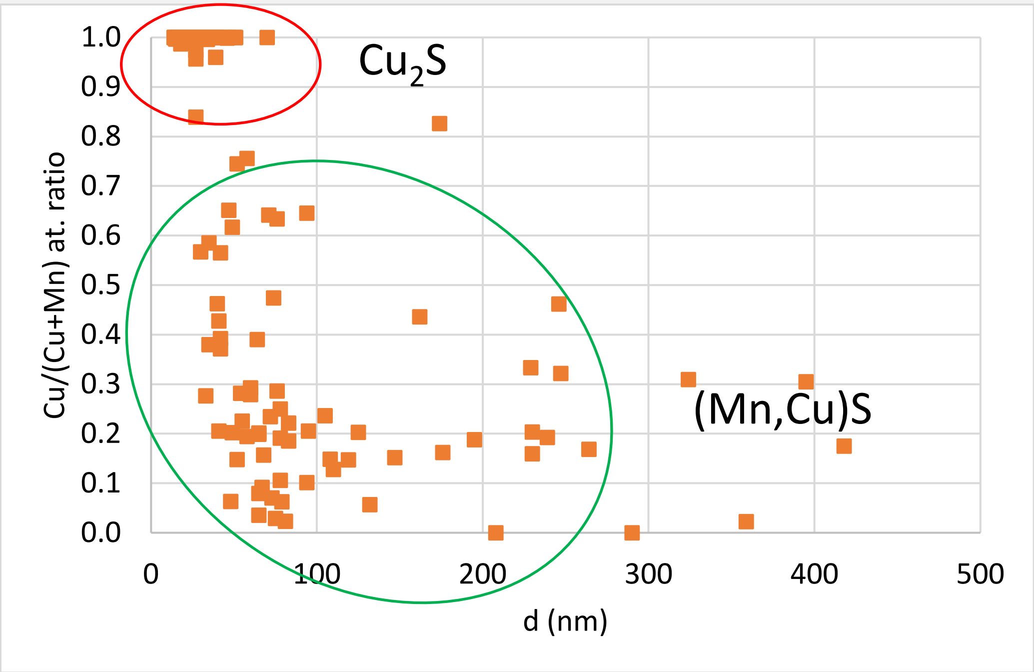


- few AlN, similar number of Ti(C,N) and sulphides
- mixed Cu-Mn sulphide with defective stoichiometry, Cu_2S around 100nm, (Mn,Cu)S from 50 to 400 nm

	mean (nm)	stdev (nm)
Ti(CN)	189	63
(CuMn)S	125	97
AlN	90	47

Hi-Si Reference, cold rolled & annealed SRT=1050°C – no Hot Band Annealing

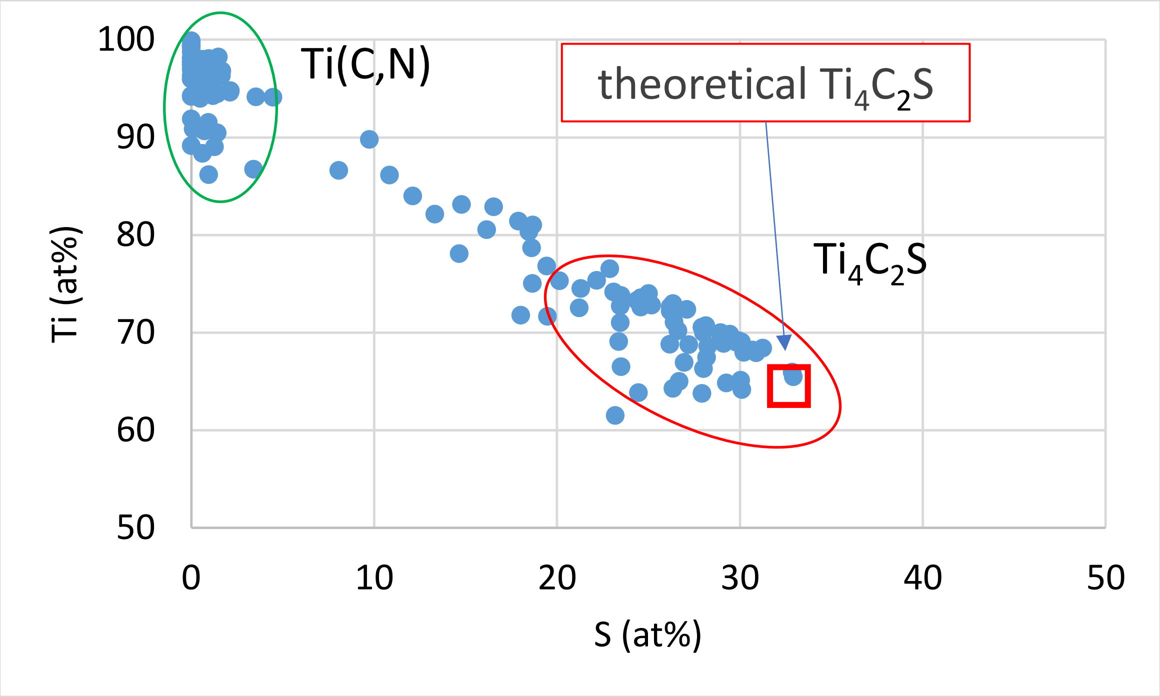


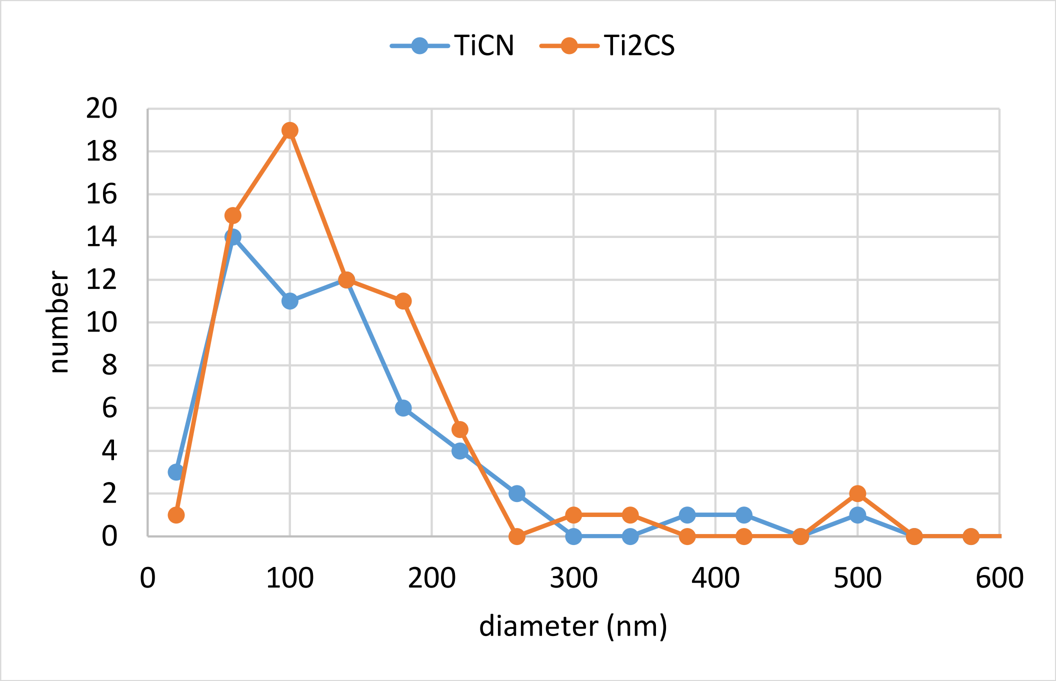


- only mixed Cu-Mn sulfides with defective stoichiometry, Cu_2S around 50nm, (Mn,Cu)S from 50 to 400 nm
- ***higher fraction of small-sized precipitates compared to the treatment with HBA***

	mean (nm)	stdev (nm)
(CuMn)S	78	81

Hi-Si 0.2% Ti
SRT=1050°C – no Hot Band Annealing

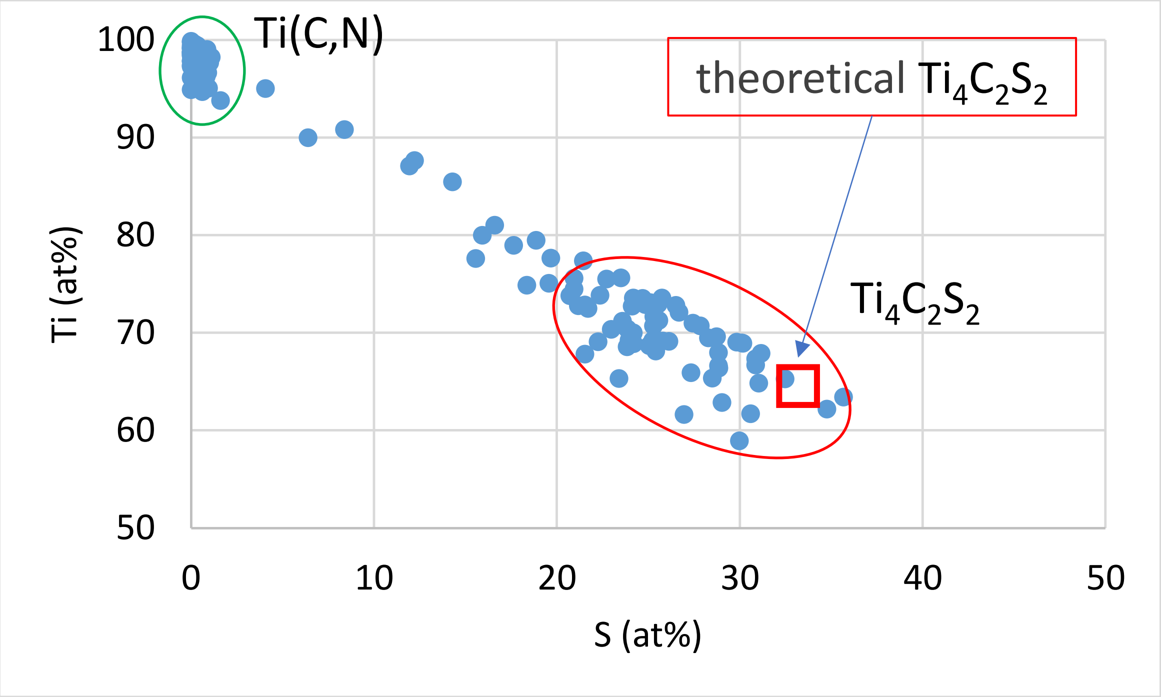


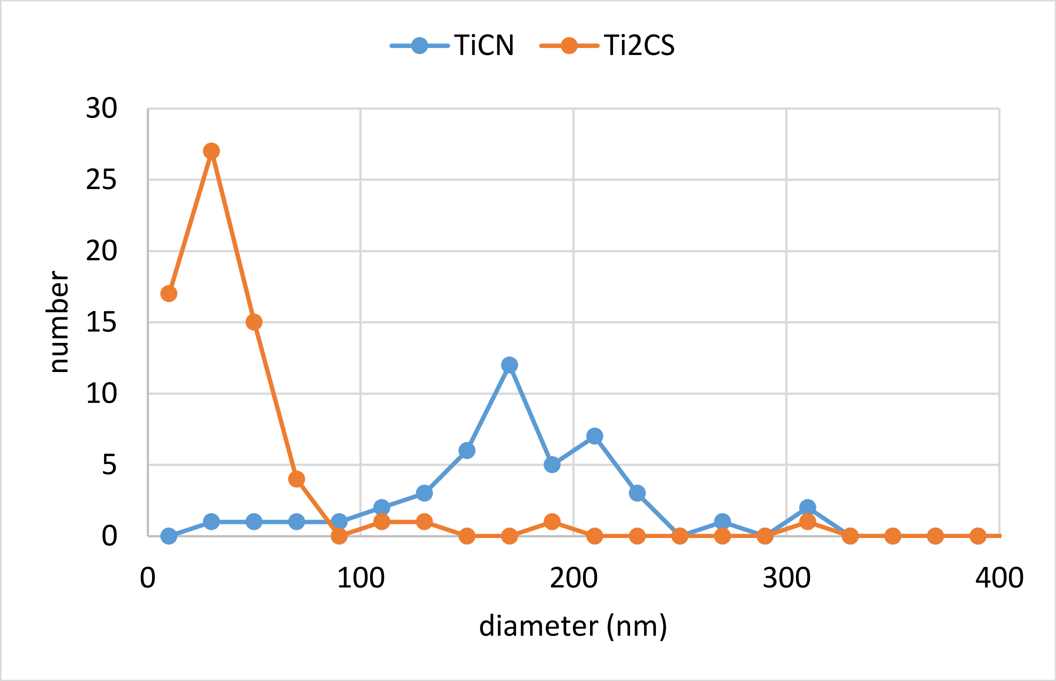


- Titanium carbonitrides and carbosulphides with mean size of about 150 nm

	TiCN	$Ti_4C_2S_2$
<d> (nm)	151	138
stdev (nm)	115	88

Hi-Si 0.2% Ti
SRT=1250°C + Hot Band Annealing





- small titanium carbosulphides (80 nm) and few coarser titanium carbonitrides (200 nm)

	Ti(C,N)	$Ti_4C_2S_2$
<d> (nm)	354	80
stdev (nm)	806	200

Summary of the precipitation characterization

Reference materials

- contain Cu-Mn sulphides (and few titanium carbides since Ti was present as impurity)
- the hot band annealing treatment seems to increase the fraction of precipitates in the size range observable by TEM

Ti-added materials

- precipitation is composed of titanium carbonitrides and carbosulphides without any AlN or Cu-Mn sulphides
- in the average the fraction of precipitates in the observed size range is larger than that in the Ti-free reference materials
- consequently, also the inhibition to grain growth is higher and this explains the need of increasing the temperatures of intermediate and final annealing

	<d> (nm)	surface density (μm^{-2})	relative volume fraction	relative inhibition
Hi-Si Ref. NOHBA	78	5.18E+04	***1.0***	***1.0***
Hi-Si Ref. + HBA	152	4.60E+05	8.9	4.6
Hi-Si 0.2%Ti NOHBA	145	8.98E+05	17.3	9.4
Hi-Si 0.2%Ti + HBA	204	3.44E+06	66.4	25.5

This has led to the production of a new alloy with 0.5% Ti to further reduce the fraction of fine particles

ACKNOWLEDGEMENT

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For more info:

Thank you for your attention