POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

Corso di Laurea Magistrale
in Ingegneria dei Materiali

Tesi di Laurea Magistrale

Effetto della composizione chimica e la dimensione del grano austenitico sulla trasformazione martensitica

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1) Introduzione

La maggior parte degli acciai avanzati di terza generazione ad alta resistenza: 3G AHSS (advanced high strength steels) contengono una certa quantità di austenite residua nella loro struttra finale. Questa austenite residua si trasforma in martensite durante uno caricamento meccanico: effetto TRIP (transformation induced plasticity) il che conferisce al materiale un buon compromesso tra resistenza meccanica e duttilità. La figura 1 sottostante rappresenta l'allungamento a rottura (duttilità) in funzione della resistenza meccanica delle differenze famiglie di acciaio industriale. In questa figura, il campo di esistenza degli acciai 3G AHSS si colloca in una zona dove sono elevate sia la resistenza meccanica che l'allungamento a rottura e quindi sono interessanti per lo sviluppo di prodotti industriali.

Tuttavia, la stabilità di questa fase austenitica rimane poco nota. Quindi questo lavoro è stato pensato per studiare la stabilità **termica** dell'austenite in funzione della composizione chimica del materiale e della dimensione del grano austenitico di partenza.

Per fare ciò, diversi trattamenti termici sono stati realizzati su campioni di acciaio laminati a caldo e a freddo utilizzando un dilatometro Bähr. I dati forniti in output dal dilatometro sono stati analizzati per determinare la temperatura di inizio trasformazione martensitica Ms (parametro che rappresenta la stabilità termica dell'austenite) e la cinetica di trasformazione. Inoltre, analisi di micrografie ottiche ed elettroniche sono state condotte per misurare la dimensione del grano austenitico di partenza.

Prima di entrare nella problematica, uno studio bibliografico è stato realizzato per comprendere meglio i fenomeni fisici associati e, paragonare gli studi statistici dei diversi autori per individuare quello che meglio si avvicina al nostro.

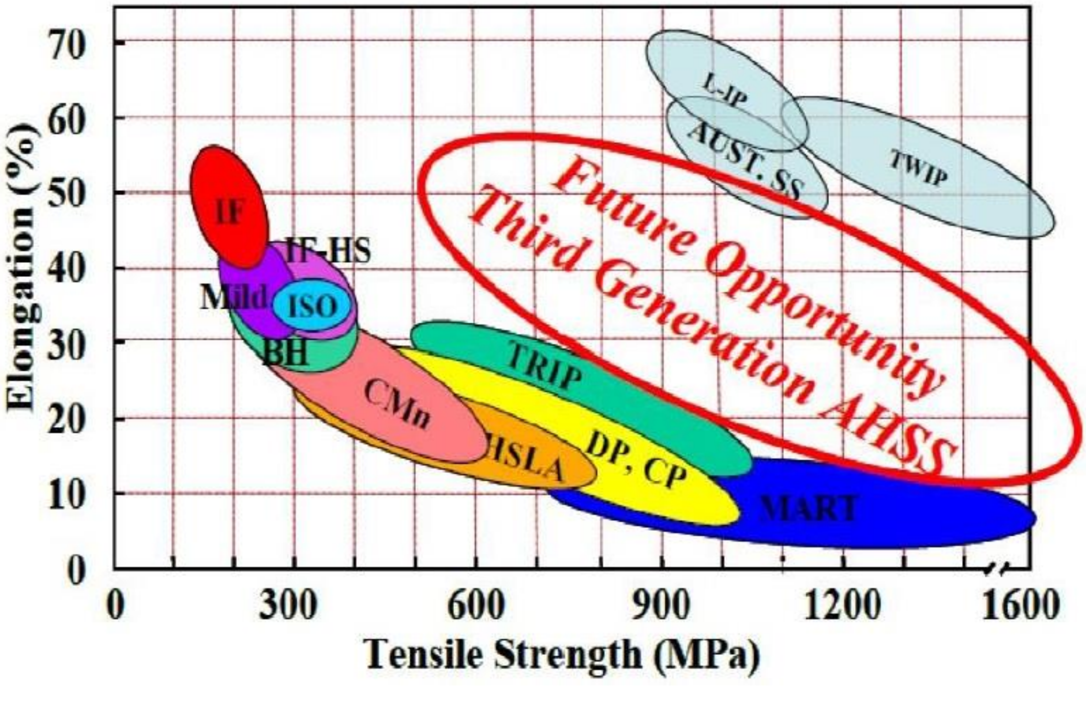


Figura 1: Grande famiglia degli acciai industriali

2) Studio bibliografico

La trasformazione martensitica è un processo non diffusivo che si verifica quando un materiale in acciaio viene temprato dal campo austenitico. La formazione di una assicella (martensite di tipo aciculare) di martensite è accompagnata da un meccanismo di taglio che genera un campo di deformazione elastica nel genitore austenite circonstante come visualizzabile in figura 2:

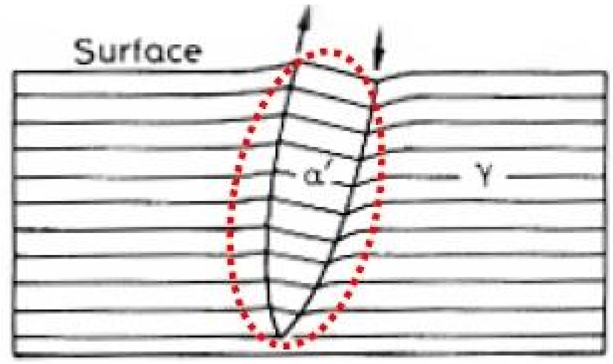


Figura 2: formazione di un nucleo di martensite (assicella) ed energia elastica associata

Questo campo di deformazione stimolerà la formazione di altre assicelle al raffreddamento del materiale: questo meccanismo è detto **cinetica di transformazione martensitica**.

La singola assicella si forma a una temperatura caratteristica detta: temperatura di inizio trasformazione martensitica: **Ms.**

La temperatura Ms dipende sia dalla composizione chimica del materiale che dalla dimensione del grano austenitico di partenza.

2.1) Influenza della composizione chimica del materiale su Ms

Alcuni autori hanno proposto delle leggi matematiche basate su studi puramente statistici per il calcolo della temperatura Ms in funzione della composizione chimica del materiale togliendosi l'effetto dimensione del grano. Il grande dibattito sta intorno alla relazione fra la temperatura Ms e la percentuale in massa di carbonio. Distingueremo due diverse correlazioni tra la temperatura Ms e la percentuale in massa di carbonio: **una correlazione polinomiale e una correlazione esponenziale**. Chiameremo queste Ms di predizione Ms_chimica in quanto non tengono conto dell'effetto dimensione di grano austenitico.

Correlazione polinomiale fra Ms e la percentuale di carbonio

In questa sezione sono elencati alcuni autori che sostengono una dipendenza polinomiale fra la temperatura Ms e la percentuale di carbonio. Fra questi abbiamo le leggi di **Andrews[2]**:

- **Equazione lineare**

$$Ms(°c)=539-423*C-30.4*Mn-17.7*Ni-12.1*Cr-7.5*Mo \qquad (1)$$

- **Equazione prodotto**

$$Ms(°c)=512-453*C-16.9*Ni+15*Cr-9.5*Mo+217*(C)^2-71.5*(C)*(Mn)-67.6*(C)*(Cr) \qquad (2)$$

La composizione degli elementi in lega è in **wt.%**

L'equazione prodotto tiene conto dei termini di secondo ordine nonché le differenze interazioni fra gli elementi di lega.

L'artificial neutral network (ANN) ha proposto un altro modello che tiene conto di tutte le differenze interazioni tra gli elementi di lega. L'equazione proposta è data da:

$$Ms(°c)=540{,}06-584{,}9*C-23{,}1*Si-117{,}7*Mn-42{,}5*Cr+49{,}9*Mo-62{,}5*\omega_{C-Si}+178{,}3*\omega_{C-Mn}-10*\omega_{C-Cr}+52{,}5*\omega_{C-Mo}+117{,}2*\omega_{Si-Mn}+50{,}9\omega_{Si-Cr}-142{,}2*\omega_{Si-Mo}-29{,}2*\omega_{Mn-Cr}-9{,}7*\omega_{Mn-Mo}+69{,}9*\omega_{Cr-Mo} \qquad \textbf{(3)}$$

$$\text{Con } \boldsymbol{\omega_{A-B}=\sqrt{}A-B}$$

Correlazione esponenziale fra Ms e la percentuale di carbonio

In questa sezione sono presentate alcune formule che danno una correlazione esponenziale fra Ms e il tenore in carbonio nel materiale. Queste formule stanno sulla base del fatto che il carbonio ha l'effetto maggiore di riduzione di Ms. La più famosa di queste è stata proposta da **Van Bohemen[4]:**

$$Ms(°c)=565-600*(1-Exp(-0.96*C\%))-31*Mn\%-13*Si\%-10*Cr\%-8*Ni\%-12*Mo\%. \qquad \textbf{(4)}$$

Babier[5] ha proposto un altra formula che tiene conto di più elementi di lega con forchette composizionali più ampie:

$$Ms(°c)=545-601.2*(1-Exp(-0.868*C))-34.4*Mn-13.7*Si-9.2*Cr-17.3*Ni-15.4*Mo+10.8*V+4.7*Co-1.4*Al-16.3*Cu-361*Nb-2.44*Ti-3448*B. \qquad \textbf{(5)}$$

il confronto fra le varie correlazioni (lineare ed esponenziale) è presentato in figura 3 seguente:

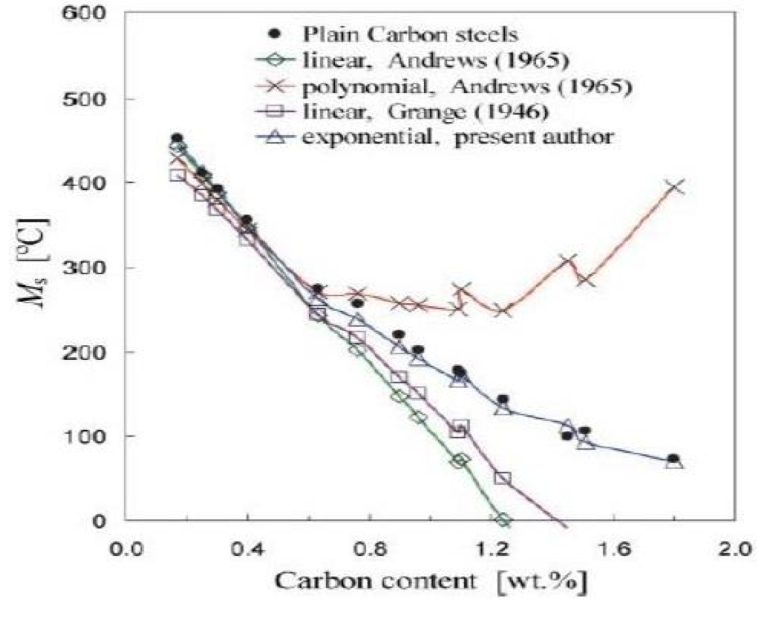


Figura 3: confronto fra le formule di predizione di Ms in fuzione de la composizione chimica**.**

La figura 3 permette di confrontare le differenze correlazioni fra Ms e il tenore in carbonio con i risultati esperimentali ottenuti negli studi di **Van Bohemen e Siestma J.[4].** Dal grafico, si nota che le correlazioni polinomiali ed esponenziali descrivono bene i risultati esperimentali per un tenore di carbonio minore di circa 0,6%. Oltre questo valore di carbonio, la correlazione esponenziale è l'unica che riproduce con buona approssimazione i risultati sperimentali. Il confronto fra le varie formule proposte nella bibliografia applicata alle nostre composizioni chimiche con i risultati sperimentali ottenuti è dato:

REF	%C	%Mn	d(µm)	Ms_exp(°c)	ΔMs(°c)
2270A	0,045	7,32	6,1±0,91	291	60
2270C	0,16	7,33	6,1±0,91	231	

Equazione lineare di Andrews

2270A: Ms = 539-423*0,045-30,4*7,32=297,437°c
2270C: Ms =539-423*0,16-30,4*7,33=248,488°c
ΔMs = 49°c

Equazione di Van Bohemen

2270A: Ms =565-600*[1-exp(-0,96*0,045)]-31*7,32=312,712°c
2270C: Ms =565-600*[1-exp(-0,96*0,16)]-31*7,33=252,339°c
ΔMs = 60°c

Equazione di Babier

2270A: Ms = 545-601,2*(1-Exp(-0,868*0,045))-34,4*7,32=270°c
2270C: Ms = 545-601,2*(1-Exp(-0,868*0,16))-34,4*7,32=215°c
ΔMs = 55°c

Questo confronto ci consente di concludere che l'equazione proposto da Van Bohemen predisce meglio il valore sperimentale di Ms dovuto alla sola composizione chimica. Quindi è stata ritenuta in questo lavoro per il calcolo di Ms_chimica.

2.2) Influenza della dimensione del grano austenitico di partenza su la temperatura Ms

Per studiare l'effetto della dimensione di partenza del grano austenitico su Ms, si deve prima togliere l'effetto composizione chimica. Per fare ciò, si considera un materiale con una certa composizione chimica, e si fa variare la dimensione del grano austenitico cambiando la temperatura di mantenimento nel campo di esistenza dell'austenite. Alcune equazioni sono state proposte per predire Ms in funzione della dimensione de grano austenitico di partenza:

Equazione di Yang & Bhadeshia

$$M_s^0\text{-}T = \frac{1}{b}\ln\left[\frac{1}{aV_\gamma}\left\{exp\left(-\frac{\ln(1-f)}{m}\right)-1\right\}+1\right] \qquad \textbf{(6)}$$

dove

M_s^0: temperatura Ms per un grano austenitico infinitamente grande
a, b: due costanti di raccordo, **f** frazione volumica di martensite alla temperatura T
m: rapporto di aspetto di una assicella di martensite, **V_γ** volume medio del grano austenitico.

M_s^0, a, b e **m** sono fissati per una determinata composizione chimica mentre **V_γ** varia.

Equazione di Seok-Jae Lee

$$\mathbf{Ms(°c)=545-423wt\%C-30.4wt\%Mn-60.5V_\gamma^{-1/3}} \qquad \mathbf{(7)}$$

dove $\mathbf{V_\gamma}$ rappresenta il volume medio del grano austenitico

il confronte fra queste due equazioni con i risultati sperimentali ottenuti dal lavoro di Garcia Junceda, è presentato in figura 4:

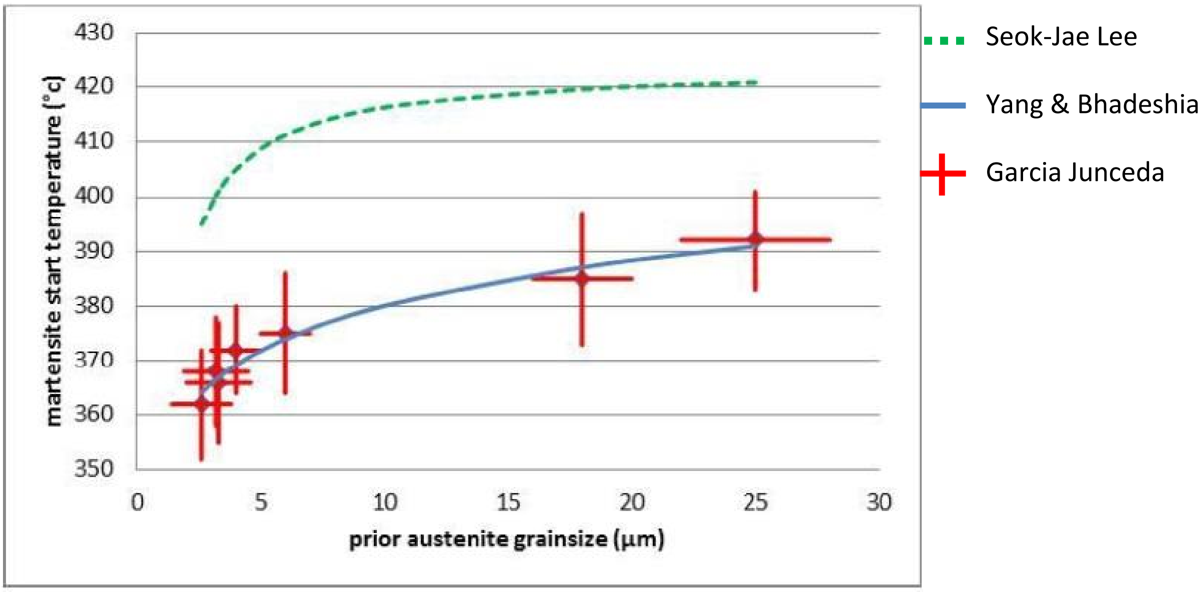


Figura 4: confronto dell'equazione di Yang & Bhadeshia e Seok-Jae Lee con il lavoro sperimentale di Garcia Junceda

Dal confronto di figura 4, si vede che l'equazione di Yang & Bhadeshia è più adatta per la descrizione dell'evoluzione di Ms con la dimensione del grano austenitico di partenza. La curva che descrive l'evoluzione di Ms con la dimensione del grano austenitico proposto da Seok-Jae Lee ha comunque la stessa forma di quella sperimentale.

3) Procedura sperimentale

La procedura sperimentale è stata effetuata su due step:

- trattamenti termici utilizzando un dilatometro Bähr con lo scopo di determinare la cinetica di trasformazione martensitica.
- Studio metallografico per misurare la dimensione del grano austenitico di partenza.

3.1) Trattamenti termici

I trattamenti termici sono stati realizzati su campioni di materiale laminati a caldo (forma cilindrica) e a freddo (forma di un parallelepipede) nel campo austenitico ad una determinata temperatura e tempo di mantenimento. La figura 5 mostra i campioni utilizzati nonché i cicli termici applicati:

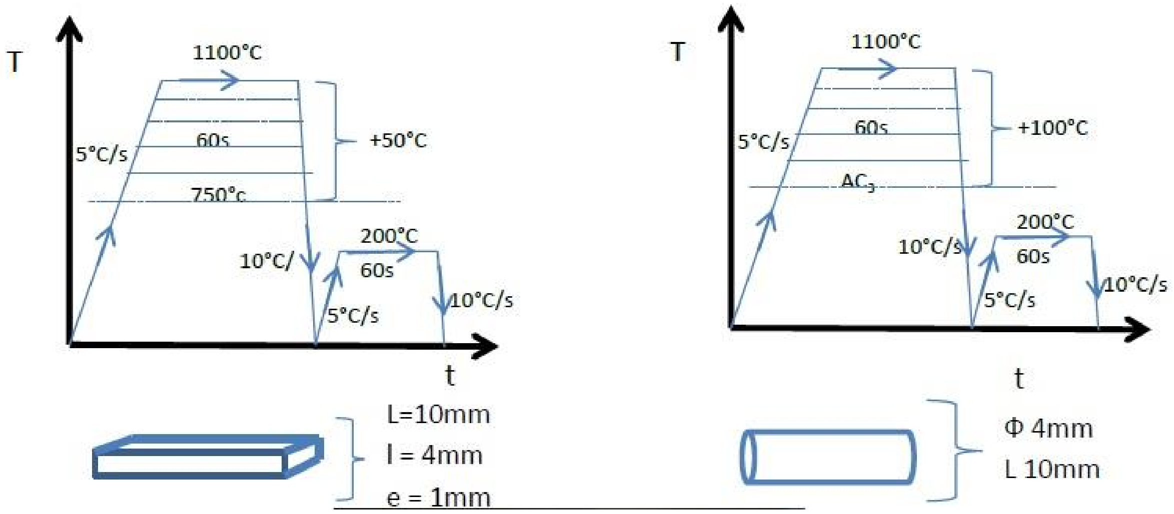


Figura 5: campioni e cicli termici per l'esperienza di dilatometria

I campioni laminati a freddo sono stati riscaldati dalla temperatura ambientale fino a una temperatura di mantenimento compresa fra [750°c-1100°c] con una velocità di 5°c/s. Il tempo di mantenimento per ogni ciclo è di un minuto. Seguito da un raffreddamento fino alla temperatura ambiente con una velocità di 10°c/s (questa velocità era sufficiente per formare la martensite perche i campioni erano auto-tempranti). Un altro ciclo termico è stato agguinto dopo il raffreddamento alla temperatura ambiente. Esso consiste in un riscaldamento con una velocità di 5°c/s fino a 200°c, seguito da un mantenimento di un minuto e un successivo raffreddamento con 10°c/s fino alla temperatura ambiente. Questo ultimo ciclo è necessario per determinare con buona approssimazione la cinetica di trasformazione martensitica. Gli stessi cicli sono stati applicati ai campioni laminati a caldo. In questo caso, le temperatura di mantenimento sono comprese tra [AC_3-1100°c] con passo di variazione di 100°c invece di 50°c per i laminati a freddo. La dimensione del grano austenitico è controllata dalla temperatura e tempo di mantenimento, quindi a temperatura di mantenimento maggiore corrisponde un grano più grande a parità di tempo di mantenimento. Durante l'esperienza, la dilatazione termica del campione viene misurata in funzione della temperatura e del tempo. I risultati ottenuti sono presentati in figura 6:

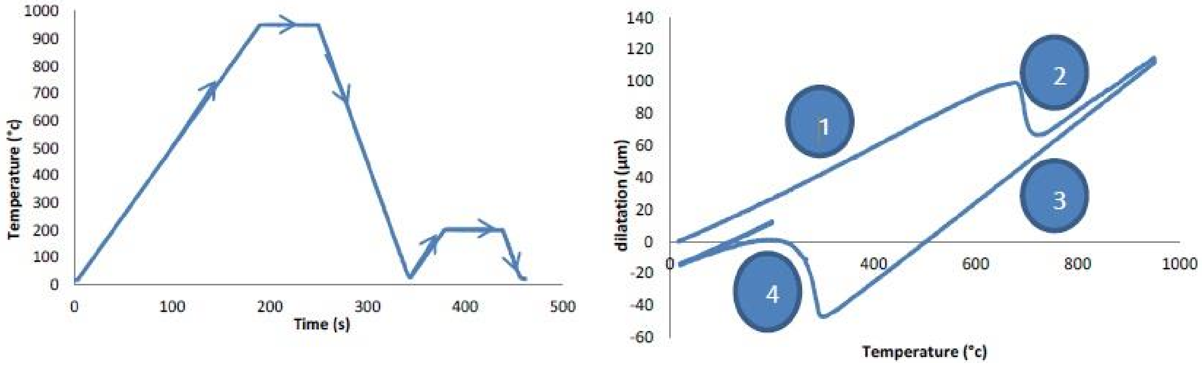


Figura 6: dati di output dell'esperienza di dilatometria

La curva di dilatazione in funzione della temperatura mostra una prima regione lineare (regione 1) che corrisponde alla dilatazione della microstruttura iniziale del campione. Questa regione si prolunga fino alla temperatura AC_1 dove si verifica un cambiamento di pendenza corrispondente all'inizio della trasformazione austenitica. L'austenite continua a formarsi durante l'esperienza fino ad AC_3 dove tutta la microstruttura iniziale si è trasformata in austenite, il materiale continua a dilatarsi in modo lineare (regione 2). Quando inizia il raffreddamento, l'austenite continua a dilatarsi in modo lineare ma questa volta in compressione come mostrato nella regione 3. Questa dilatazione lineare di compressione prosegue fino alla temperatura Ms (martensite start) dove inizia a formarsi la martensite. Si verifica un cambiamento di pendenza man mano che si forma la martensite fino a temperatura ambiente (regione 4).

Calcolo della cinetica di trasformazione martensitica

Per determinare la cinetica di trasformazione martensitica per un determinato ciclo termico, si considerano le regioni 3 e 4 della curva di dilatazione in funzione della temperatura mostrate in figura 6. A queste regioni viene applicato un algoritmo di calcolo presentato in figura 7:

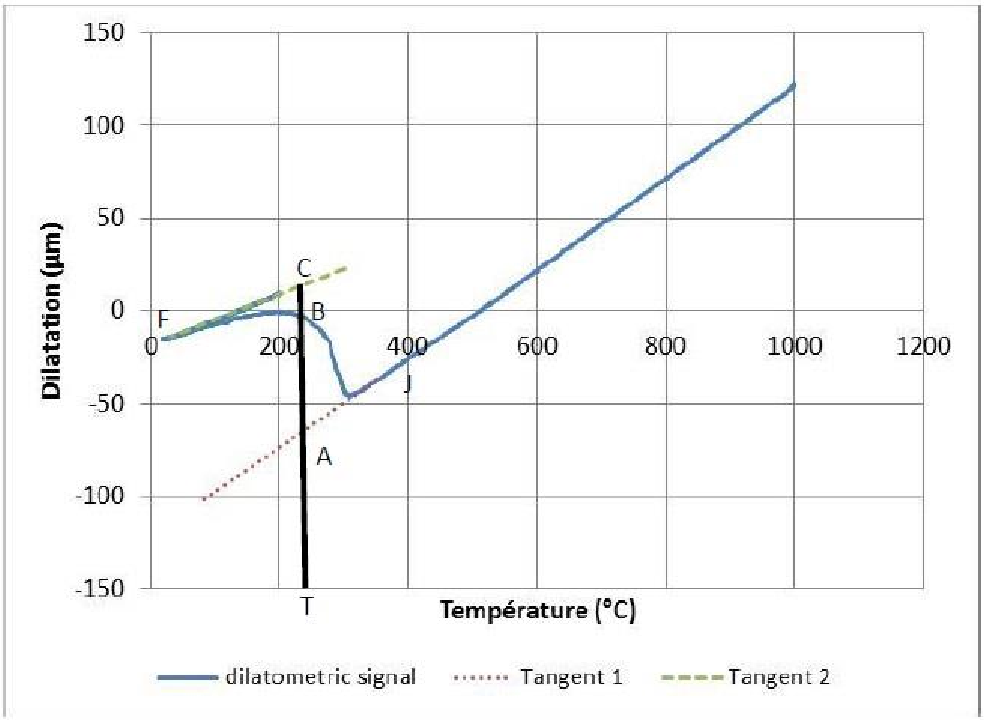


Figura 7: determinazione della curva della cinetica di trasformazione martensitica

Con l'utilizzo di una macro Excel, l'algoritmo di determinazione della cinetica di trasformazione martensitica è composto dai seguenti step:

- posizionamento della tangente viola che rappresenta la dilatazione dell'austenite in assenza di trasformazione martensitica.
- Posizionamento della tangente verde che rappresenta la dilatazione della microstruttura finale (martensite + austenite residua) quando si fa un rinvenimento.

- Tra i punti F e J si tracciano delle isoterme. Ad ogni isoterma T si applica la legge del braccio di leva per determinare la frazione volumica di martensite formata a quella temperatura. La frazione di martensite ottenuta viene moltiplica per la frazione volumica di austenite residua. Si ottiene:

$$f_{\alpha}' = \frac{AB}{AC} x(1\text{-}RA)$$

Dove f_{α}' rappresenta la frazione volumica di martensite alla temperatura T; **RA** è la frazione volumica di austenite residua.

Applicando la stessa procedura per tutti gli isotermi compresi fra F e J, si ottiene la curva che descrive la cinetica di trasformazione martensitica visualizzabile in figura 8:

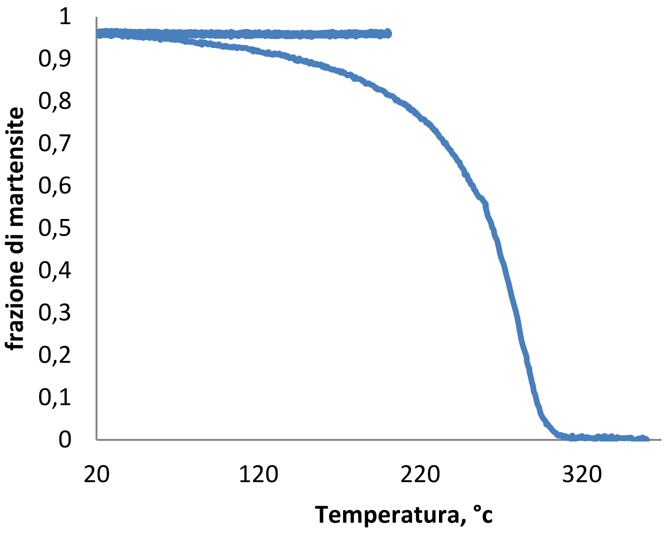


Figura 8: cinetica di trasformazione martensitica

Per ogni curva di cinetica, la temperatura Ms corrisponde alla temperatura per la quale la frazione volumica di martensite formata è di 0,05. Per assicurare la riproduttività dei risultati, l'esperienza di dilatometria è stata condotta tre volte per ogni temperatura di mantenimento. In questo modo la temperatura Ms ritenuta è la media delle tre temperature determinate.

3.2) Studio metallografico

Lo scopo di questa parte è di misurare la dimensione del grano austenitico di partenza per ogni temperatura di mantenimento nell'esperienza di dilatometria. Per fare ciò, il campione all'uscita del dilatometro viene tagliato in corrispondenza delle termocoppie come mostrato in figura 9:

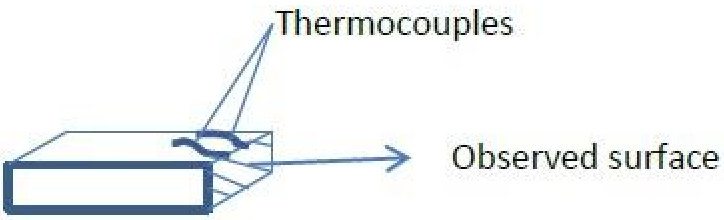
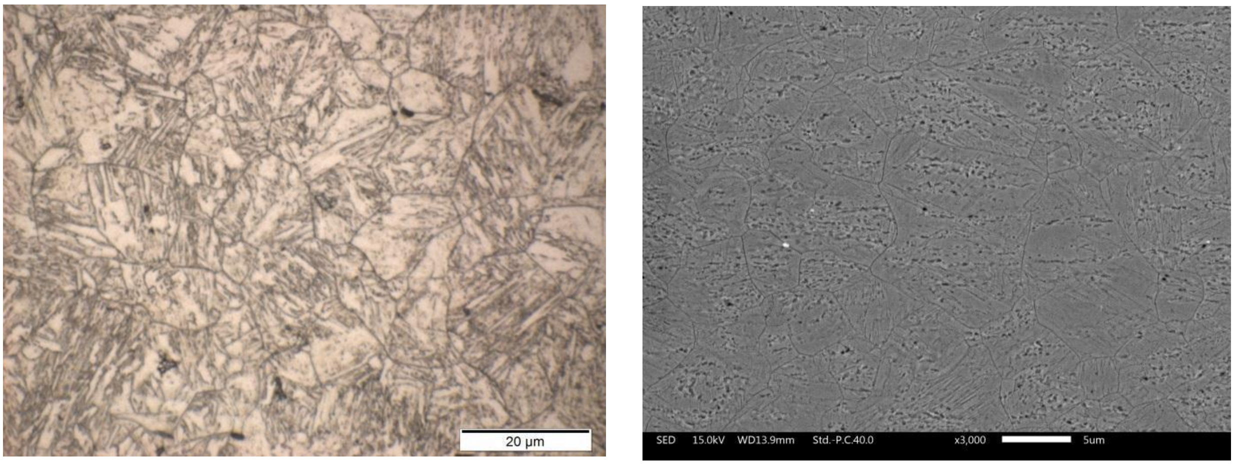


Figura 9: campione utile per lo studio metallografico

La parte di campione in figura 9 viene racchuisa in una resina conduttrice, poi seguono fasi di lucidatura ed attacco chimico. Lo step finale consiste nell'osservazione microscopica utilizzato il microscopio ottico ed elettronico a scansione. Le micrografie ottenute sono presentate in figura10:



micrografia ottica

micrografia elettronica a scansione

Figura 10: micrografie per la misura della dimensione del grano austenitico di partenza

La misura della dimensione del grano austenitico si è effettuata con un software chiamato "**APHELION"** che sfrutta il concetto di intercetta lineare media. Per avere una buona statistica del valore medio della dimensione del grano, erano necessarie l'utilizzo di almeno 12 micrografie per ogni temperatura di mantenimento. L'incertezza di misura è data dalla somma dell'intervallo di confidenza fornito da Excel più il 10% del valore di dimensione del grano ottenuto dal software.

4) Risultati e discussione

Le composizioni chimiche utilizzate in questo studio sono mostrate in tabella 1 e 2:

Tabella1: composizione chimica di campioni analizzati nello stato laminato a caldo e a freddo

REF	**C(wt.%)**	**Mn (wt.%)**	**S (wt.%)**	**P (wt.%)**
2270A	0,045	7,32	0,005	0,005
2270C	0,16	7,33	0,005	0,005

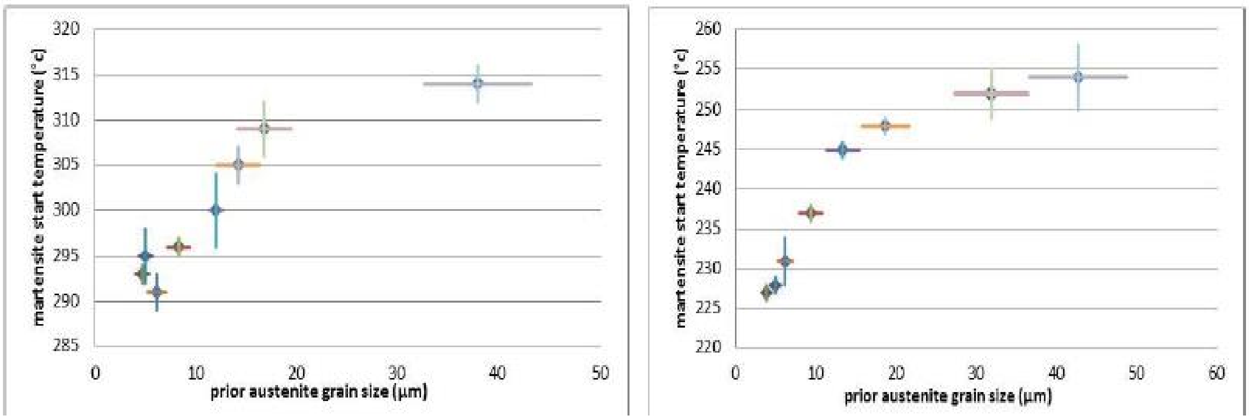
Tabella2: composizione chimica di campioni analizzati nello stato laminato a freddo

REF	**C wt.%**	**Mn wt.%**	**S wt.%**	**P wt.%**	**Si wt.%**	**Al wt.%**	**Cr wt.%**	**N ppm**	**B ppm**
2260B	0,098	4,73	0,001	0,005	0,001	0,003	0,003	7,2	6

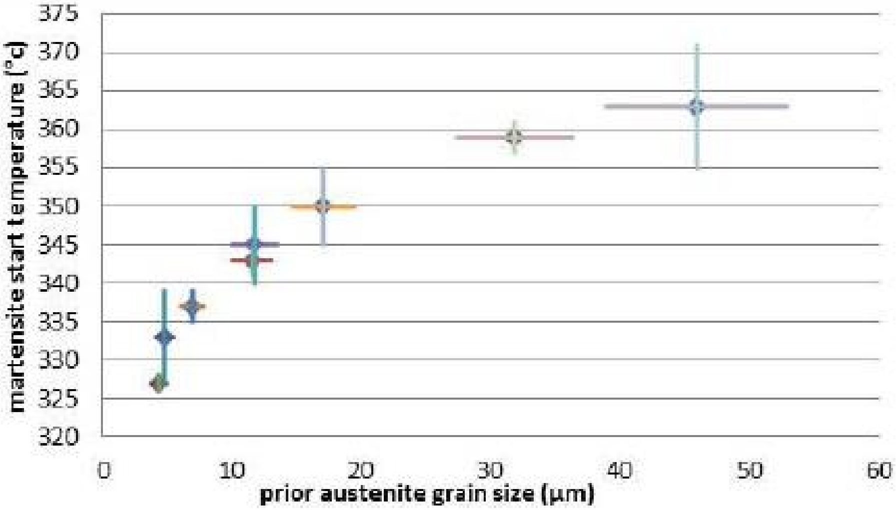
Temperatura di inizio trasformazione della martensite (Ms)

Come detto prima, la temperatura Ms dipende sia dalla composizione chimica del materiale che dalla dimensione del grano austenitico di partenza. Per il contribuito dei due effetti, uno può tracciare l'evoluzione di Ms globale in funzione della dimensione del grano austenitico come visualizzabile in figura 11:

Materiali laminati a freddo

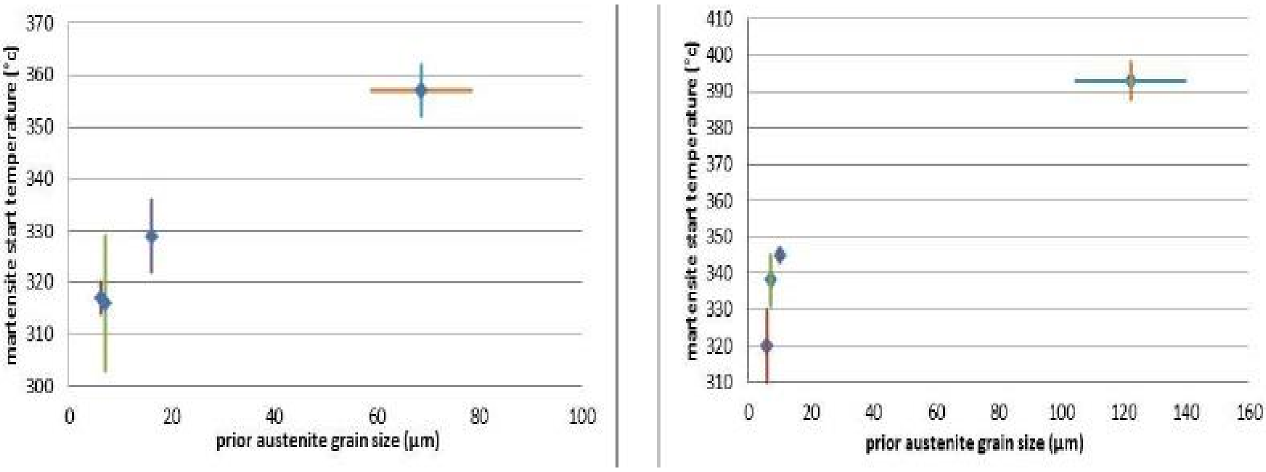


2270A **2270C**



2260B

Materiali laminati a caldo

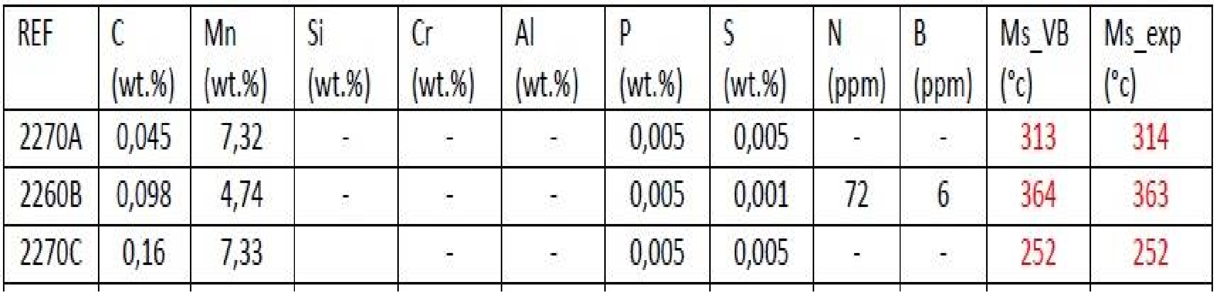


2270A **2270C**

Figura 11: evoluzione di Ms globale con la dimensione del grano austenitico di partenza

Dai grafici di figura 11 si vede che la temperatura Ms globale descrive una evoluzione logaritmica con la dimensione de grano. Questa forma di cruva era predita da Yang & Bhadeshia nella loro equazione. Inoltre, si nota l'esistenza di un plateau quindi un valore critico della dimensione del grano oltre il quale non si osserva più un aumento di Ms globale. Da questo valore critico in poi si può concludere che la Ms osservata è dovuta al solo contribuito della composizione chimica. Questa Ms è stata chiamata in precedenza Ms_chimica ed è descritta con buona approssimazione dall'equazione proposta da Van Bohemen. Per confermare ciò, sono state calcolate le temperature Ms dei materiali utilizzati in questo studio utilizzando l'equazione di Van Bohemen, e confrontate con i valori sperimentali ottenuti. La tabella 3 seguente mostra i confronti:

Tabella 3: confronto fra Ms calcolati e Ms sperimentali



REF	C (wt.%)	Mn (wt.%)	Si (wt.%)	Cr (wt.%)	Al (wt.%)	P (wt.%)	S (wt.%)	N (ppm)	B (ppm)	Ms_VB (°c)	Ms_exp (°c)
2270A	0,045	7,32	-	-	-	0,005	0,005	-	-	313	314
2260B	0,098	4,74	-	-	-	0,005	0,001	72	6	364	363
2270C	0,16	7,33		-	-	0,005	0,005	-	-	252	252

Le ultime due colonne della tabella 3 mostrano valori simili fra Ms calcolati con l'equazione di Van Bohemen e Ms sperimentali in corrispondenza di alti valori di dimensione di grano austenitico di partenza. Da questo risultato si può concludere che:

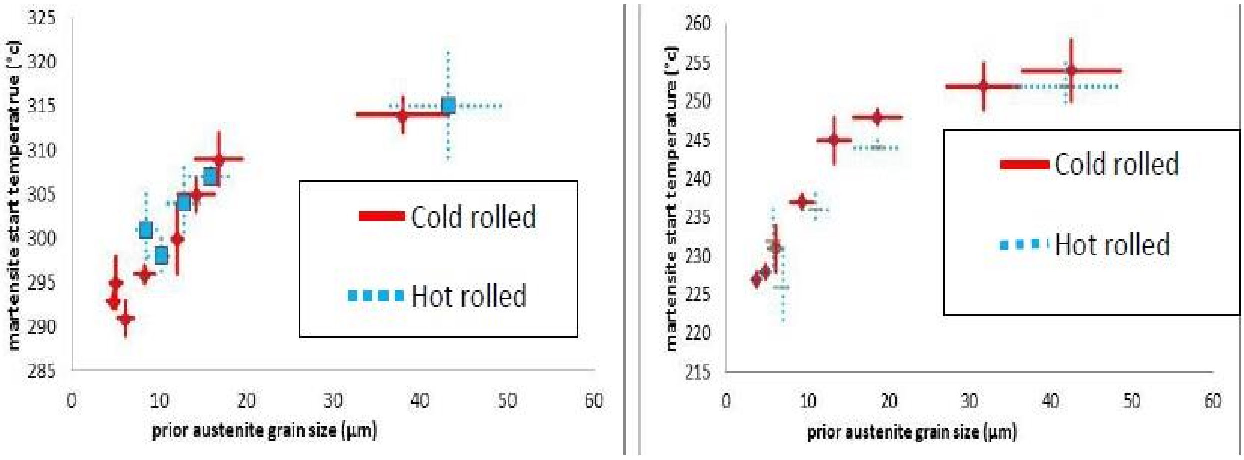
- La temperatura Ms a partire da un valore elevato (circa 15µm) di dimensione di grano austenitico è dovuta al solo contribuito della composizione chimica, ed è chiamata in questo lavoro Ms_chimica.
- La Ms_chimica è ricavabile con l'equazione di Van Bohemen per composizione chimiche entro il range utilizzato nel suo studio.

4.1) Confronto fra materiale laminato a caldo e a freddo

Uno degli scopi di questo studio era di studiare l'effetto dello stato laminato di un acciaio in termini di trasformazione martensitica. Per fare ciò, il confronto di due stati di laminazione (a caldo e a freddo) di un acciaio è stato fatto in termini di :

- Evoluzione di Ms globale in funzione della dimensione del grano austenitico di partenza
- Curve di trasformazione martensitica a una stessa temperatura di mantenimento

I risultati del confronto sono presentati in figura 12 che segue:



2270A 2270C

T=800°c; 2270A T=1100°c; 2270C

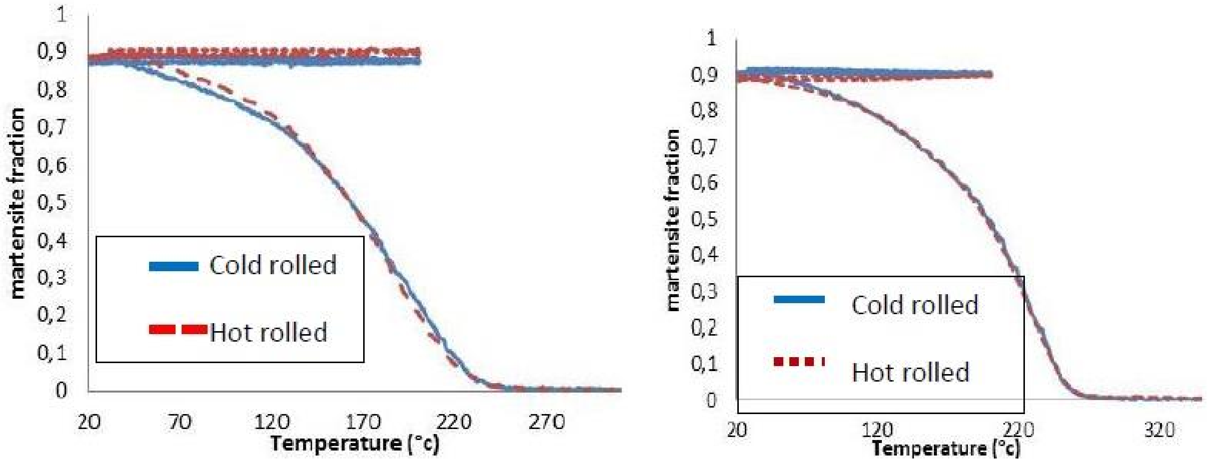


Figura 12: confronto di stati di laminazione (caldo e freddo):2270A e 2270C

Il confronto di figura 12 mostra un comportamento simile tra i due stati di laminazione per i due tipi di acciaio 2270A e 2270C sia in termini di evoluzione di Ms globale con la dimensione del grano sia in termini di cinetica di trasformazione martensitica. Quindi si può concludere che lo stato di laminazione non influisce su la trasformazione martensitica dell'acciaio.

4.2) Influenza del contenuto di carbonio sulla temperatura Ms

Per studiare l'effetto del carbonio sulla temperatura Ms, due acciai di diversa percentuale in carbonio sono stati confrontati: **2270A: Fe-0,045C-7,32Mn; 2270C: Fe-0,16C-7,32Mn.** Quindi per un $\Delta C=0{,}115$wt.% abbiamo un $\Delta M_s= 60$°c. Questa differenza in Ms si verifica per tutti i valori di dimensione del grano austenitica come si può vedere nel grafico di figura 13 seguente:

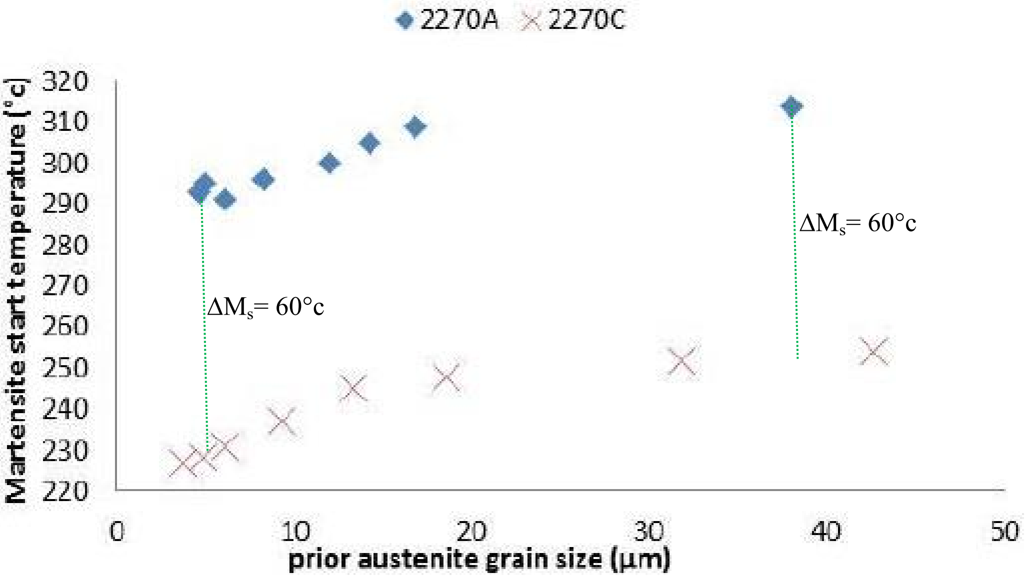


Figura 13: Effetto de carbonio sulla temperatura Ms

Questa differenza di ordine di grandezza nei valori di Ms per una piccola variazione del contenuto di carbonio mette in luce la forza di riduzione del carbonio su Ms. In altre parole il potere stabilizzante del carbonio della fase austenitica è molto elevato.

4.3) Influenza della dimensione del grano austenitico di partenza sulla temperatura Ms

Avendo chimato Ms_chimica ilcontribuito dell'effetto chimico sulla temperatura Ms globale e supponendo un effetto additivo con quello della dimensione del grano, possiamo scrivere:

$$\mathbf{Ms_{PAGS}= Ms\_exp-Ms\_chimica}$$

Dove **Ms_{PAGS}:** contribuito della dimensione del grano austenitico primario su Ms
Ms_exp: la temperatura Ms sperimentale globale.
Riportando su un grafico semi-logaritmico i valori di **Ms_{PAGS}** in funzione della dimensione del grano austenitico, si ottiene la figura 13 seguente:

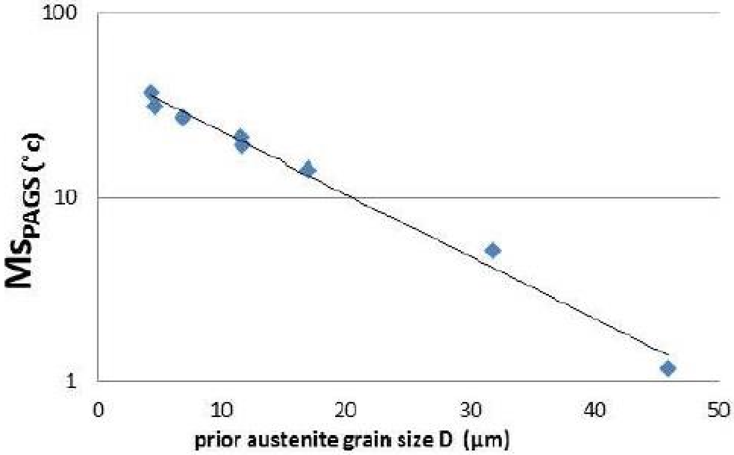


Figura 13: evoluzione di **Ms_{PAGS}** in funzione della dimensione del grano.

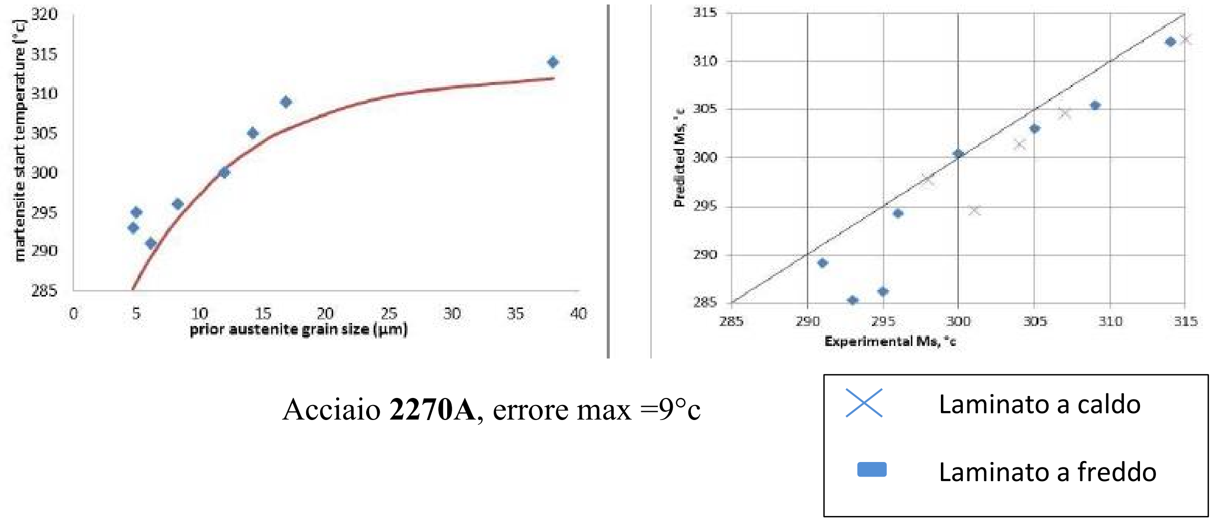
Da questa evoluzione di $\mathbf{Ms_{PAGS}}$ in funzione della dimensione del grano viene fuori una relazione esponenziale del tipo:

$$Ms_{PAGS} = \alpha e^{-\beta * D}$$

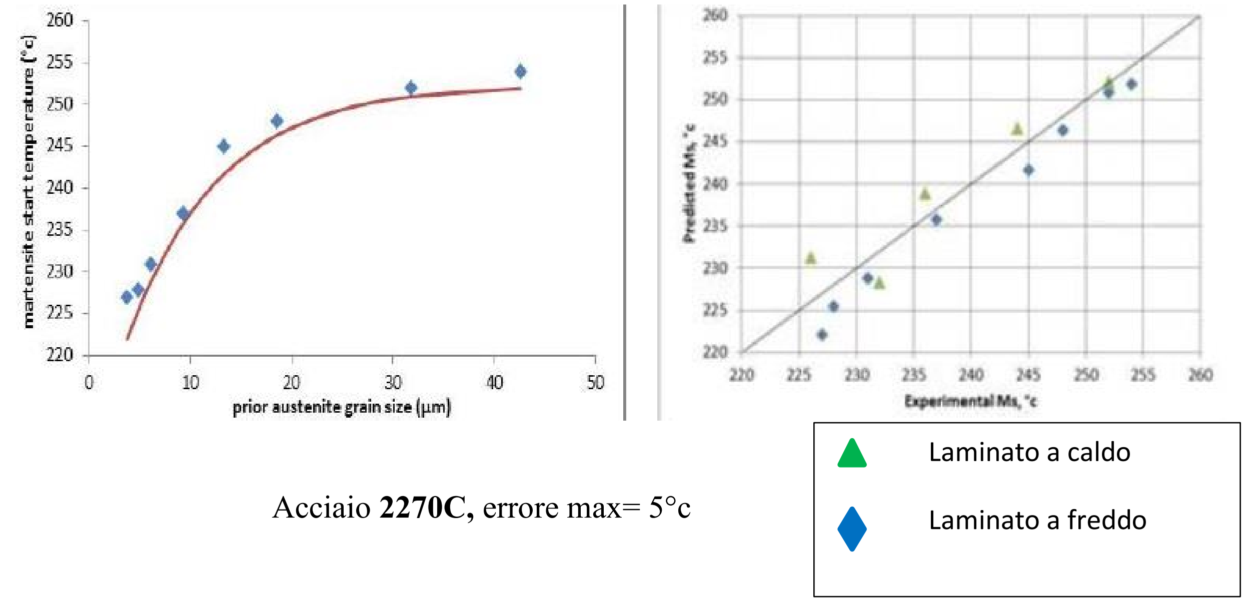
dove: **α** e **β** sono due costanti e **D** la dimensione del grano austenitico di partenza.
Da questo relazione è stato possibile proporre una equazione di predizione della temperatura di inizio trasformazione martensitica Ms in funzione della composizione chimica dell'acciaio nonché la dimensione del grano austenitico di partenza:

$$\mathbf{Ms = Ms\_van\ Bohemen} + \alpha e^{-\beta * D}$$

Applicando questa legge sugli acciai utilizzati in questo studio e confrontando con i risultati sperimentali ottenuti, si ottiene i seguenti dati di figura 14:



Acciaio **2270A**, errore max =9°c



Acciaio **2270C,** errore max= 5°c

Figura 14: Confronto tra Ms calcolato con l'equazione proposto in questo studio e Ms sperimentale scegliendo $\alpha = 46$ e $\beta = 0{,}11$.

Il confronto di figura 14 mostra una buona riproduzione dell'andamento di Ms sperimentale in funzione della dimensione del grano austenitico utilizzando la nuova formula proposta. Inoltre, i valori di Ms ottenuti con questa equazione sono molto simili a quelli sperimentali, con errori massimi contenuti entro 10°c in entrambi i casi.

5) Conclusione

Questo lavoro è stato pensato per studiare l'influenza della composizione chimica e la dimensione del grano austenitico di partenza sulla stabilità termica dell'austenite per acciai laminati a caldo e a freddo. Stabilità termica che viene descritta dal parametro Ms: temperatura di inizio trasformazione martensitica. Dallo studio bibliografico viene fuori che tutti gli elementi di lega riducono la temperatura Ms. L'effetto maggiore di riduzione è assegnato al carbonio. Tra le equazioni proposte nella bibliografia, quella di Van Bohemen risulta più adatta per predire la Ms in funzione della composizione chimica. Yang & Bhadeshia hanno proposto un'equazione che tiene conto dell'effetto dimensione del grano austenitico di partenza per descrivere la temperatura Ms, e questa equazione riproduce con buona approssimazione l'evoluzione di Ms sperimentale con la dimensione del grano austenitico di partenza.

La procedura sperimentale ha consistita nella realizzazione di esperienze di dilatazione a diverse temperature e tempo di mentenimento nel campo austenitico per determinare la cinetica di trasformazione martensitica. I campioni trattati sono stati sottoposti a studi metallografici per misurare la dimensione del grano austenitico di partenza.

I risultati ottenuti mostrano una similitudine nella trasformazione martensitica per un materiale laminato a caldo e a freddo. In effetti, l'evoluzione di Ms globale in funzione della dimensione del grano austenitico nonché la cinetica di trasformazione martensitica sono gli stessi in entrambi gli stati di laminazione.

La temperatura Ms globale ha un'evoluzione logaritmica con la dimensione del grano austenitico fino a raggiungere un valore di plateau a partire dal quale l'effetto dimensione del grano su Ms diventa trascurabile. Da questo punto è stato possibile determinare l'effetto composizione chimica su Ms che è ben descritto dall'equazione di Van Bohemen. Supponendo un effetto additivo tra i due parametri, è stato proposto un equazione del tipo:

$\alpha e^{-\beta * D}$ per descrivere l'effetto dimensione del grano austenitico su Ms.

Con questo risultato, è stato possibile proporre un'equazione di predizione della temperatura Ms in funzione dei due parametri:

$$\mathrm{Ms}(°\mathrm{c}) = \mathrm{Ms\_VB} - \alpha e^{-\beta * D}$$

con α e β due costanti, D il diametro medio della dimensione del grano austenitico.

Per α = 46 e β = 0,11 si è riuscito a riprodure con buona approssimazione i risultati sperimentali con errori massimi inferiori a 10°c.

ACKNOWLEGEMENTS

First of all, I would like to thank God for his support an inspiration during my entire life. He filled me with motivation and work spirit and is responsible of all the achievements in my life.

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I would also like to express my gratitude to my supervisors: ARTEM ARLAZAROV and DIDIER HUIN. They helped me think and act with an engineer spirit, gave me my autonomy to orient my work in relationship with my goals. Our numerous discussions contributed to the development of this work and allowed good understanding of the happening phenomena.

I am extremely thankful to NORA KABO my assistant supervisor for her availability and welcome in ArcelorMittal research center. She acts to me like a mother through her advices and orientation to facilitate my work and insertion in the industry world. A particular thank to Giuseppe SOLLAZZO for his assistance in metallography work and his sympathy.

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I. Company presentation

My engineer internship took place to the research and development center of ArcelorMittal located in Maizières-lès-Metz in Moselle department (France). ArcelorMittal is the world's number one steel company with 260000 employees. It has led the consolidation of the world steel industry and today ranks as the only truly global steelmaker with an industrial presence in 27 countries.

ArcelorMittal is the leader in all major global markets, including automotive, construction, household appliances and packaging. ArcelorMittal global R&D is spanning the globe with 11 sites dedicated to research (operating in process, products, application and steel solution) within 7 countries and more than 20 nationalities. Among these research centers is central Maizières-lès-Metz:

Delta: département automobile

Maizières-lès-Metz ArcelorMittal research center

The Maizières-lès-Metz campus is divided in four departments presented in the flowing:

Process:
Development and deployment of process solution

Automotive Products
Develop new steels products

Packaging
Develop products and associated processes in the packaging market

Mining & Mineral Processing
Characterisation and evaluation of new raw materials

INTRODUCTION

Most of the so-called Third generation of Advanced High Strength Steels (3G AHSS) contain a certain amount of retained austenite in the final microstructure. This retained austenite transforms in martensite during mechanical loading (TRIP effect) and provide interesting compromise between strength and ductility as shown in figure 1. This makes the 3G AHSS very attractive for the product development. In order to obtain even better mechanical behavior the fraction of retained austenite should be increased and its stability should be controlled precisely. However, there is certain knowledge about the control of austenite stability; there is still important number of questions, especially, about the influence of austenite size as well as chemical composition on its stability. Hence the present work has been thought to predict the austenite stability as a function of these two parameters. To achieve this, several thermal treatments will be performed on hot and cold rolled states steels grades using a Dilatometer bähr. In addition, Analysis of dilatometer data in order to determine the evolution of Ms (Austenite stability) and kinetics of martensite transformation will be conducted. Finally Image analysis in order to determine the Austenite grain size is also planned. Before get to that, literature study is necessary to better understand the physical phenomena related on this topic and to compare the statistical studied performed by different authors in order to identify the one that match better to our experimental results.

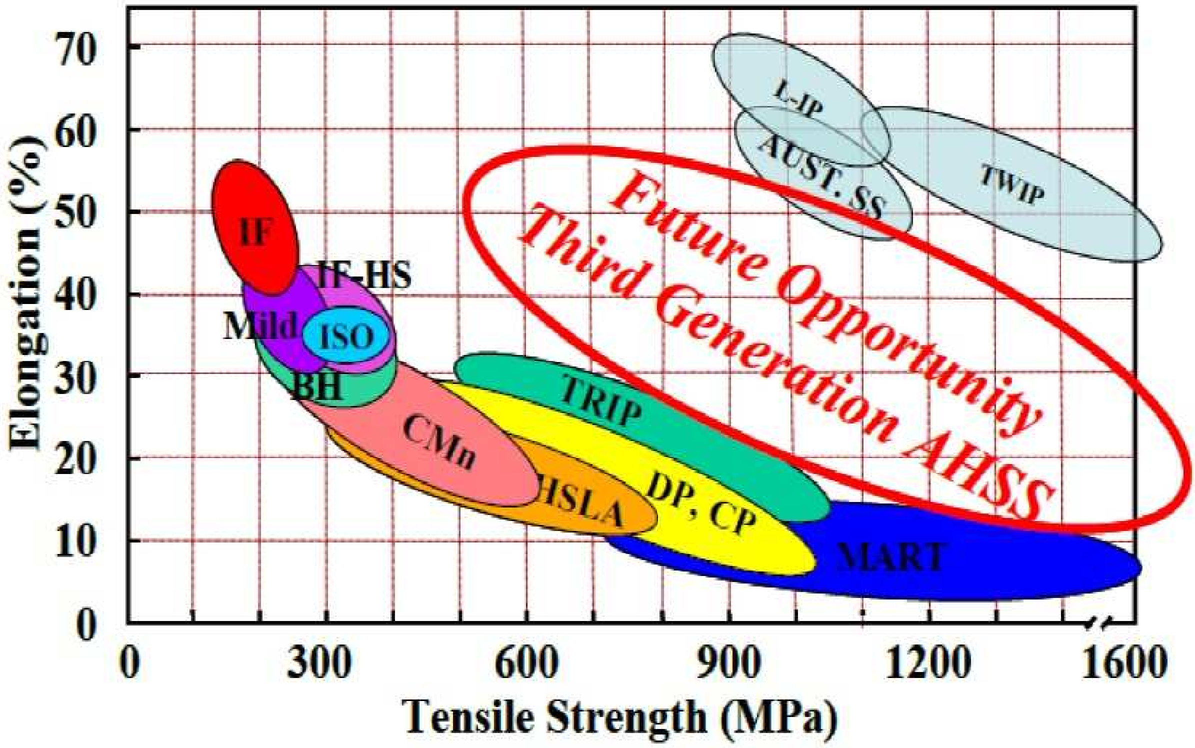


Figure 1: tensile strength and Elongation of different generations of steels

II. Literature

Athermal martensite transformation is a diffusionless transformation where steel is quenched from the austenitic field. Atoms change position in a regimented manner during the transformation which is termed "military" in contrast to diffusion-controlled transformations termed civilian. The rapid cooling rate necessary for the transformation to occur brings the majority of carbon atoms to remain in solution in the γ-Fe phase during the quenching process. Since allotropic transformation of the fcc lattice of γ-Fe phase in bcc one of α-Fe phase occurs, these Carbon atoms will be trapped in the bcc lattice, as shown in figure 2, And distort it into the bct lattice of martensite.

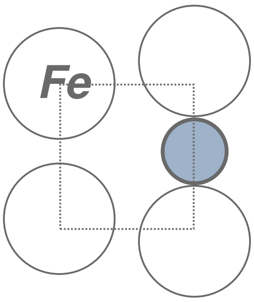


Figure 2: carbon trapped in the α-Fe lattice.

The bct lattice can be obtained by applying the **Bain Model.** According to this model, an elongated unit cell of the bct structure can be drawn within two fcc cells as shown in figure 3:

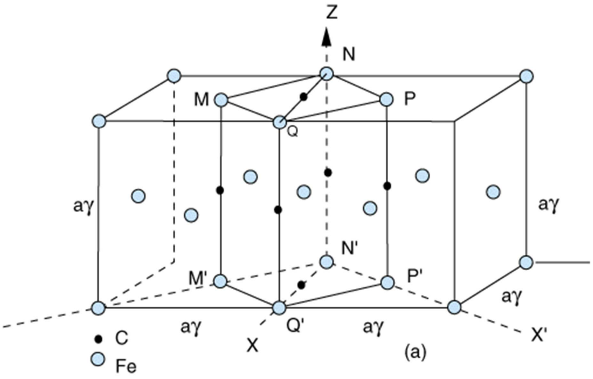


Figure 3: bct structure obtained from two fcc structures.

Transformation to a bct unit cell is achieved by expanding the bcc cell of 20% in the z-direction and contracting it of 12% along the x-and y-axes as shown in the following figure 4:

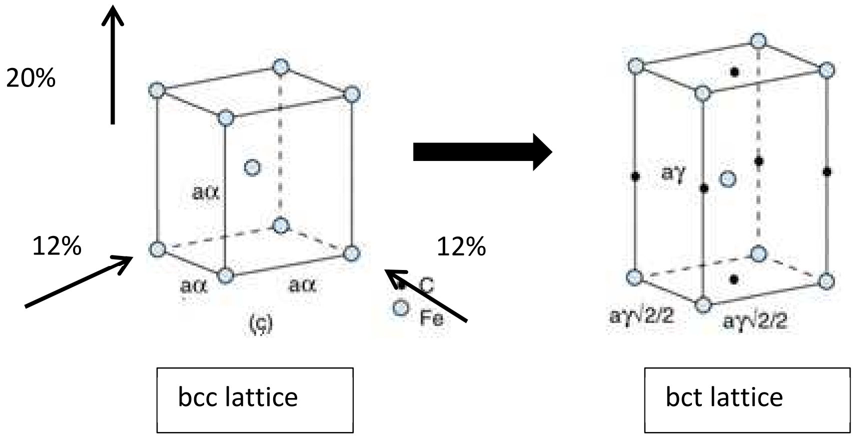


Figure 4: Bain deformation model from bcc to bct structure.

Rearrangement of carbon atoms take place during the transformation which leads to different positions occupied by carbon atoms in the bct structure than those in the parent fcc structure.

The shearing mechanism associated with martensite formation induces stresses in the surrounding austenite which suggest a coherent interface between the martensite nucleus and the parent austenite as shown in figure 5:

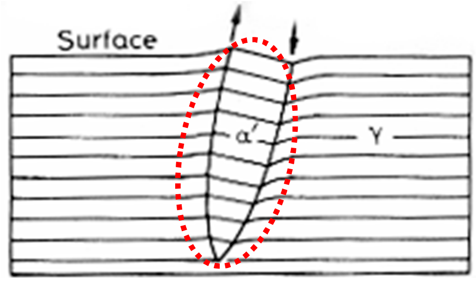


Figure 5: formation of a martensite nucleus in the parent austenite.

The total increase in Gibbs free energy associated with the formation of a fully coherent inclusion of martensite in the parent austenite can be expressed as:

$$\Delta G = A\gamma + V\Delta G_s - V\Delta G_v \qquad (1)$$

Where

γ is the interfacial free energy
ΔG$_s$ is the strain energy
ΔG$_v$ is the volume free energy release
V is the volume of the nucleus
A is the surface area

This Gibbs free energy represented with the red circle in figure 5 will stimulate the nucleation events of nuclei in the surrounding austenite. These phenomena will take place at a characteristic temperature called “martensite start temperature (Ms)”. The growth process of a nucleus is rapid enough and stop when encounter any discontinuity in the parent austenite such as another martensite lath, dislocation, grain boundary. Therefore the martensite transformation kinetics is given by the volume fraction of martensite transformed upon additional undercooling. This is theoretically described by the equation proposed by Koistinen Marburger **[1]:**

$$\mathbf{f = 1\text{-}exp\,[-0,\ 0\ 11*(M_s\text{-}T)]} \qquad \mathbf{(2)}$$

where **M_s** is the martensite start temperature.

This equation can be graphically represented in figure 6 that follows:

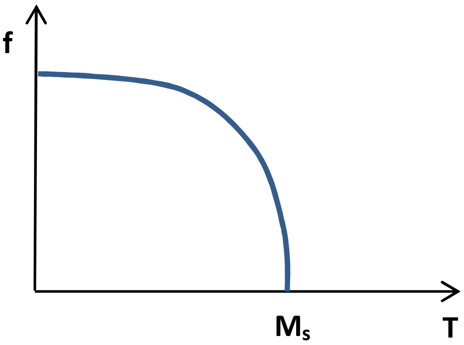


Figure 6: Martensite transformation kinetics according to Koistinen and Marburger equation

It is known that martensite start temperature (M_s) depends at least on the chemical composition of the steel. Several mathematic formulations based on statistical studies have been proposed in the literature in order to predict the martensite start temperature. Two different theories regarding the carbon effect on Ms are available in the literature: a polynomial and exponential one.

II.1 Influence of chemical composition on Ms: polynomial

Several authors proposed a polynimial dependence of carbon content on martensite start temperature. One of these famous authors to propose martensite start temperature equation is **Andrews [2]** with two different equations:

- **Linear equation**

$$M_s(°c)=539-423*C-30.4*Mn-17.7*Ni-12.1*Cr-7.5*Mo \qquad \mathbf{(3)}$$

- **Product equation**

$$M_s(°c)=512-453*C-16.9*Ni+15*Cr-9.5*Mo+217*(C)^2-71.5*(C)*(Mn)$$

$$-67.6*(C)*(Cr) \qquad \mathbf{(4)}$$

with alloying element composition in **wt.%**

The product equation takes into account the possible influence of second order terms as well as the interactions between alloying elements. The product (C)*(Mn) accounts for all the manganese variations without a linear term. The product (C)*(Cr) suggests that the chromium effect on Ms is influenced by its interaction with carbon especially when chromium exceeds 2%. This can be emphasized through three steels taken randomly where the differences between experimentally determined and calculated Ms for the chromium content is given below:

%Cr		0,98	3,16	4,61
Difference	(a) linear equation	+6,1°C	-17,3°C	-28,4°C
Observed – calculated	(b) product equation	+2,1°C	-6,1°C	-0,8°C

Regarding the chromium content, according to the above example, the product equation gives statistically a better prediction of Ms with respect to the linear one. These equations have been established for a total of 184 samples with a compositional database summarized in the following table 1:

Table 1: chemical composition used in Andrews study

wt.%	C	Mn	Ni	Cr	Mo
Composition ranges	0,110 – 0,123	0,040 – 0,528	0,000 – 1,441	0,000 – 0,714	0,000 – 0,495

In order to take into account all the possible interactions between alloying elements, another equation has been proposed in an **"artificial neural network (ANN) model" [3].** The compositional database and the corresponding equation are given in table 2 and equation 5 respectively:

Table 2: chemical composition used in ANN model

wt.%	C	Mn	Si	Cr	Mo
Composition ranges	0,2 – 0,5	0,5 – 2	0,5 – 2	0,5 – 2	0,1 – 0,7

$$M_s(°c)=540,06-584,9*C-23,1*Si-117,7*Mn-42,5*Cr+49,9*Mo-62,5*\omega_{C\text{-}Si}+178,3*\omega_{C\text{-}Mn}-10*\omega_{C\text{-}Cr}+52,5*\omega_{C\text{-}Mo}+117,2*\omega_{Si\text{-}Mn}+50,9\omega_{Si\text{-}Cr}-142,2*\omega_{Si\text{-}Mo}-29,2*\omega_{Mn\text{-}Cr}-9,7*\omega_{Mn\text{-}Mo}+69,9*\omega_{Cr\text{-}Mo} \quad \textbf{(5)}$$

Where $\boldsymbol{\omega_{A\text{-}B}}=\sqrt{\boldsymbol{A}*\boldsymbol{B}}$ and alloying element composition in wt.%

According to this equation, **Mo** increases the Ms temperature unlike to what is predicted by the others equations of the literature. In addition, the C-Mn, C-Cr, and C-Mo interactions weaken the effect of C because of their carbide formers nature while the C-Si interaction intensifies the effect of C. This equation has the advantage to consider a broader compositional range than that in the Andrew's study. However, the statistical interaction between C-Mn predicted in the ANN model is less realistic than that in the Andrew's one. The former predicts an increase of Ms due to the C-Mn interaction. Let us consider the following example based on our experimental work:

PAGS= prior austenite grain size=6,1µm

REF	C (wt. %)	Mn (wt. %)	Ms_experimental	Ms_Andrews_linear	Ms_ANN
2270A	0,045	7,32	291°c	297°c	-245°c
2270C	0,16	7,32	231°c	249°c	-222°c

By considering the compositional database limited on the only carbon and manganese content, we can observe from the example that the ANN model predicts a negative Ms as well as an increase of its value when increasing the amount of carbon in steel grade 2270C. In the other site, Andrews reproduces the experimental evolution of Ms when increasing the carbon content. In conclusion, for a polynomial dependence between carbon content and Ms, Andrews's equation is more adapted to reproduce the experimental evolution of Ms.

II.2 Influence of chemical composition on Ms: exponential

This section presents some formulae that suggest an exponential relationship between martensite start temperature and carbon content. According to **Van Bohemen [4]**, carbon has the strongest reduction effect on Ms, and therefore it is exponentially related with martensite start temperature. The chemical composition used in his studies is given below:

Table3: composition ranges in Van Bohemen study

wt.%	C	Mn	Si	Cr	Ni	Mo
Composition ranges	0,1 – 1,9	0 – 3	0 – 2	0 – 4	0 – 5	0 – 0,8

In his work, all the alloying elements present in the steel were completely dissociated in order to quantify their proper effect. The equation proposed by Van Bohemen is given as follow:

$$M_s(°c)=565-600*(1-Exp(-0.96*C\%))-31*Mn\%-13*Si\%-10*Cr\%-8*Ni\%-12*Mo\%. \qquad \textbf{(6)}$$

This model has been compared with those proposed by Andrews and Grange for plain carbon steels as shown in figure 7:

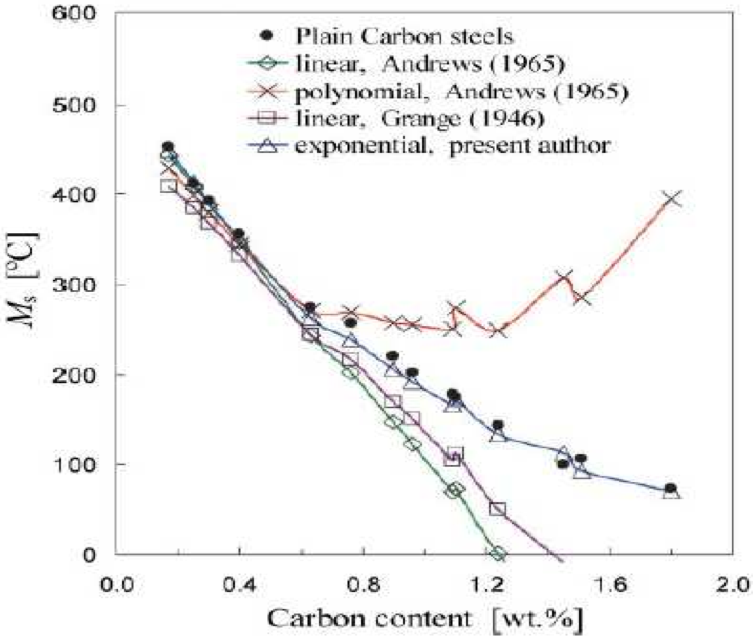


Figure 7: Experimental data and predictions of Ms Temperature for 14 plain carbon steels **[4]**

It can be noted from data in figure 7 that all the models predict with good approximation the experimental Ms for steels with 0,1-0,6wt-%C. in fact the limited development of equation 6 for very low carbon content lead to:

$$Ms(°c)=565-576*C-31*Mn-13*Si-10*Cr-8*Ni-12*Mo \qquad \textbf{(7)}$$

This is very similar to equation 3 with the coefficient of carbon bigger. The comparison of equation 3 and 7 in figure 7 for low carbon content shows a greater slope for equation 7 due to the coefficient of carbon. For carbon content more than 0,6wt.% only the Van Bohemen 's model predicts the experimental data of Ms temperature. in the polynomial model, as a consequence of the quadratic term, the Ms temperature will increase for carbon content greater than ~ 1wt-% in the case of Fe-C alloy.

The work of **Barbier [5]** goes in the same way as Van Bohemen suggesting an exponential dependence between martensite start temperature and carbon content. He goes further by taking into account a larger database in terms of alloying elements as well as their respective ranges of validity. The proposed equation with the respective compositional database is given below:

$$M_S(°c)=545-601.2*(1-Exp(-0.868*C))-34.4*Mn-13.7*Si-9.2*Cr-17.3*Ni-15.4*Mo+10.8*V+4.7*Co-1.4*Al-16.3*Cu-361*Nb-2.44*Ti-3448*B. \qquad \textbf{(7)}$$

Table4: composition ranges in Barbier's study

wt.%	C	Mn	Si	Cr	Ni	Mo	V	Co	Al	Cu	Nb	Ti	B
Composition ranges	0,002 - 1,86	0 - 10,24	0 - 1,9	0 - 17,98	0 - 29,55	0 - 5,4	0 - 1,19	0 - 16,08	0 - 3,007	0 - 2,17	0 - 0,11	0 - 1,614	0 - 0,004

Comparing the two exponential models of Barbier and Van Bohemen in the same composition ranges, one can observe a similar prediction of Ms temperature as shown in figure 8:

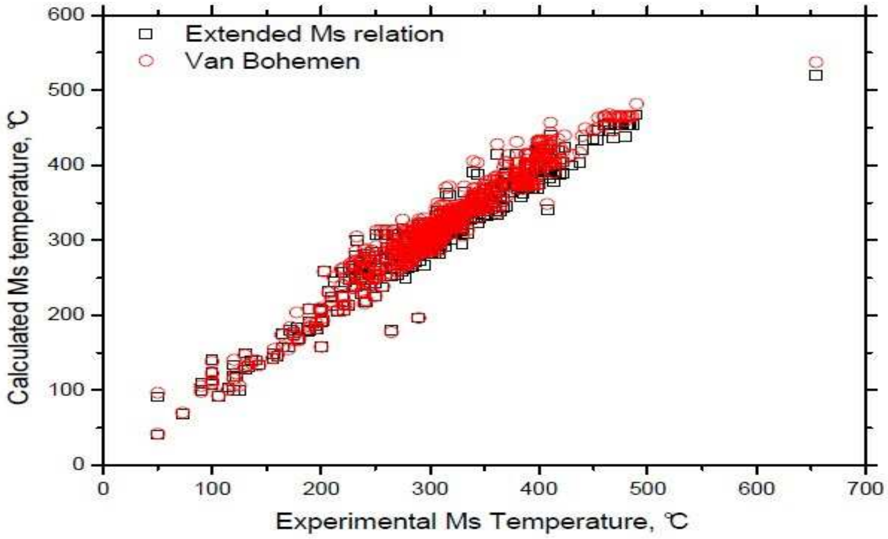


Figure 8: Comparison of the predicted Ms Temperature obtained with Barbier and Van Bohemen's equations on the same composition ranges **[5]**

What should be noted from the correlation between carbon content and Ms temperature is the linear relationship which is predicted by all authors from the literature when carbon content is less than 1% wt. this should be applied for most of the industrial steels since they contain less than 1wt. % C. However, one among these equations is very close to the experimental Ms. By considering from this study two alloys with the same prior austenite grain size, one can study the influence of chemical composition on Ms Temperature:

T=850°c

REF	%C	%Mn	d(µm)	Ms_exp(°c)	
2270A	0,045	7,32	6,1±0,91	291	➡ ΔM_s =60°c
2270C	0,16	7,33	6,1±0,91	231	
		T=1100°C			
2270A			38±5,3	314	➡ ΔM_s =60°c
2270C			42,6±6,06	254	

Andrews_Linear (3)

2270A: Ms = 539-423*0,045-30,4*7,32=297,437°c
2270C: Ms =539-423*0,16-30,4*7,33=248,488°C
➡ ΔM_s =49°c

Van Bohemen (6)

2270A: Ms_chimie=565-600*[1-exp(-0,96*0,045)]-31*7,32=312,712°c
2270C: Ms_chimie=565-600*[1-exp(-0,96*0,16)]-31*7,33=252,339°c
➡ ΔM_s =60,4°c

Barbier (7)

2270A: Ms_chimie=545-601,2*(1-Exp(-0,868*0,045))-34,4*7,32=270°c
2270C: Ms_chimie=545-601,2*(1-Exp(-0,868*0,16))-34,4*7,32=215°c
➡ ΔM_s =55°c

In this example we studied the influence of carbon content. Van Bohemen equation gives the best prediction of martensite start temperature. Barbier is also close to the experimental Ms.

II.3 Influence of prior austenite grain size on martensite start temperature

The temperature at which martensite plate/lath begin to form is also related to the prior austenite grain size. Even if the real physical explanation is not yet clear, some formulae have been proposed to demonstrate the evolution of martensite start temperature with the prior austenite grain size. One of these has been elaborated by Yang & Bhadeshia **[6]** based on **"the geometrical partitioning model of Fisher et al" [7]:**

$$M_s^0\text{-}T=\frac{1}{b}\ln\left[\frac{1}{aV_\gamma}\left\{exp\left(-\frac{\ln(1-f)}{m}\right)-1\right\}+1\right] \qquad \textbf{(8)}$$

where: M_s^0 is the martensite start temperature of a large grain determined thermodynamically

a, b are two empirical fitting constants

m: the aspect ratio of a lath martensite

f: formed martensite volume fraction at the temperature T

V_γ : the average volume of an austenite grain considered to be spherical

The set of parameters in equation 8 corresponds to a given chemical composition. The comparison of equation 8 with the experimental work performed by Garcia Junceda **[8]** on the evolution of Ms with austenite grain size is given in figure 9:

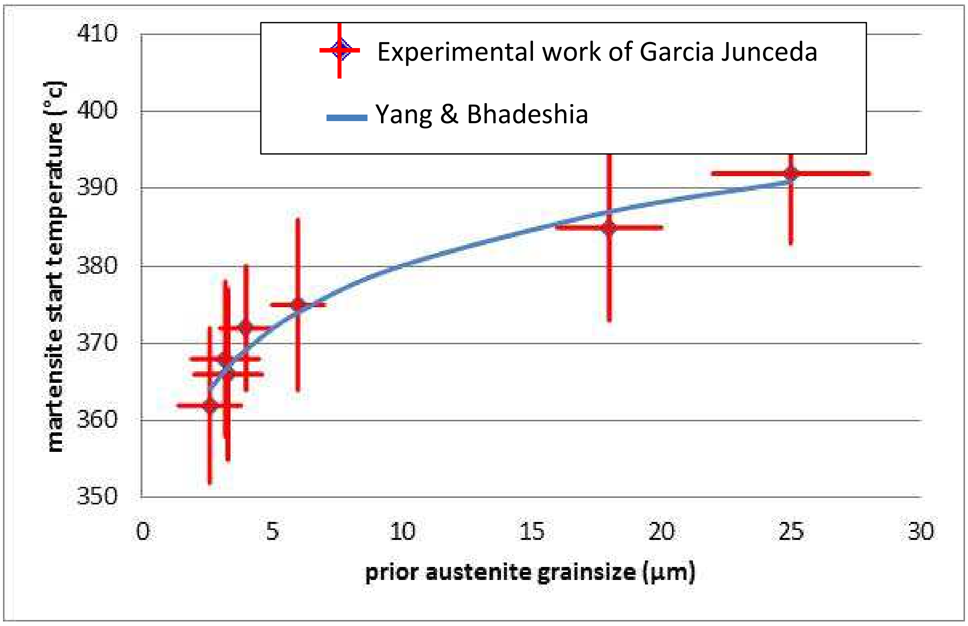


Figure 9: Evolution of Ms with austenite grain size: comparison of the experimental work of Garcia Junceda with the prediction given by Yang & Bhadeshia

The comparison in figure 9 shows that equation 8 reproduces very well the experimental evolution of Ms with austenite grain size. The corresponding set of parameters chosen for the fitting is:

Ms^0= 581; a = 1,57x10^-25µm^-3; b= 0,253; m=0,075.

Seok-Jae Lee et al **[9]** proposed another equation which gives the combined effect of chemical composition and prior austenite grain size on Ms for Mn6C5 alloy obtained with a full austenitization:

$$M_s(°c)=545-423wt\%C-30.4wt\%Mn-60.5V_\gamma^{-1/3} \quad (9)$$

Where V_γ is the average volume of a spherical austenite grain

The comparison of the two models with the experimental work of Garcia Junceda is presented in figure 10:

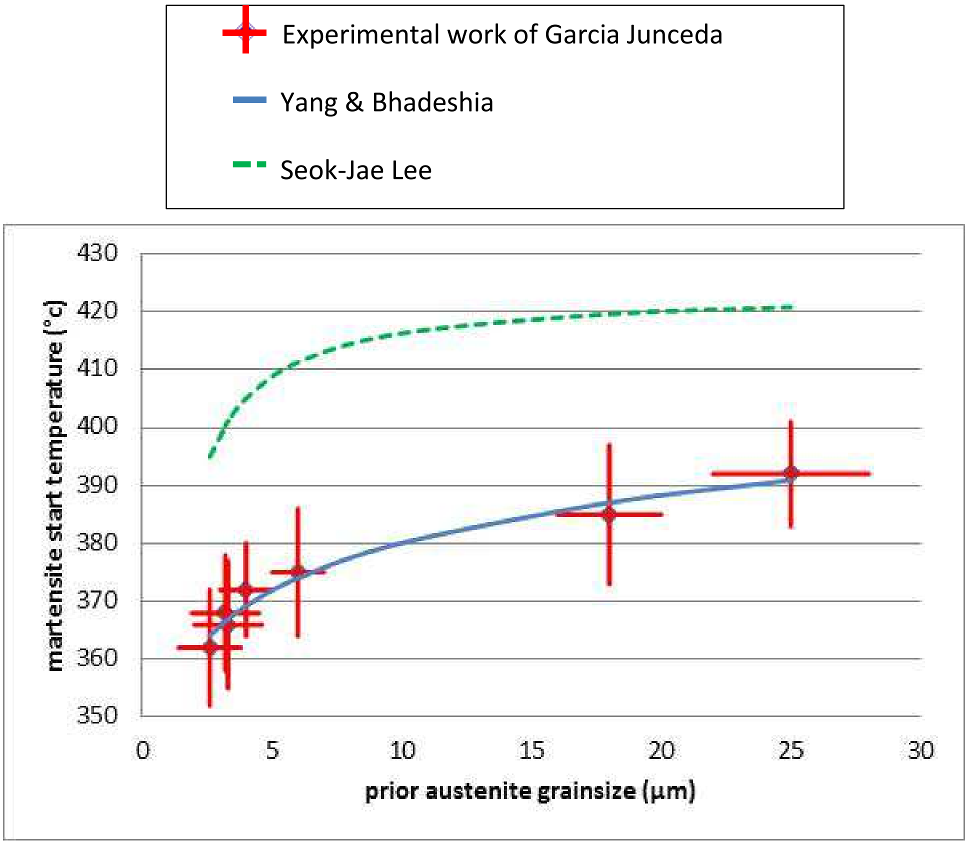


Figure 10: comparison of the equation of Yang & Bhadeshia and Seok-Jae Lee with the experimental work of Garcia Junceda

The comparison in figure 10 shows that equation 9 proposed by Seok-Jae Lee does not reproduces the experimental results of Garcia Junceda. However, its prediction of the evolution of Ms with austenite grain size has the same trend than that of the experimental one i.e. Ms increases with increasing austenite grain size until reach a plateau value. We can conclude that between the two predictions equations, the one of Yang & Bhadeshia is more adapted to reproduce the evolution of Ms with austenite grain size.

The equations predicting Ms with chemical composition for the polynomial and exponential forms are all based on the fcc lattice stabilizers nature of some alloying elements. In fact, these elements including carbon, manganese, nickel and others, stabilize the austenite phase at lower temperature. This makes it difficult to transform during the quenching process and thus reduce the martensite start temperature. Among these chemical elements, carbon appears to have the highest effect on reducing the martensite start temperature. This explains the biggest coefficient appearing in front of its contribution in the prediction of Ms temperature in the polynomial equations or exponential ones. However we also notice through the different equations that bcc lattice stabilizers elements such as Cr, Mo, Si, Al have also a reduction effect on Ms Temperature. This could be explained by the combination of various effects including mechanical reinforcement of alloying elements, thermodynamic and crystallographic effect. Further work need to be done to identify the real origin of this phenomenon.

II.4 Physical theory of austenite stabilization by interstitial alloying elements

Some researchers gave a physical explanation of the influence of interstitial alloying elements such as Carbone on the thermal stabilization of austenite at low temperature. Among them we can list the theory proposed by **Kinsman and Shyne [10]** where the stabilization parameter is noted **θ.** If the quenching process is interrupted at $T_a<Ms$ the martensite transformation does not occur until additional cooling below T_a. If there is no stabilization, the transformation will take place at T_a but if thermal stabilization is verified, the martensite transformation will begin at a temperature $Ms^{'}<T_a$. Indeed the quantity $\theta = Ta-Ms^{'}$ is the best experimental estimation of thermal stability as shown in figure 11:

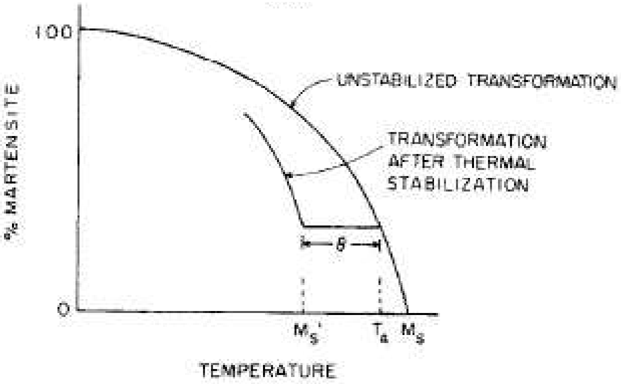


Figure 11: thermal stabilization of austenite.

The value of θ depends on the aging temperature and the aging time below martensite start temperature.

Hypotheses of their theory:

- Thermal stabilization of austenite equal to the suppression of the martensite nucleation step.
- Above the martensite start temperature, all nuclei have a subcritical size and the larger of them will form at Ms temperature while the others will form at a temperature under Ms.
- Martensite nucleus is an oblate spheroid of martensite bounded by an array of dislocations which provides a mobile linkage with the surrounding austenite phase.

It is proposed that the thermal stabilization of austenite is a result of immobilization of the semi-coherent interface between the martensite nucleus and the austenite matrix because of interstitial solute atom segregation (carbon) to the dislocation array that comprise the interface. The strength of the pinning of the interface dislocations is manifested through the value of θ which must be a function of the excess concentration of segregated solute atoms at the interface $N_B^x(t)$. This latter has a qualitative evolution with aging time and temperature presented in figure 12:

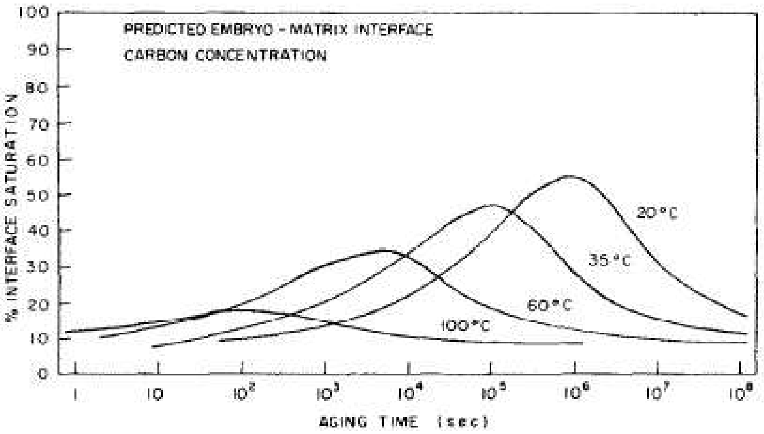


Figure 12: θ as a function of aging temperature and time.

Since θ is a function of $N_B^X(t)$ (assumed linear), it increases with increasing the aging time until reaching a maximum value and then a continuous decrease for long aging time. In addition, θ_{max} decreases with increasing the aging temperature and the maximum value is obtained in shorter aging time as shown in figure 12.

II.5 Physical theories of the influence of prior austenite grain size on martensite start temperature

Regarding the influence of prior austenite grain size on martensite start temperature, several theories have been developed to explain this dependence. **Guimaraes and Gomes [11]** suggested a **"Burst"** phenomenon which takes place at the beginning of the transformation phase. The burst is the first detectable martensite fraction which forms at the beginning of the phase transformation at a temperature called Mb=Ms. Considering a single austenite grain, reducing its size will cause less burst, i.e. a very small transformed martensite volume. Additional cooling will be needed in order to procede with the transformation until reach a detectable transformed martensite volume. This will therefore lower the martensite start temperature. The propagation of the burst to neighboring grains is stimulated by the elastic strain caused by the first formed marteniste plate. This elastic strain is proportional to the size of the plate and hence to the size of the austenite grain. For large grains, the number of grain per unit volume is small causing a more powerful and extended burst as shown in figure 13:

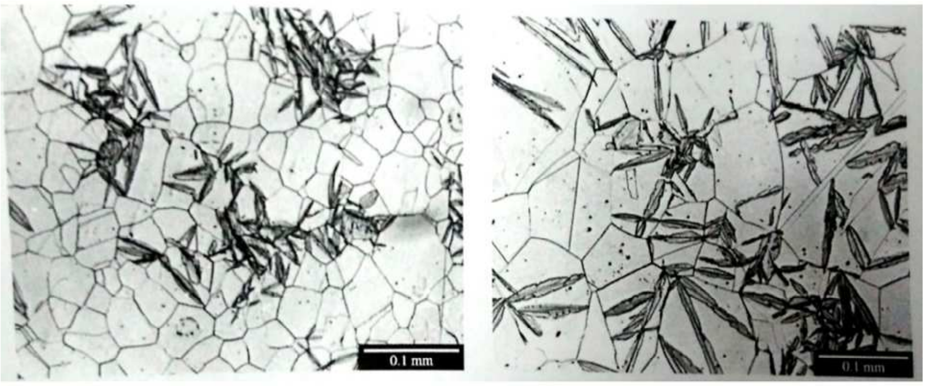


Figure 13: Burst martensite in Fe-Ni-C alloys for different prior austenite grain sizes **[11]**

As we can see in figure 13, large grain size promotes transformation all over the beginning while in fine grained austenite clusters of partially transformed grains are observed.

Another theory to explain the influence of prior austenite grain size on martensite start temperature is brought by **Brofman and Ansell [12]** based on the Hall-Petch effect. Two basic approaches are used in explaining the Hall-Petch effect: dislocation pile-ups and dislocation density. In the former, dislocation-grain boundary interactions result in strain fields that produce back stresses impeding dislocation motion. A finite stress will be experienced by all mobile dislocations throughout the grain. At very fine grain diameters, the magnitude of this back stress will be fairly high throughout the grain volume, thus increasing resistance to plastic deformation even at a microyield level.

The dislocation density model is based on the theoretical expression:

$$\boldsymbol{\rho \; \alpha \; \frac{1}{D_{\gamma}}}$$

Where **ρ** is the dislocation density and **$D_γ$** is the grain diameter.

Hall-Petch strengthening results from increasing dislocation density with decreasing grain size. Reducing grain size will therefore increase the resistance of austenite to plastic deformation locally as well as macroscopically. This increased austenite resistance will directly impede the martensite transformation by increasing the nonchemical free energy opposing the transformation.

KAJIWARA [13] goes in the same direction as Brofman and Ansell by suggesting a Hall-Petch effect. According to him, only some specific grain boundaries are favorable sites for martensite nucleation. Dislocations only enable the deformation by slip of the matrix in order to accommodate the shape strain of the martensite plate. In a polycrystal material, the deformation by slip to accommodate the martensite shape strain cannot be confined to one grain, but it must be propagated into neighboring grains. The critical stress to cause such slip propagation corresponds to the yield stress in polycrystals which is increased with decreasing grain size. The increased difficulty in the plastic accommodation of martensite shape strain is the reason for the suppression of the transformation in fine-grained specimens.

One of the most used theory to explain the dependence between prior austenite grain size and martensite start temperature is the one proposed by **Fisher et al. [7].** According to his work, the martensite start temperature is the temperature at which the probability to find a martensite plate of a certain size equal to 0,5. Only plates with supercritical size as well as a coherent interface with the matrix are expected to grow during the transformation. Since martensite transformation is an heterogeneous process i.e. which occur through a nucleation and growth step, the growth of a nucleus will be impeded by any discontinuity within the grain i.e. dislocations, others nuclei, grain boundaries. The volume of a typical transformed region is proportional to **$D_γ^3$** where **$D_γ$** is the mean grain diameter, leading to the relationship

$$\textbf{(transformed fraction)} \sim D_{\gamma}^{3}$$

during the early stages of transformation. A ten-fold decrease in grain diameter decrease the volume transformed to martensite by a factor of a thousand, thereby lowering the experimental M_s temperature.

The mechanisms explaining the influence of austenite grain size on marteniste start temperature presented in the literature analysis of this work are all converging in a same point: the martensite fraction formed at the beginning of the transformation is large and hence detectable for large austenite grains. Austenite grain refinement induces an increase in the strength of the parent austenite matrix and its resistance to local plastic deformation creating in this way an impediment to martensite transformation effectively shifting the transformation to lower temperatures.

II.6 Physical theories of the influence of prior austenite grain size on martensite transformation kinetics

It is also suggested that the prior austenite grain size has an influence on the martensite transformation kinetics. In fact, according to **Guimaraes and Gomes [11]** the martensite transformation kinetics can be divided in two steps occurring simultaneously: **propagation and fill-in.** In the first one, the kinetics consists in the increase in the number of austenite grain partially transformed per unit volume of material. It occurs by stimulation across grain boundaries because of the shear elastic stress concentration ahead of a martensite plate which is proportional to the square of its length and that is likely to be of the order of the austenite diameter for the first formed plates. Small grains specimens will have a lot of grain boundaries per unit volume of material which induces an increase in the strength of the parent austenite and its resistance to plastic deformation. This will therefore slow the kinetics of martensite transformation. The **fill-in process** is the uniform transformation of austenite grains which was partially transformed. This process will be very important for small grains specimens because of the high heterogeneity of the reaction.

Fisher et al [7] also believe that there is a link between prior austenite grain size and martensite transformation kinetics. As mentioned before, the size of the first few martensite plates that form in a specimen of austenite containing no undissolved carbides is determined by the austenite grain size. But the size of the latter martensite plates is determined by the size of the pockets of untransformed austenite remaining among previously formed martensite plates. Therefore, calculation of martensite transformation kinetics requires an estimation of the size of these austenite pockets as a function of austenite grain size and number of martensite plates.

In this work, we hypothesize that martensite transformation kinetics is an autocatalytic process that can be thought to occur in two steps. The first one deals with an autocatalytic phenomenon where the first martensite laths formed will stimulate through the grain boundaries the nucleation events in the neighboring grains by the stress field generated during their formation as shown in figure 14.

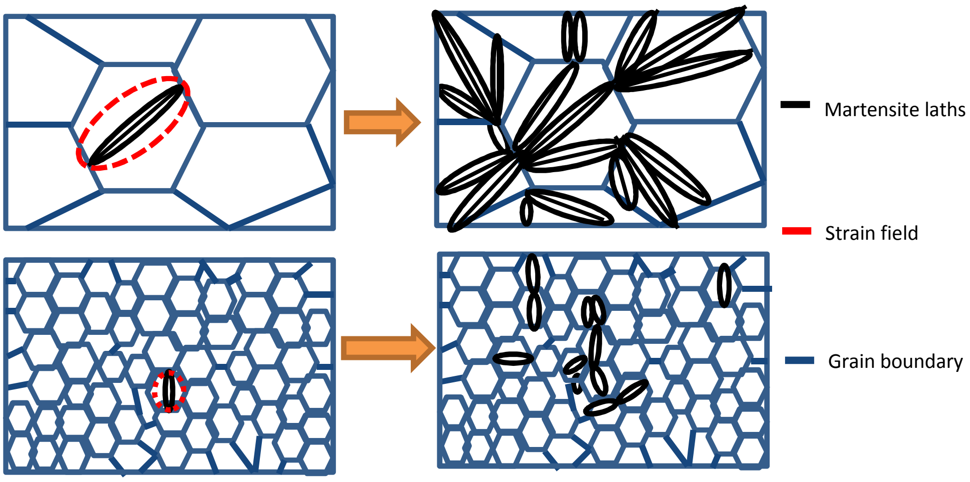


Figure 14: first stage of martensite transformation kinetics

The effectiveness of the stimulation will be more powerful and extended in large austenite grains since these grains are less resistant to plastic deformation than small one. In these last types of grains, the stress field ahead of the first formed laths is very small and the material is more resistant to plastic deformation because of Hall-Petch strengthening as well as containing more grains per unit volume of material. These effects will reduce the transformation kinetics defined as the increasing number of austenite grains partially transformed per unit volume of material. The high transformation kinetics observed in large austenite grain during the first stage of the process will cause a larger transformed volume fraction than in the finer grain. Hence the kinetics will become slower in the second step as shown in figure 15.

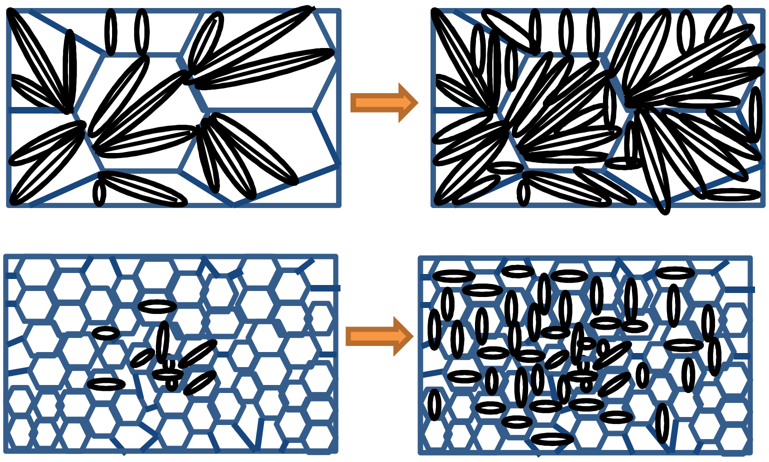


Figure 15: second stage of martensite transformation kinetics

The decrease in martensite transformation kinetics observed in large grains in the second step is due to the strengthening of the untransformed regions which is caused by the surrounding transformed ones. In fact the retained austenite in the large grains will be full of dislocations coming from plastic deformation and stress field caused by the large martensite laths in the transformed region. This will increase the resistance to plastic deformation of the untransformed austenite causing a decrease of the transformation kinetics which becomes smaller than that of the finer grains. In these last one, further transformation will proceed because of large untransformed regions.

III. Experimental procedure

Martensite transformation kinetics can be defined as the fraction of formed martensite, or the remaining fraction of untransformed austenite, as a function of quenching temperature for specimens cooled as rapidly as possible from the austenitizing temperature. This has been determined by means of dilatometry experience using a Dilatometer Bähr DIL805. Two different geometries of specimens were used for the study:

- A rectangular parallelepiped cold rolled sample of 10mm in length, 4mm width and 1mm thick.
- A cylindrical hot rolled sample of 10mm in length and 4mm in diameter.

These samples geometries were subjected to thermal treatments of austenitization and He cooling as described in figure 16. The samples were held in position at the center of the induction coils by hollow cylindrical quartz rods minimizing the thermal gradient at the extremities of the samples induced by the contact with rods. He cooling was performed with a minimum He flow achievable (Valve 1) in order to minimize temperature gradients and reduce vibration in the dilatometer signal. The temperature was controlled by a thermocouple welded at the surface of the sample at the center position. Figure 16 shows the dilatometer chamber set up with thermal treatments applied on samples:

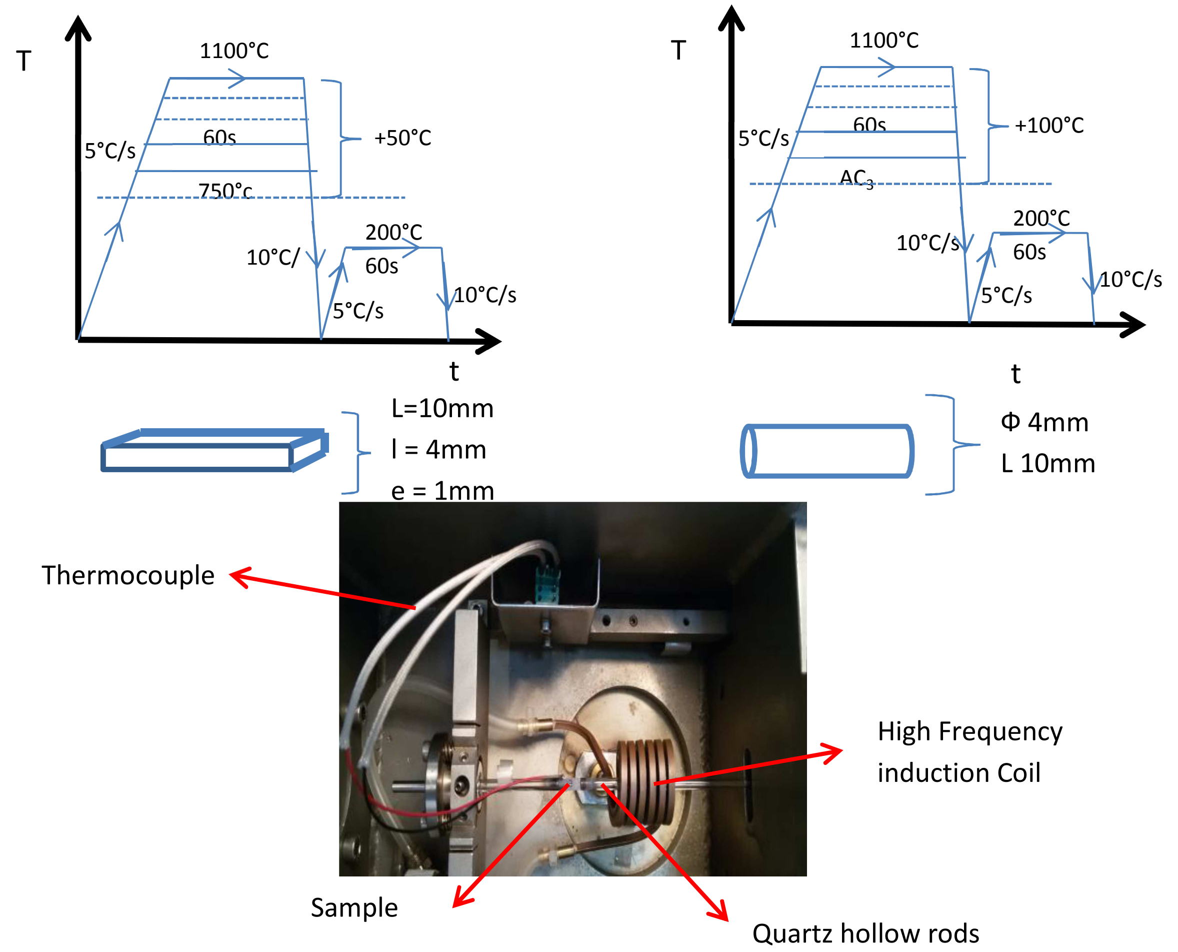


Figure 16: Dilatometry experience

For both the cylindrical and rectangular parallelepiped geometries, two types of thermal treatments were applied: the first one was performed in the fully austenitic field and the second one in the biphasic ferrite-austenite field. For the first, specimens were taken above AC_3 at different holding temperature from 750°c to 1100°c during 60 seconds with a variation step of 50°c for rectangular parallelepiped samples and from AC_3 to 1100°c during 60 seconds with a variation step of 100°c for cylindrical samples as described schematically in figure 16. The used heating rate was 5°c/s and the cooling rate was 10°c/s. This last rate used was sufficient to obtain martensite since the samples are air hardenable. The second thermal treatments conducted in the biphasic ferrite-austenite field aimed to obtain very little prior austenite grain size. Samples were heated at temperatures below AC_3 and held for very long time 10, 15, 20 and 30 hours in order to recrystallize. These treatments were not done because of lack of time. Parameters which define austenite grain size are the holding temperature and the holding time. The first one plays a relevant role in the kinetics of the growth process through the mobility of the grain boundaries. At high temperature, substitutional alloying elements will have enough of thermal energy to diffuse easily in the specimen; this will free the austenite grain boundaries which could move easily and lead to a growth process with a high kinetics. Holding time also impacts the prior austenite grain size but with an effect which is less than that of the holding temperature.

During the experience, the dilatation of specimens in µm is measured as a function of time and temperature. We obtain in output a file with tree columns containing respectively time dilatation and temperature of the specimens. From this file, one can draw the thermal treatment applied and the corresponding dilatation as a function of temperature as shown in figure 17:

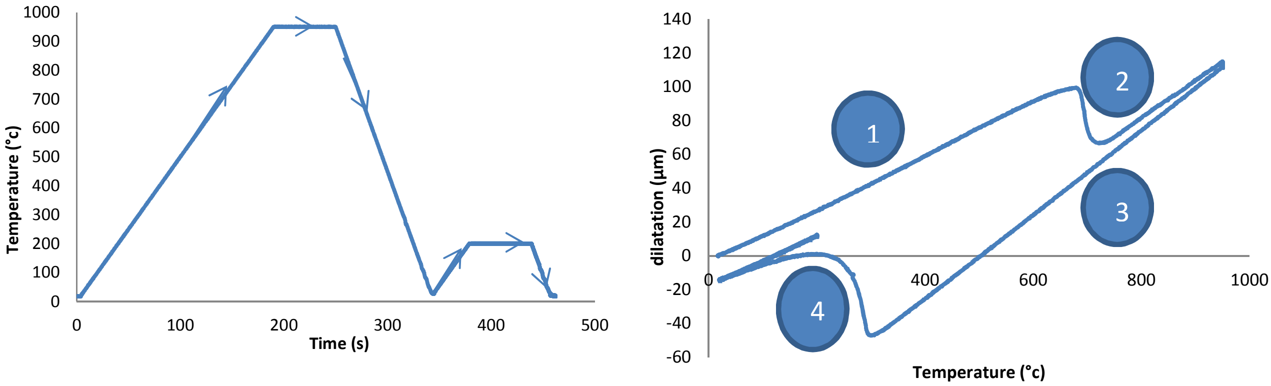


Figure 17: Output data from dilatometry experience.

Considering the dilatation curve of the specimens as a function of temperature, one can identify four regions numbered with circles from 1 to 4 as shown in figure 17:

- The first region numbered 1 corresponds to the dilatation of the initial microstructure of the sample (martensite-bainite in this study).
- The second region numbered 2 deals with the austenitic transformation which takes place at the temperature called Ac_1. This transformation is marked by the deviation from the linear behavior and proceeds until it reach AC_3 which is the end of the austenitic transformation.

This new formed phase will dilate until the cooling process with a positive linear behavior as in region 1 during the heating process.

- By cooling the sample with the austenitic microstructure, the dilatation behavior is still linear as shown in region 3 but with a contraction trend with respect to the current length of the sample. This linear contraction continuous while cooling the sample until a certain temperature where another transformation takes place: the martensite transformation.
- The martensite transformation takes place at the so called martensite start temperature (Ms) which matches with the change from the linear behavior as shown at the beginning of region 4. The transformation proceeds while cooling the specimens under Ms with an expansion of volume. At the end of the cooling process (at room temperature), a tempering treatment is needed to know how the final microstructure dilate. This is useful in order to calculate with a good approximation the martensite transformation kinetics. For this purpose, the chosen tempering process consists of heating the sample with 5° c/s from room temperature to 200° c with a holding time of 60 second and subsequently cools it with 10°c/s to room temperature.

III.1 Determination of Martensite transformation kinetics curve

The martensite transformation kinetics can be determined from the dilatation curve of the sample as a function of temperature. For this aim, regions 3 and 4 of figure 17 are needed. The graphical method adopted for the determination of martensite transformation kinetics is shown in figure 18:

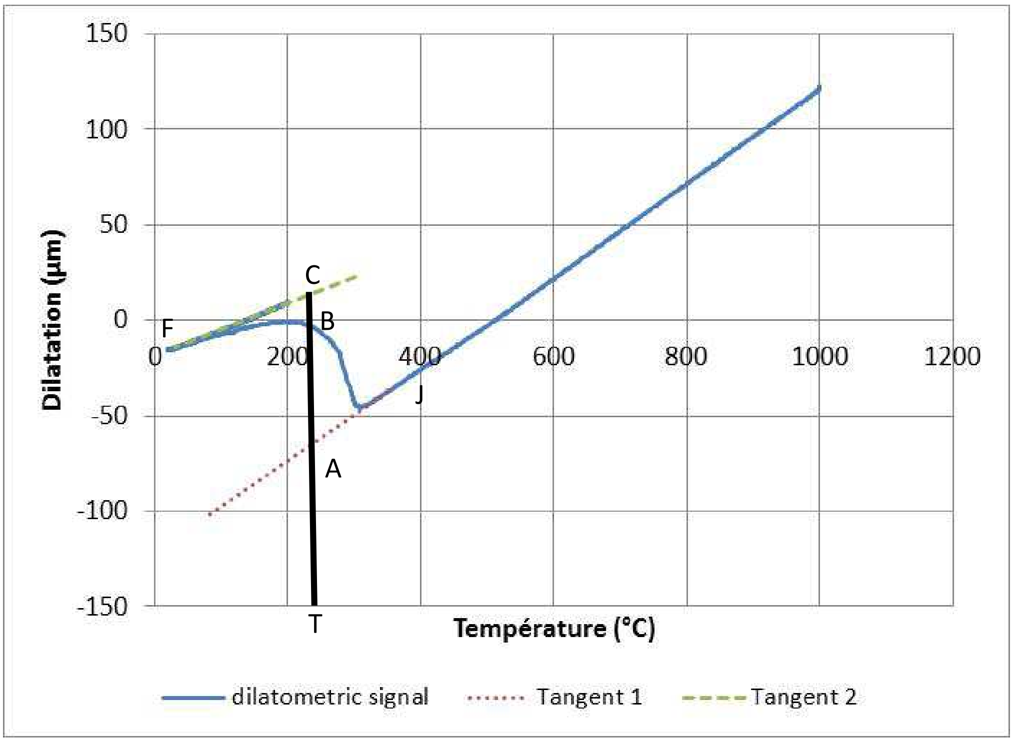


Figure 18: Determination of martensite transformation kinetics

The algorithm used to determine the martensite transformation is:

- Place tangent 1 which represents the extrapolation of austenite dilatation
- Place tangent 2 which is the real dilatation of the final microstructure at the end of the first cooling process.
- Draw between points F and J isothermal segments.
- For every isothermal segment (for example the black segment drawn at temperature T) we apply the level rule to obtain the volume fraction of martensite formed at that temperature as follows:

$$\mathbf{f_{\alpha}}' = \frac{AB}{AC}$$

where $\mathbf{f_{\alpha}}'$ stands for the volume fraction of martensite formed at temperature T.

It should be noted that by placing tangent 2 as in figure 18 we suggest that the austenite phase has been transformed entirely into martensite, which is not the case. In fact, an additional experience called "sigmametry" was needed to determine the untransformed austenite volume fraction (residual austenite) at the end of the dilatometry experience. This residual austenite fraction should be taken into account in the calculation of the volume fraction of martensite formed at a given temperature below martensite start. Therefore the real formula used to calculate the formed martensite volume fraction at a given temperature is given as follows:

$$\mathbf{f_{\alpha}}' = \frac{AB}{AC}\mathbf{x(1\text{-}RA)}$$

where **RA** stands for residual austenite.

By applying the same algorithm for all temperatures between points F and J of figure 18, one can determine the martensite transformation kinetics. An example is given in figure 19:

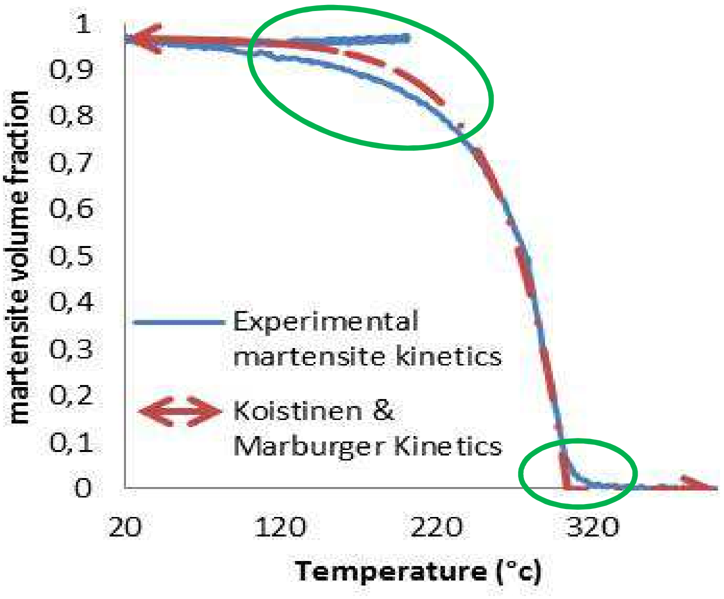


Figure 19: martensite transformation kinetics

As we can see in figure 19, the experimental martensite kinetics has a sigmoidal evolution unlike the exponential form described by Koistinen & Marburger. This difference in shape makes it difficult for the predicted kinetics to reproduce the experimental one. In this work, the martensite start temperature has been taken as the temperature at which the martensite volume fraction formed is 0,05. For every holding temperature, the dilatometric experience has been performed three times for the statistical reproducibility.

III.2 Metallography study

Determination of Prior Austenite Grain size

The second step of the experimental part was to determine the prior austenite grain size at the end of the dilatometry experience. This was done through a metallographic study conducted on the treated specimen. The procedure consists in cutting the sample near to the thermocouple and observing the cut section shown in figure 20:

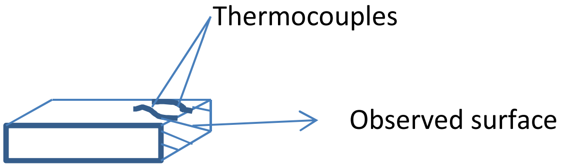
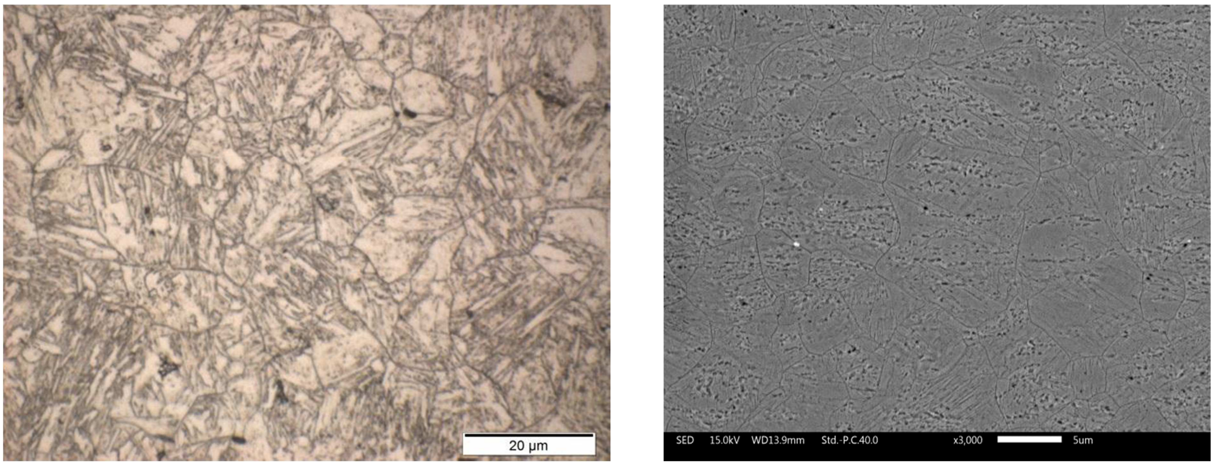


Figure 20: part of the sample for the metallographic study

To facilitate the microscopic analysis of the microstructure, the part of the sample in figure 20 was previously embedded into a polymeric resin, polished with an automatic polisher and then etched with different reagents such as: Picral (a mixture of Picric acid and ethanol); Marshall (a mixture of distilled water, hydrogen peroxide, sulfuric acid and oxalic acid). Some examples of images taken in the Light and Scanning electron microscope are shown in figure 21:



Optical Micrography

SEM Micrography

Figure 21: images analyzed for the determination of prior austenite grain size

The obtained micrographies were analyzed with Image Analyzer software called **"APHELION".** This software uses the mean linear intercept method to determine the mean prior austenite grain size. For the statistic, about 12 images were analyzed for every holding temperature. The global uncertainty of the austenite grain size value was obtained by summing to the confidence interval given by Excel 10 percent of the statistical value of austenite grain size given by the Image analyzer.

IV. Results and discussion

Materials

Two types of steels were selected for this study: cold rolled and hot rolled steel. The chemical compositions of selected materials are summarized in table 5 and 6:

Table 5: chemical composition of steels analyzed at hot rolled/cold rolled state

REF	C(wt.%)	Mn(wt.%)	S(wt.%)	P(wt.%)
2270A	0,045	7,32	0,005	0,005
2270C	0,16	7,33	0,005	0,005

Table 6: chemical composition of steel analyzed only at cold rolled state

Ref	C wt. %	Mn wt. %	S wt. %	P wt. %	Si wt. %	Al wt. %	Cr wt. %	N ppm	B ppm
2260B	0.098	4.73	0.001	0.005	0.001	0.003	0.003	7.2	6

Also, some others hot rolled steels coming from a different study have been taken into account in this work in order to have a larger database. Their chemical composition is given in table7:

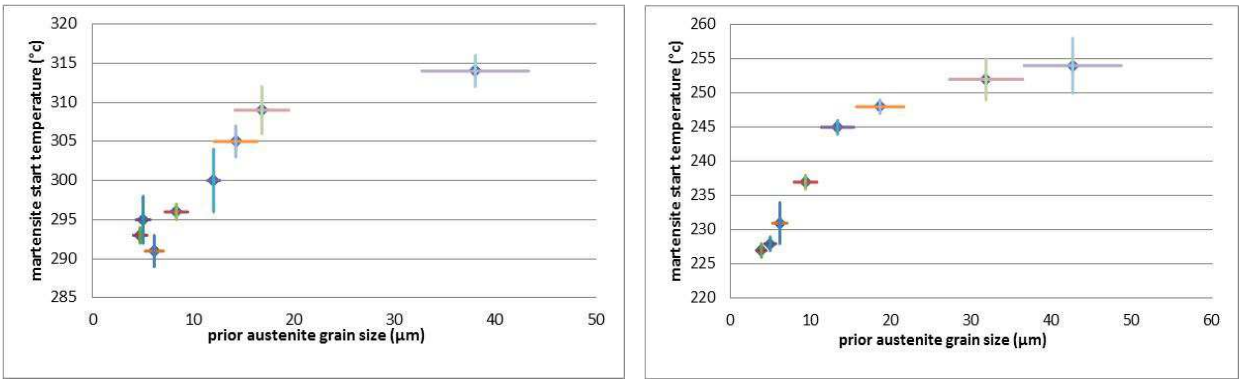
Table7: chemical composition of steel coming from another study

REF	C(wt.%)	Mn(wt.%)	Si(wt.%)	Cr(wt.%)	Al(wt.%)	P(wt.%)	S(wt.%)	N(wt.%)
X173	0.220	2.51	0.66	0.2	0.002	0.009	0.003	5
X165	0.230	2.52	0.19	2.03	0.02	0.008	0.003	5

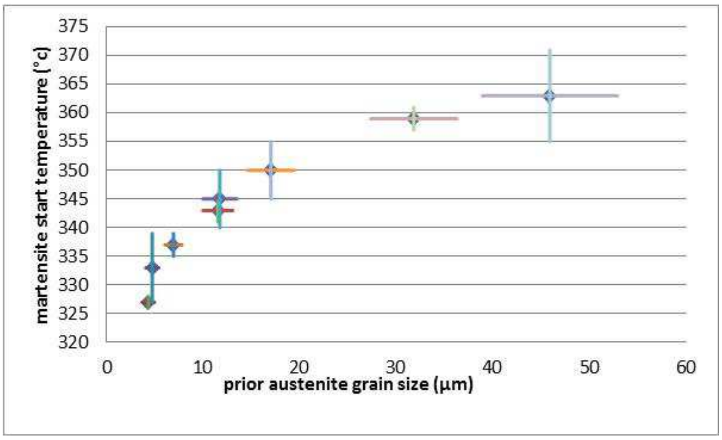
IV.1 Martensite start temperature

As discussed previously, martensite start temperature (Ms) is influenced by the chemical composition of the steels as well as the prior austenite grain size. For each steel, one can draw the evolution of the experimental Ms with the prior austenite grain size as shown in figures 22 and 23:

Cold rolled samples



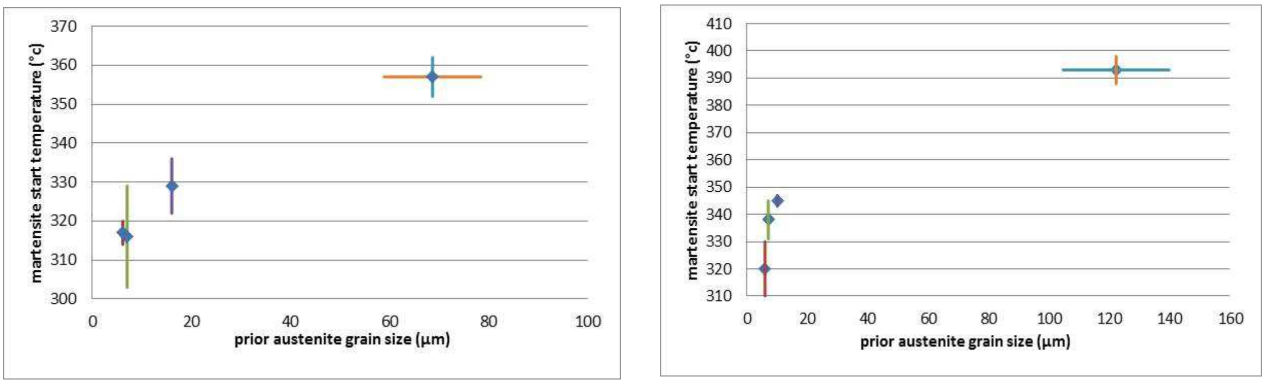
a) Steel grade 2270A **b) steel grade 2270C**



c) Steel grade 2260B

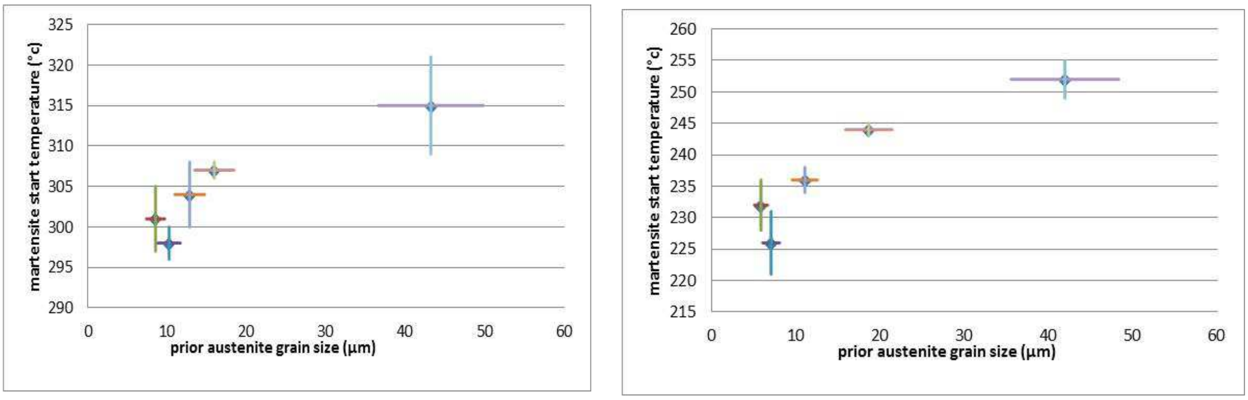
Figure 22: Evolution of Ms temperature with prior austenite grain size for cold rolled specimens

Hot rolled samples



a) Steel grade 2270A

b) steel grade 2270C



c) Steel grade X165

d) Steel grade X173

Figure 23: Evolution of Ms temperature with prior austenite grain size for hot rolled specimens

The combined effect of chemical composition and prior austenite grain size on Ms temperature describes a logarithmic evolution with prior austenite grain size as shown in figures 22 and 23. Such evolution is predicted by Yang & Bhadeshia equation drawn in figure 9. In addition, we also notice a saturation trend where the prior austenite grain size effect becomes negligible. Starting from this point, it can be considered that the value of Ms temperature is only due to the chemical composition. Therefore one can discriminate the chemical composition effect to the one of austenite grain size on Ms temperature. We have demonstrated previously that Van Bohemen equation was the most adapted one to describe the chemical composition effect. By using this latter equation, we calculated the only effect of chemical composition on Ms temperature for the studied steels. The results are summarized in table8:

Table8: Chemical composition effect on martensite start temperature

REF	C (wt.%)	Mn (wt.%)	Si (wt.%)	Cr (wt.%)	Al (wt.%)	P (wt.%)	S (wt.%)	N (ppm)	B (ppm)	Ms_VB (°c)	Ms_exp (°c)
2270A	0,045	7,32	-	-	-	0,005	0,005	-	-	313	314
2260B	0,098	4,74	-	-	-	0,005	0,001	72	6	364	363
2270C	0,16	7,33		-	-	0,005	0,005	-	-	252	252
X173	0,220	2,51	0,66	0,2	0,02	0,009	0,003	5	-	362	393
X165	0,23	2,52	0,19	2,03	0,02	0,008	0,003	5	-	345	357

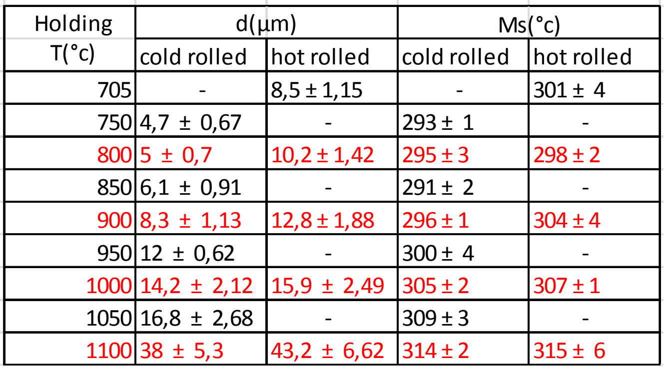
The comparison of the predicted Ms temperatures proposed by Van Bohemen with the experimental one is very similar except for steel X173. This result confirms the validity of van Bohemen's equation in the prediction of chemical composition effect on Ms temperature.

Comparison between cold rolled and hot rolled state

This study also includes materials with different states. The purpose was to see if there is any difference in steel obtained in both states. The comparison was done in terms of the evolution of Ms with the austenite grain. We will also look at the martensite transformation kinetics. Table 9 gives the values of austenite grain size and Ms for both states:

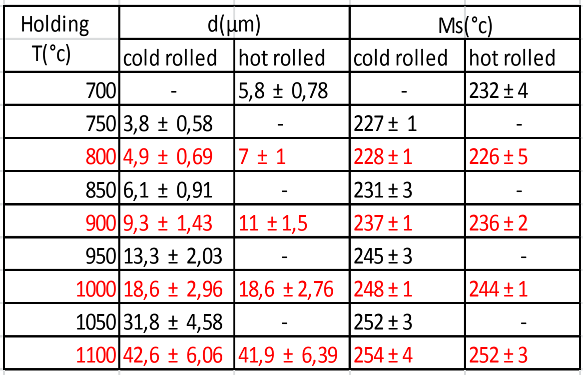
Table 9: Comparison between cold and hot rolling

2270A



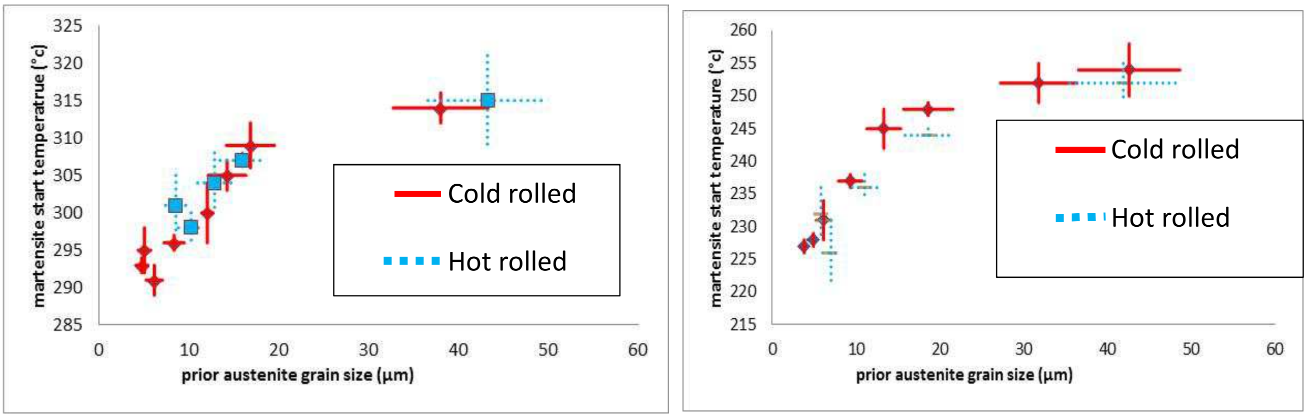
Holding T(°c)	d(µm)		Ms(°c)	
	cold rolled	hot rolled	cold rolled	hot rolled
705	-	8,5 ± 1,15	-	301 ± 4
750	4,7 ± 0,67	-	293 ± 1	-
800	5 ± 0,7	10,2 ± 1,42	295 ± 3	298 ± 2
850	6,1 ± 0,91	-	291 ± 2	-
900	8,3 ± 1,13	12,8 ± 1,88	296 ± 1	304 ± 4
950	12 ± 0,62	-	300 ± 4	-
1000	14,2 ± 2,12	15,9 ± 2,49	305 ± 2	307 ± 1
1050	16,8 ± 2,68	-	309 ± 3	-
1100	38 ± 5,3	43,2 ± 6,62	314 ± 2	315 ± 6

2270C



Holding T(°c)	d(µm)		Ms(°c)	
	cold rolled	hot rolled	cold rolled	hot rolled
700	-	5,8 ± 0,78	-	232 ± 4
750	3,8 ± 0,58	-	227 ± 1	-
800	4,9 ± 0,69	7 ± 1	228 ± 1	226 ± 5
850	6,1 ± 0,91	-	231 ± 3	-
900	9,3 ± 1,43	11 ± 1,5	237 ± 1	236 ± 2
950	13,3 ± 2,03	-	245 ± 3	-
1000	18,6 ± 2,96	18,6 ± 2,76	248 ± 1	244 ± 1
1050	31,8 ± 4,58	-	252 ± 3	-
1100	42,6 ± 6,06	41,9 ± 6,39	254 ± 4	252 ± 3

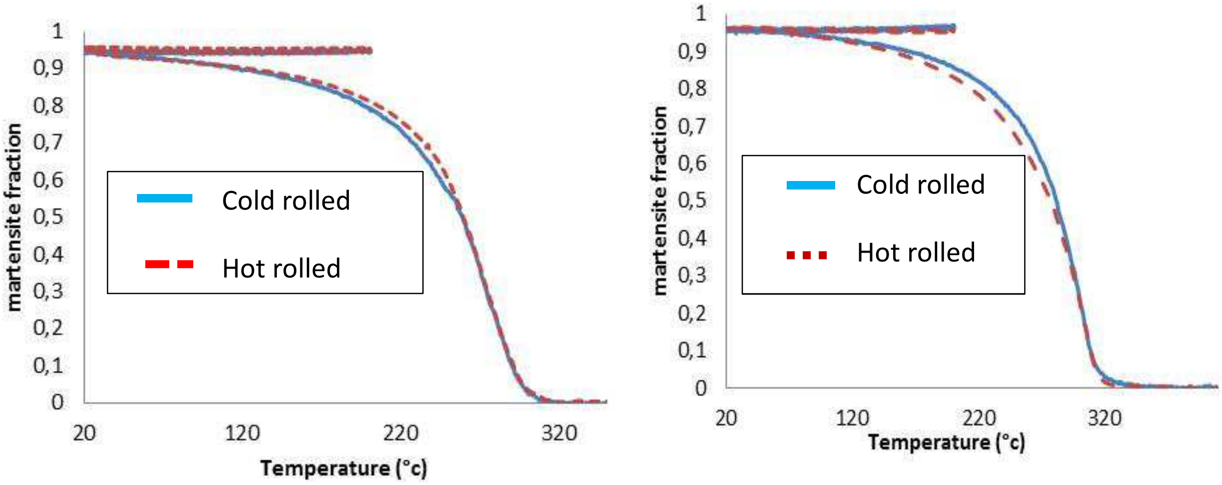
From the comparison between cold and hot rolling steel presented in table 9, one can notice the similarity which exists between Ms values for both steel 2270A and 2270C. In addition, the evolution of Ms with austenite grain size for both states has the same trend as shown in figure 24:



2270A **2270C**

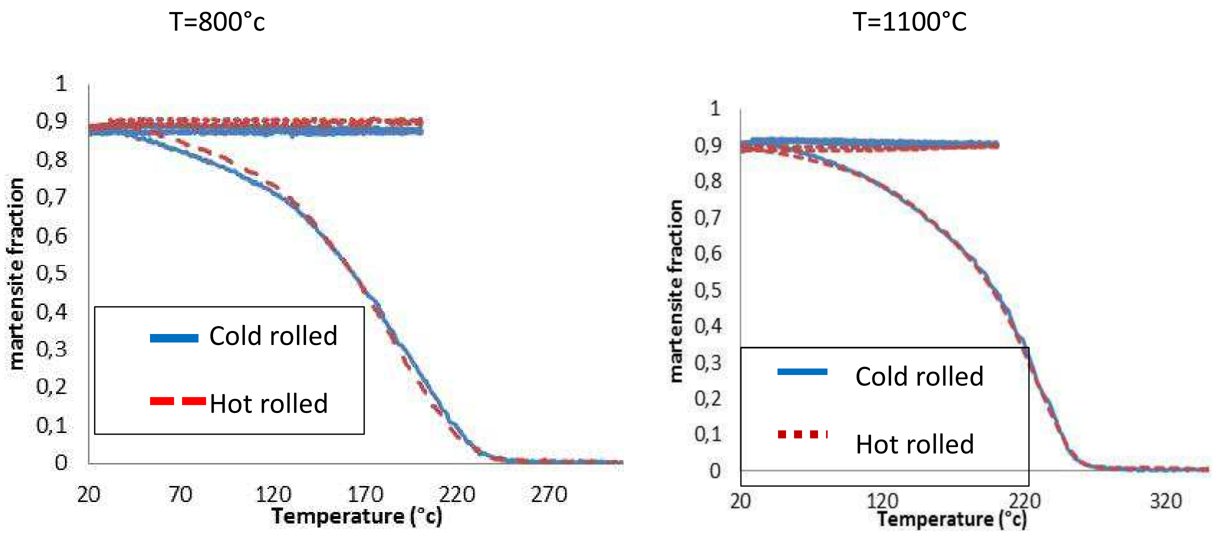
Figure 24: Evolution of Ms with austenite grain size for hot and cold rolled steels.

Before conclude on the comparison between cold and hot rolled steels, let's have a look on their respective martensite transformation kinetics. It was necessary to plot in the same graph the curve of martensite transformation kinetics for both states at each holding temperature as shown in figure 25 and 26. Here is given the comparison for two holding temperatures for each steel, the others are given in annexes:



T= 800°c T=1100°c

Figurre 25: Comparison of martensite kinetics between hot and cold steel: 2270A


T=800°c

T=1100°C

Figurre 26: Comparison of martensite kinetics between hot and cold steel: 2270C

As we can see from the curves in figure 25 and 26, the martensite transformation kinectics for both states is almost the same. It should be noted that for cold rolled steel, a particular attention should be payed regarding the parallelism of the two opposite faces of the sample in contact with the hollow cylindrical quartz rods. This is the source for thermal gradient at the edge of the sample responsible of measurement uncertainties. Thus martensite transformation kinetics of cold and hot rolled steel can be considered as the same as well.

IV.1.1 Influence of Carbon content

In order to emphasize the impact of carbon content on Ms Temperature, we have compared two steels with different carbon content:

2270A: Fe-0,045C-7,32Mn and 2270C: Fe-0,16C-7,32Mn.

By plotting the evolution of Ms with austenite grain size for both steels, we obtain the results shown in figure 27:

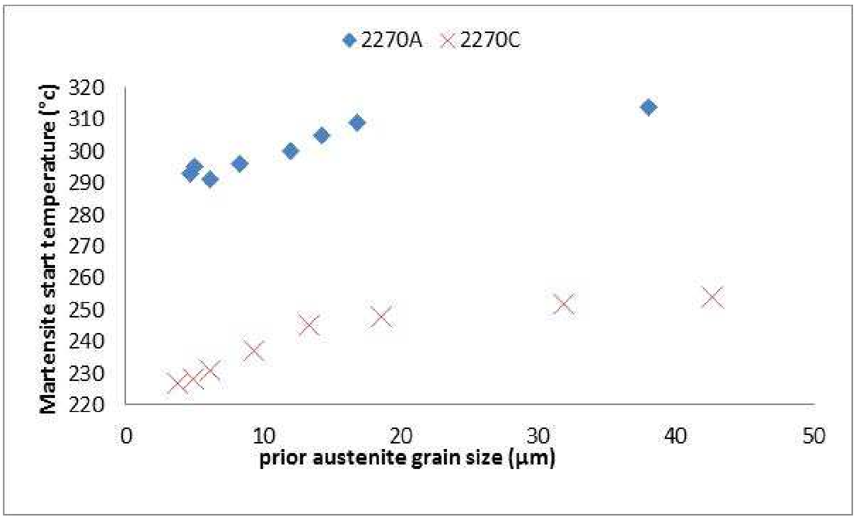


Figure 27: evolution of Ms with austenite grain size for steels 2270A and 2270C

The different order of magnitude in the values of Ms shown in figure 27 indicates how strong is the influence of carbon content in reducing martensite start temperature. For ΔC=0.115wt.% → ΔM_s=60°c. This difference of temperature on Ms values is almost the same for all the austenite grain size values as we can see in figure 27 where the gap is almost constant.

IV.1.2 Influence of chromium and silicon content.

In order to analyze the influence of both chromium and silicon content on Ms temperature, we have considered these two steels:

X173: Fe-0,22C-2,51Mn-0,66Si-0,2Cr and X165: Fe-0,23C-2,52Mn-0,19Si-2,03Cr.

As discussed previously, van Bohemen's equation is the most adapted to predict the Ms temperature as a function of chemical composition of steel.

Influence of silicon content

By using equation 6 of Van Bohemen on steels X173 and X165 without taking into account chromium content, we obtain as predicted Ms values:

$$\left.\begin{array}{l}\text{X173: } Ms = 565-600*[1-\exp(-0{,}96*0{,}22)]-31*2{,}51-13*0{,}66 = 364{,}4^\circ c \\[1em] \text{X165: } Ms = 565-600*[1-\exp(-0{,}96*0{,}23)]-31*2{,}52-13*0{,}19 = 365{,}3\ ^\circ c\end{array}\right\} \longrightarrow \boxed{\Delta Ms = 1^\circ c}$$

By increasing the silicon content of 0,47wt.% from steel X165 to steel X173, Ms temperature decreases of about 1°c which is negligible. Therefore silicon does not influence at all Ms temperature.

Influence of chromium content

By considering the chromium content for both steels X175 and X165, one can analyze the influence of chromium content using the same equation 6 proposed by Van Bohemen:

$$\left.\begin{array}{l}\text{X173: } Ms = 364{,}4-10*0{,}2 = 362{,}4^\circ c \\[1em] \text{X165: } Ms = 365{,}3-10*2{,}03 = 345\ ^\circ c\end{array}\right\} \longrightarrow \boxed{\Delta Ms = 17{,}4\ ^\circ c}$$

By increasing the chromium content of 1,83wt.% from steel X173 to steel X165 Ms temperature decrease of 17,4°c. It can be concluded that chromium content also decreases Ms temperature. Its reducing effect remains lower than that of carbon content.

IV.1.3 The influence of prior austenite grain size on martensite start temperature

As discussed previously, prior austenite grain size also have an impact on martensite start temperature. This influence can be discriminated easily since we have already studied the influence of chemical composition. For this purpose, the procedure consists of taking out from the measured experimental Ms temperature the chemical composition effect calculated with equation 6. By calling the **Prior austenite grain size effect Ms_{PAGS},** we have:

Ms_{PAGS} = $Ms_{\_exp}$ - Ms_chemical composition effect

With **Ms_exp:** experimental martensite start temperature

Ms_chemical composition effect: calculated with Van bohemen equation

By plotting the evolution of Ms_{PAGS} with the prior austenite grain size in a semi-logarithmic scale we obtain an exponential evolution as shown in figure 28.

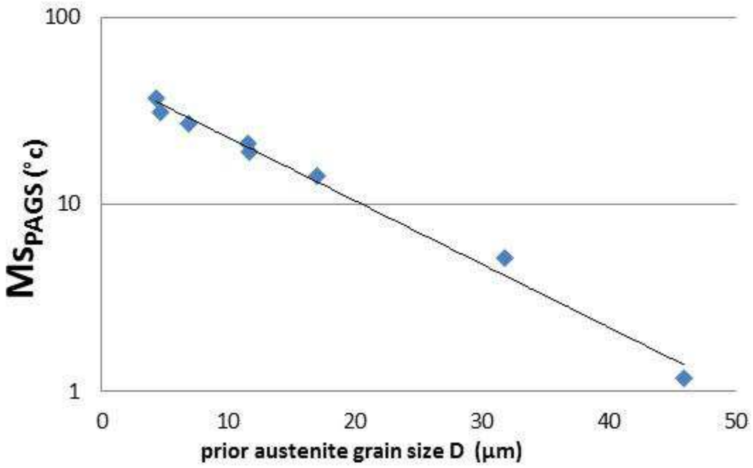


Figure 28: Evolution of Ms_{PAG} with austenite grain size for a given steel.

From this exponential evolution of Ms_{PAG} with austenite grain size, the corresponding mathematic law has the form:

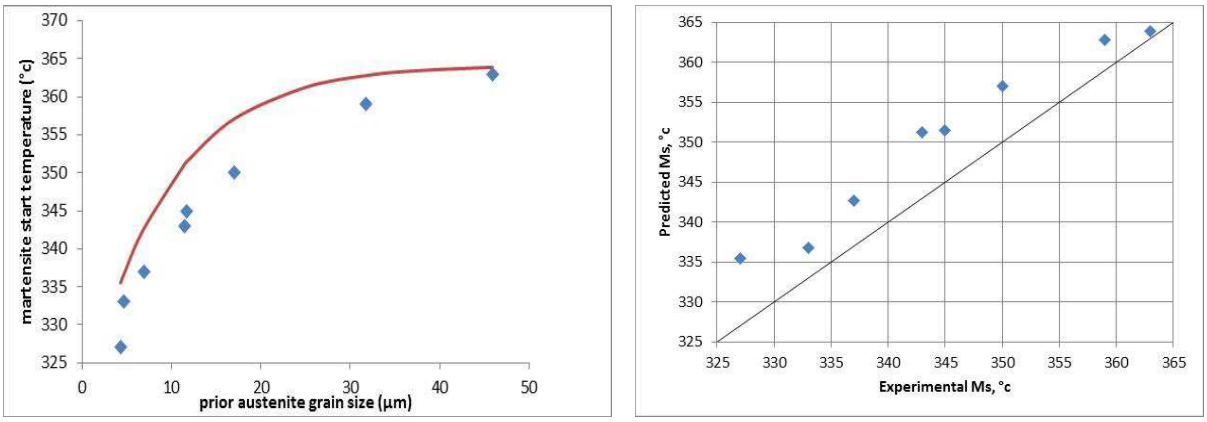
$$Ms_{PAGS} = \alpha e^{-\beta * D} \quad (10)$$

Where **α** and **β** are two constants and **D** the prior austenite grain size.

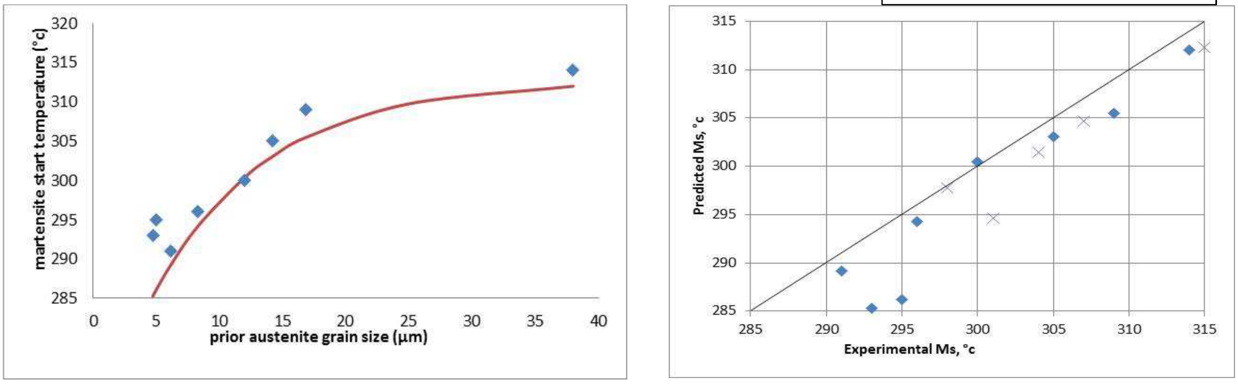
The mathematic equation which can be used to predict the martensite start temperature as a function of chemical composition and prior austenite grain size has the form:

$$Ms = 565-600*(1-e^{-0.96*C\%})-31*Mn\%-13*Si\%-10*Cr\%-8*Ni\%-12*Mo\% - \alpha e^{-\beta * D} \quad (11)$$

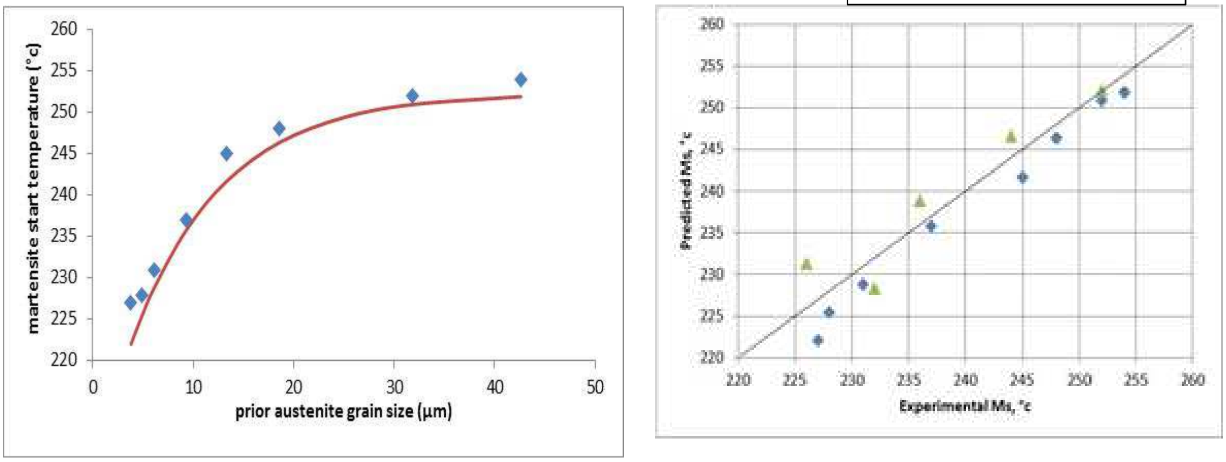
Our goal for this study was to have a unique equation that predicts the martensite start temperature as a function of chemical composition and prior austenite grain size. By taking α=46 and β=0,11 one can plot for all the studied steels Ms prediction with equation 11 as a function of Ms experimental as shown in figure 29:



Steel 2260B; maximum error = 9°C



Steel 2270A; maximum error = 9°C



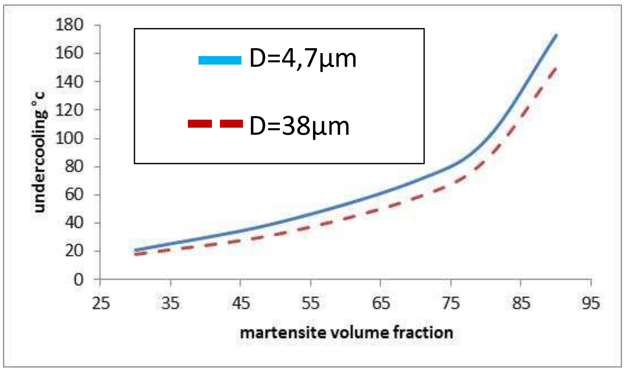
Steel 2270C; maximum error = 5°C

Figure 29: plotting of Ms predicted as a function of Ms experimental and the corresponding evolution of Ms with austenite grain size compared to the experimental one.

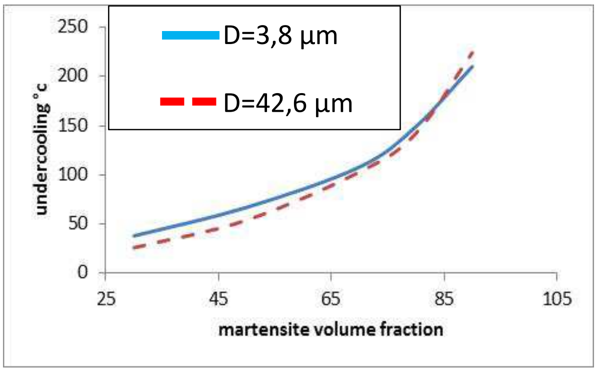
Considering steel 2260B, the maximum error obtained with the predicted Ms is 9°C but almost all the predicted values of Ms are higher than the experimental one. In addition, the evolution of the predicted Ms with austenite grain size is different from the experimental one. This bring us to conclude that the couple (α;β) used in this case is not the suitable one to describe the experimental trend. The prediction of Ms with the chosen couple of parameters is better in the case of steel 2270A where the maximum error remain 9°C but this concern only two predicted values. In fact it can be observed in this case that almost all the points are closer to the diagonal of the graph than in steel 2260B showing a better prediction trend. The same distribution is observed for the hot rolled state of this steel. The good prediction is also visible in the evolution of the predicted Ms with austenite grain size where the continuous line is closer to the experimental points. The best prediction is obtained in the case of steel 2270C. In this case, the maximum error is reduced to 5°C and all the points are closest to the diagonal of the graph as well as hot-cold state. The corresponding evolution of the predicted Ms with austenite grain has the same trend as the experimental one. The prediction matches very well with the experimental values in this case. It should be noted that the chosen values of α and β are the average of these parameters taken from the respective prediction equations for each studied steel.

V. Martensite transformation kinetics.

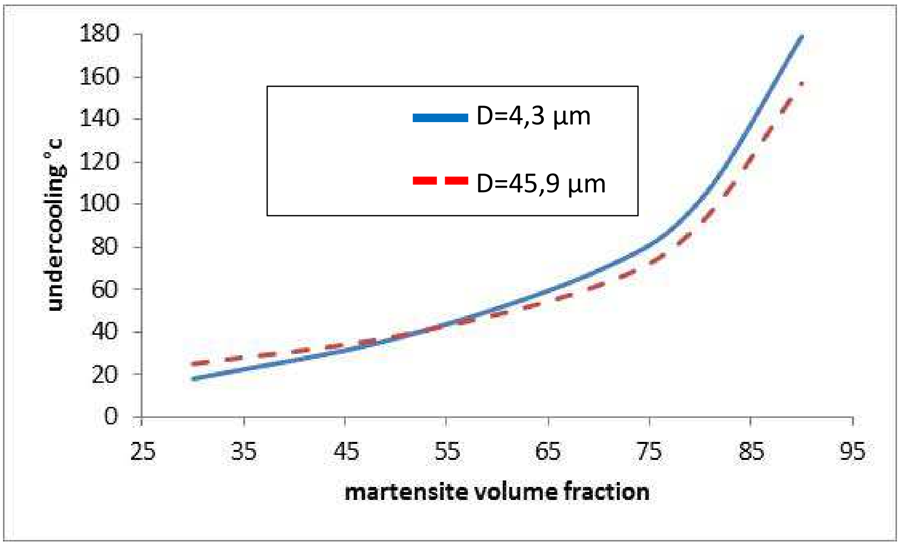
This section aims to analyze if there is any influence of the austenite grain size on martensite transformation kinetics. In order to verify the hypothesis made in section 2 where martensite kinetics is seen as an autocatalytic process occurring in two stages, it was necessary to calculate the undercooling necessary to obtain a same transformed martensite fraction for two different austenite grains size for each studied steel. To do this, the chosen transformed martensite fraction was 30, 50, 70, 80 and 90%. The evolution of the undercooling necessary for the transformation to occur, with the corresponding transformed martensite volume for each studied steel is plotted in figure 30:



2270A



2270C



2260B

Figure 30: evolution of the undercooling with the transformed martensite fraction

From the three graphs in figure 30 it can be noticed that the martensite kinetics is almost the same because the undercooling necessary to obtain a given martensite fraction is very similar. For steel 2270A the martensite kinetics is almost the same with a similar undercooling at the beginning of the transformation for both austenite grains size. For the bigger grain, the undercooling becomes smaller for the rest of the transformation standing for higher martensite kinetics. The opposite behavior is observed for steel 2270C where the martensite kinectics is higher at the beginning of the transformation for the bigger austenite grain before decrease continuously during the transformation until becomes lower than that of the small grain at the end of the martensite transformation. A different trend is observed for steel 2260B. In this last one, the martensite kinetics is smaller for the bigger austenite grain at the beginning of the transformation and continuously increases during the martensite transformation kinectis until became higher at the end. This last case was not expected since the Ms temperature is higher for bigger austenite grain showing a higher among of martensite formed at the beginning of the transformation.

From this analysis, it can be concluded that martensite transformation kinetics can be seen as a two steps process where the kinetics between two different austenite grains size is slightly different. In addition, the hypothesis made in section 2 where martensite kinetics was completely an autocatalytic transformation cannot be validated because the physical explanation given is not verified in the studied steels. The autocatalytic reaction may contribute to the course of the transformation but would not be of first order.

V.1 Comparison of the equation of Koistinen-Marburger with the experimental martensite kinetics

Koistinen-Marburger law is the most famous equation used to describe the martensite transformation kinetics. This section aims to verify if this equation is suitable to describe the transformation kinetics of studied steels. Thus comparison for the same holding temperature of the martensite transformation kinetics predicted by Koistinen-Marburger with the experimental kinetics was done. The chosen holding temperatures are 750°c, 950°c and 1100°c. The results are presented in figure 31:

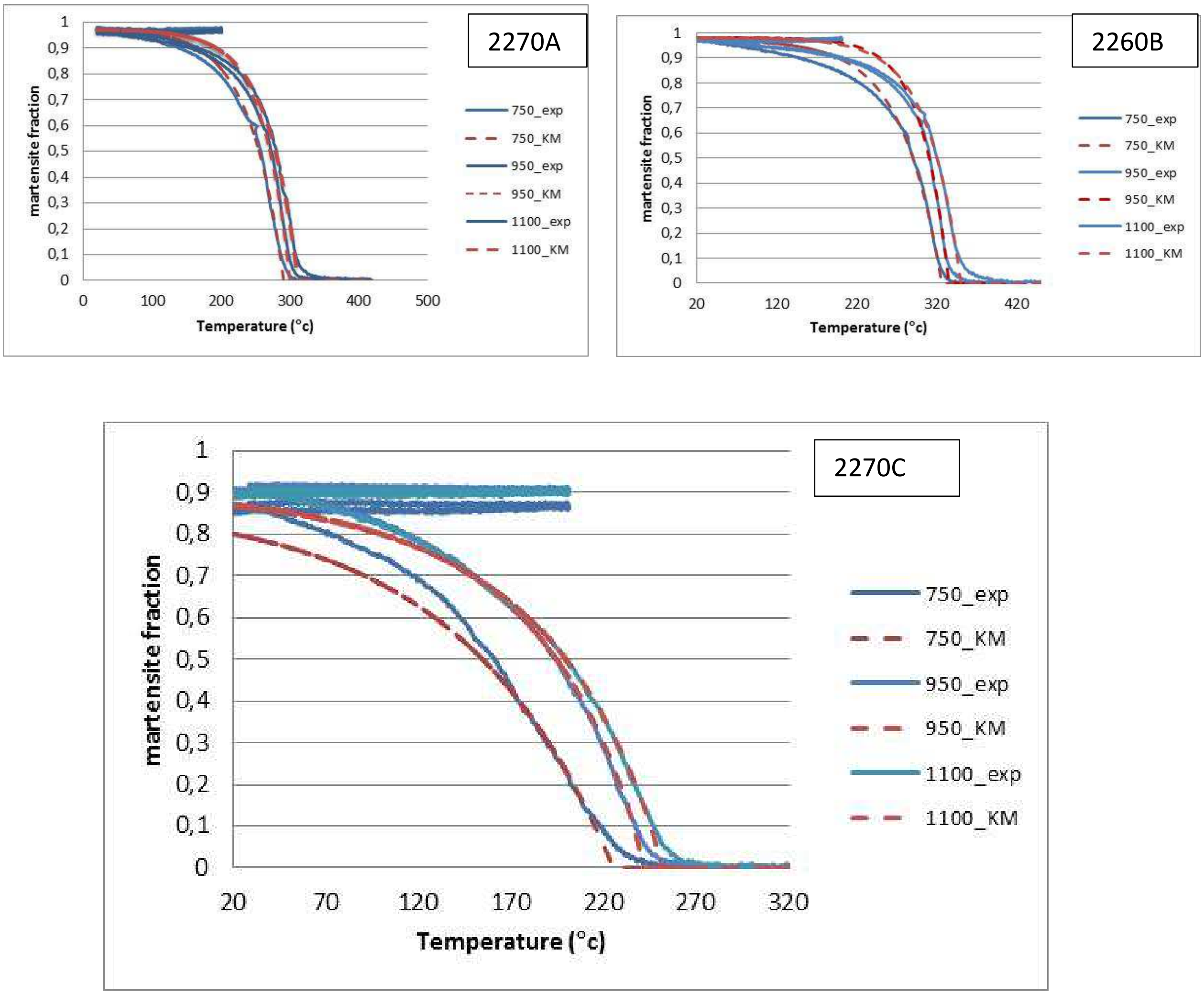


Figure 31: Comparison of martensite transformation kinetics: KM & Experimental

As we can see in figure 31, Koistinen & Marburger 's equation describes neither the beginning nor the end of martensite transformation kinetics. In fact this prediction kinetics has an exponential form whereas the experimental one is a sigmoidal evolution. Thus this equation cannot be used to describe the experimental martensite transformation kinetics for the studied steels.

V.2 Comparison of the equation of Yang & Bhadeshia with the experimental martensite kinetics

Yang & Bhadeshia also proposed an equation based on the partitioning theory of Fisher et al.to describe the martensite transformation kinetics by taking into account the influence on prior austenite grain size. The proposed equation is recalled below:

$$M_s^0 - T = \frac{1}{b}\ln\left[\frac{1}{aV_\gamma}\left\{exp\left(-\frac{\ln(1-f)}{m}\right)-1\right\}+1\right]$$

Where: a,b: are two fitting parameters

m: aspect ratio

M_s^o: Ms Temperature for a large prior austenite grain size determined thermodynamically

V_γ: volume of austenite grain.

For each steel, a set of parameters (a, b, m and M_s^o) were fixed to have the best fitting with the experimental martensite curves. Figure 32 presents the comparison with the corresponding parameters chosen for the studied steels:

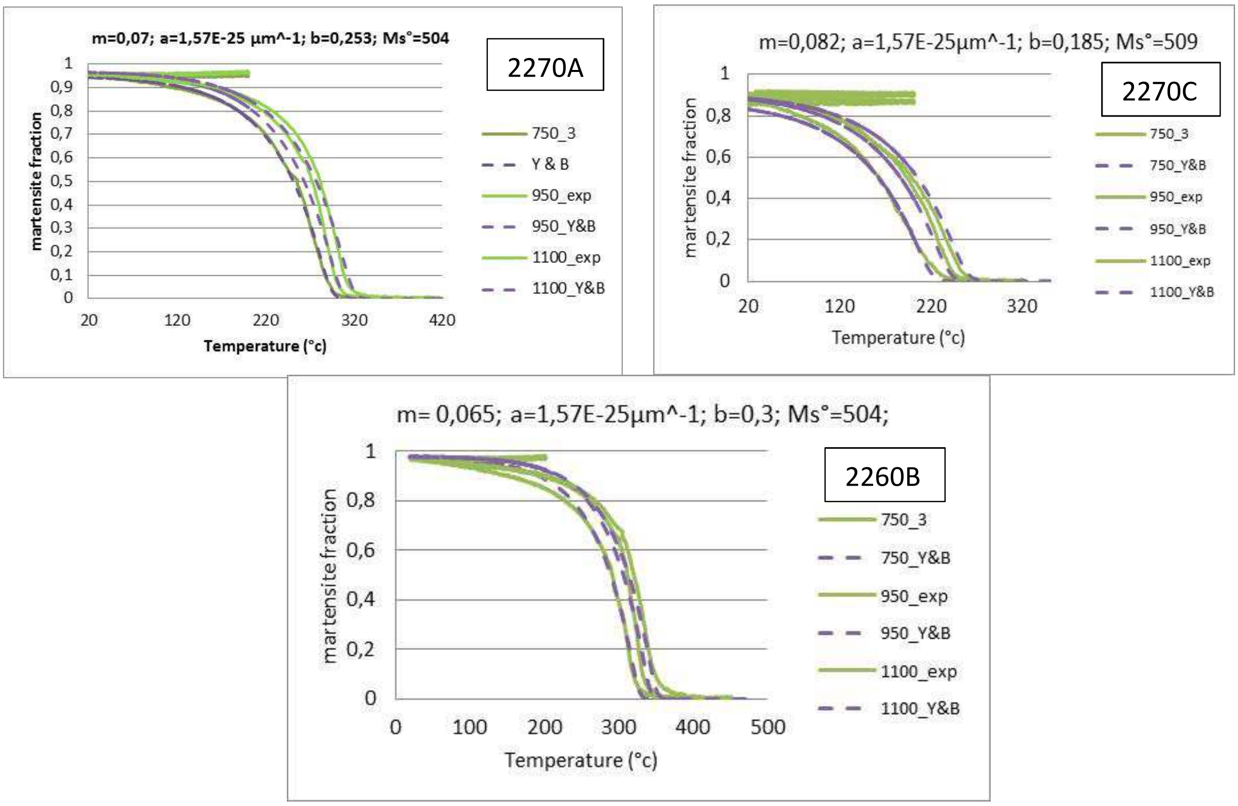


Figure 32: Comparison of the martensite transformation kinetics: Y&B vs Experimental

From the different graphs in figure 32, the martensite transformation curves predicted by Yang & Bhadeshia do not match exactly with the experimental curves despite of their sigmoidal form and to the fact that they took into account the influence of prior austenite grain size. In addition, there are many fitting constants in the proposed equation making it less attractive.

VI. Conclusions

This work was done to study the influence of chemical composition and prior austenite grain size on martensite start temperature as well as on the martensite transformation kinetics of both cold rolled and hot rolled steels. It appears from the literature study that alloying elements decrease Ms temperature. The reduction effect is higher for both carbon and manganese content. It was also observed that bcc lattice stabilizers including chromium and molybdenum decrease Ms. This remain unclear and need to be studied with further work. Among the proposed equations in the literature relating Ms with chemical compostion, Van Bohemen's equation is the most adapted to predict the experimental Ms. Yang & Bhadeshia also proposed an equation taking into account the influence of austenite grain size on Ms which reproduce the experimental results.

The experimental procedure has consisted in performing dilatometric experiments on steel at different holding temperatures to determine the martensite transformation kinetics. For the reproducible of the results, three dilatometric experiments were done for each holding temperature, and about 12 micrographies were analyzed for each holding temperature to determine the prior austenite grain size.

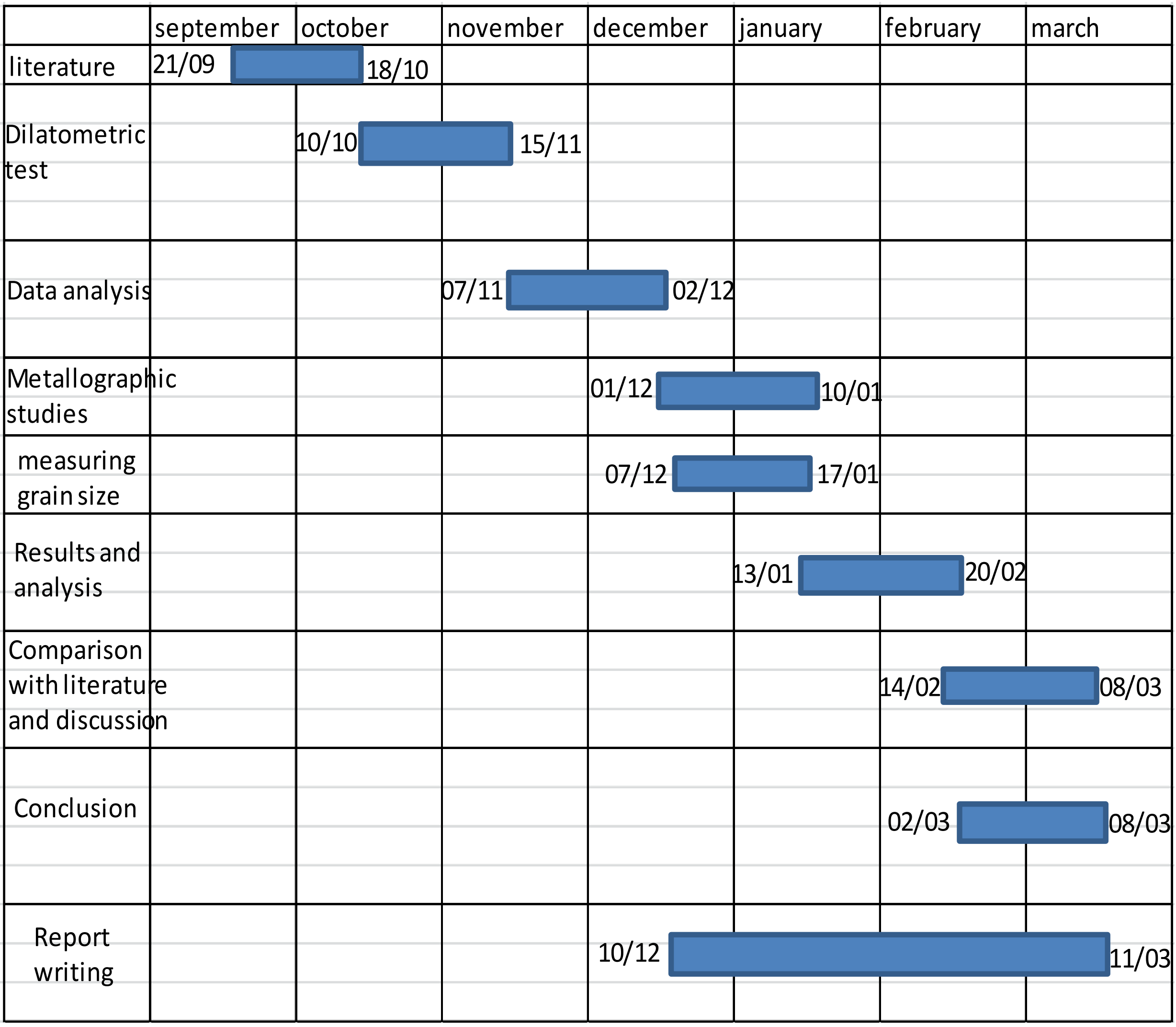
It comes out from the study that cold and hot rolled steel are the same in terms of martensite transformation kinectics. The evolution of Ms with austenite grain size for both states is similar as well.

The martensite start temperature has a logarithmic evolution with austenite grain size until a plateau value where the austenite grain effect is almost negligible. From this, it is possible to calculate the Ms due to the only chemical composition effect by using Van Bohemen's equation. The austenite grain effect on Ms in its turn can be described with an exponential law with the form: $\boldsymbol{\alpha e^{-\beta * D}}$with D the mean prior austenite grain size and α, β two constants. From this, it was possible to propose an equation that predicts the influence of both chemical composition and prior austenite grain size on Ms Temperature: **Ms(°c) = Ms_VB-** $\boldsymbol{\alpha e^{-\beta * D}}$ with Ms_VB : Ms Temperature predicted by Van bohemen. By chosen a suitable set of parameters α=46 and β=0,11, it was possible to predict the Ms evolution with austenite grain for the studied steel within 9°c of statistical uncertainties.

From the analysis of the experimental martensite transformation kinetics, it is important for a better understanding of the transformation to see it has a two steps process where the kinetics is slightly different for two different austenite grains size. An autocatalytic phenomenon can be thought to guide the transformation but not in the first order. The equations proposed by Koistinen & Marburger as well as Yang & Bhadeshia to predict the martensite transformation kinetics were not in perfect agreement with the experimental kinetics.

VII. Perspectives

- Conduct the same study for intercitical annealing in order to have values of small prior austenite grain size and complete the database.
- Expand the database in terms of alloying elements in order to study their impact on Ms Temperature as well as martensite transformation kinetics.
- Study the influence of prior austenite grain size on mechanical properties of steels.



Provisional schedule

VIII. References

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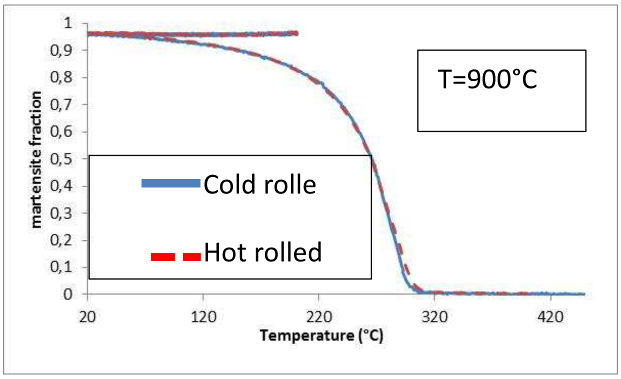
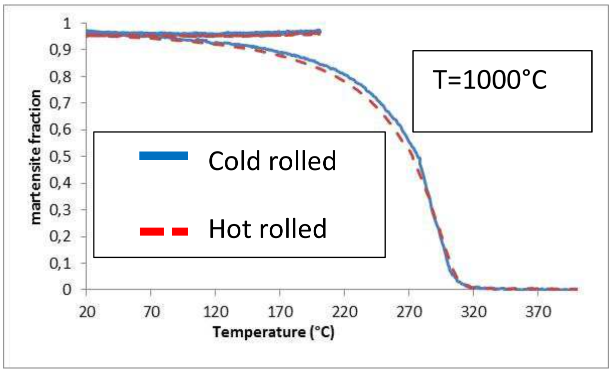
IX. Annexes

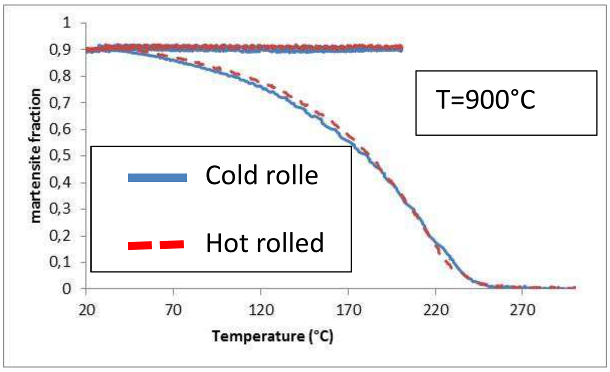
Comparison of martensite transformation kinetic for cold and hot rolled steels

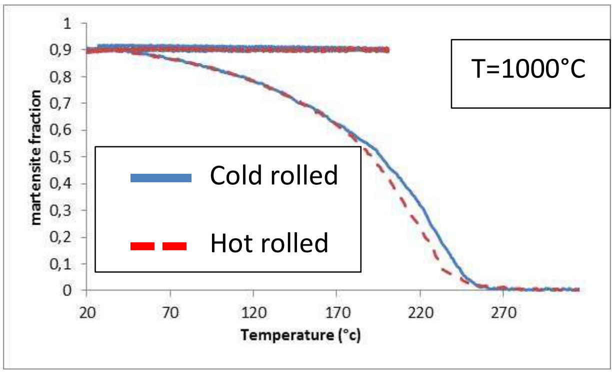
2270A





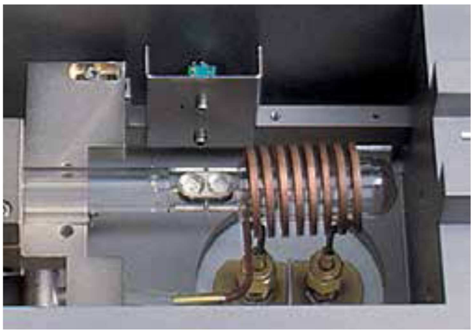
2270C



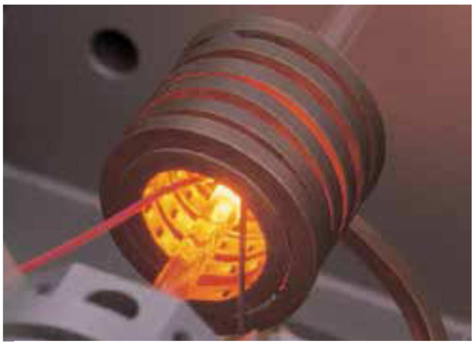


Dilatometer bähr DIL805A/D

Dilatometry system

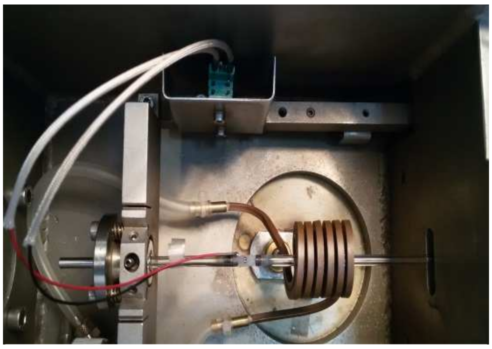


Main measurement part



Induction heating

Heating rate up to 40000°k/s

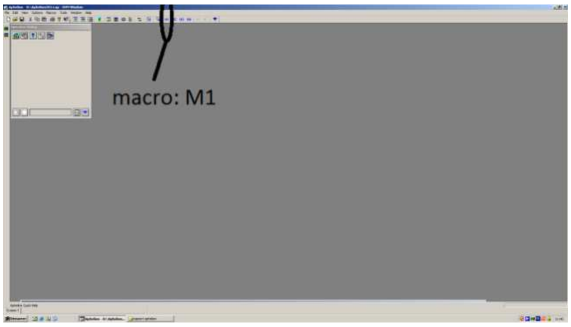


Thermocouples/ Sample in the heating system

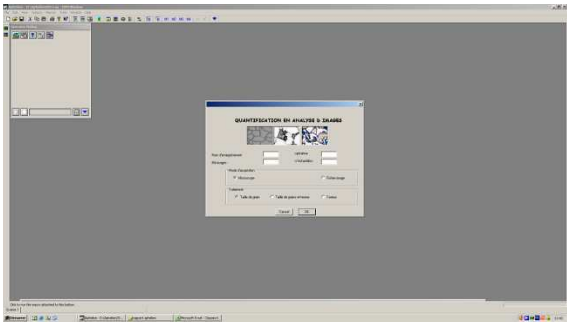
Dilatometer bähr DIL805 features

- conductivity of samples
- Resolution **ΔL/°c : 0,05µm/0,05°C**
- Strain rate : **from 0,01mm/s to 200mm/s**
- Measurement head **: DTA/DSC**

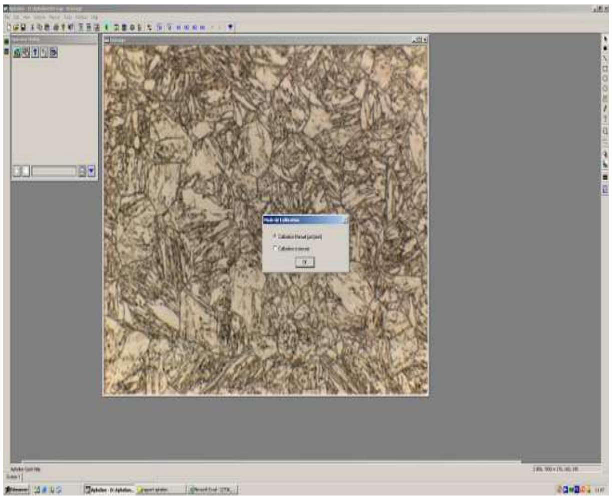
Aphelion



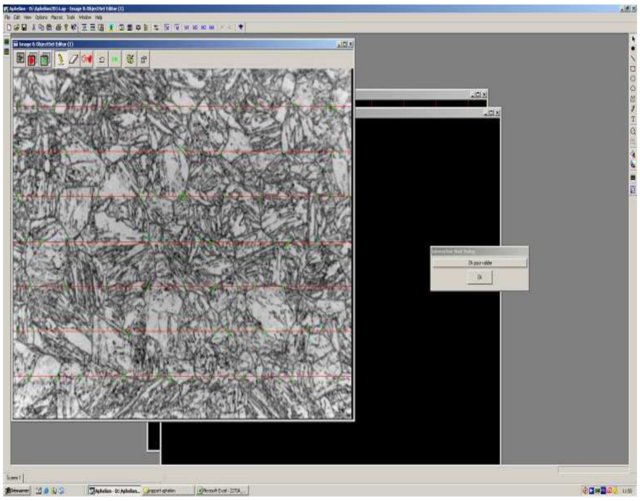
1- Step1 : clic on « macro



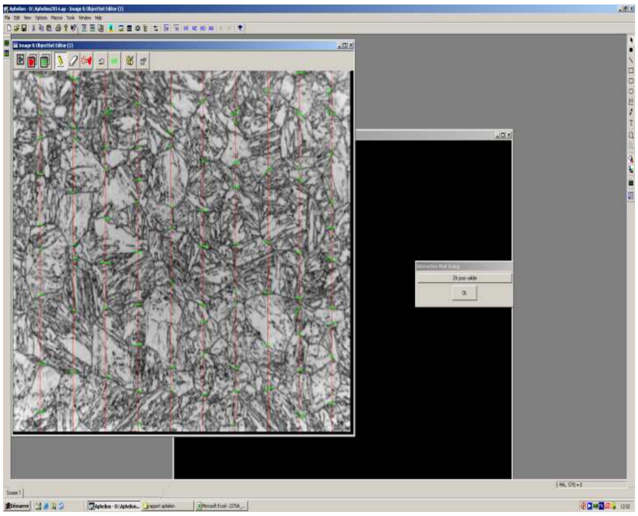
2- Step2: in the dialog, insert: registration name, username, number of images to treat.



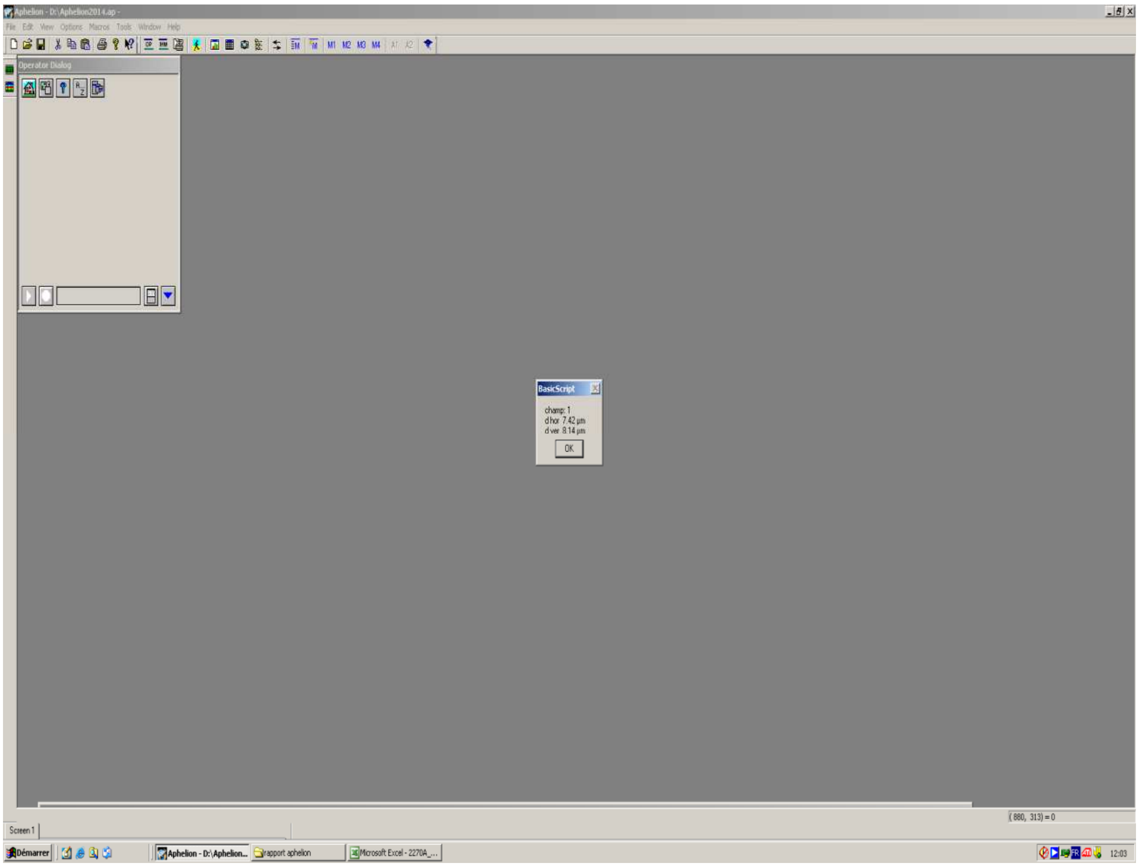
3- Step3: Choose calibration to measure; choose an image with the good scale and insert in the dialog the scale's value



4- Step4: Check all intersection of the red line with the grain boundaries: horizontal direction



5- Step5: apply the same operations as described in step4:



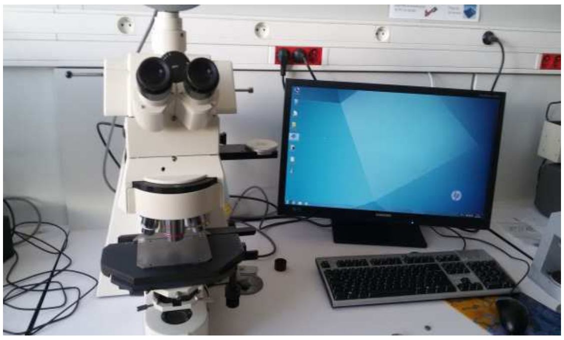
champ: 1
d hor 7.42 µm
d ver 8.14 µm

6- Step6: Austenite grain size value in both horizontal and vertical direction

Mounting

Mounted Samples.

Automatic polisher



Optical microscope

Cutting machine

Micro-Cutting machine

X. Summary

At the end of my internship in the research center of Arcelomittal in Maizières-lès-Metz, my main goals were to study: The influence of chemical composition and prior austenite grain size on martensite start temperature as well as on martensite transformation kinetics of several steels at cold rolled and hot rolled state.

From the literature analysis, Van Bohemen's equation is the most adapted to predict Ms temperature with chemical compostion. Barbier equation's also gives a good prediction of the experimental Ms.

Cold and hot rolled steels are the same in terms of martensite transformation kinetics and have the same evolution of Ms with austenite grain size as well.

The proposed equation to predict Ms temperature as a function of chemical composition and austenite grain has the form: **Ms(°c) = Ms_VB-** $\boldsymbol{\alpha e^{-\beta * D}}$ with Ms_VB : Ms Temperature predicted by Van bohemen. By taking α=46 and β=0,11 the predicted Ms is within 9°c ranges.

Martensite transformation kinetics needs to be seen as a two steps process to determine the influence of austenite grain size on the transformation. The transformation cannot be thought as an autocatalytic process in first order. The equations proposed by Koistinen & Marburger as well as Yang & Bhadeshia are not adapted to describe the experimental martensite transformation.

XI. Résumé

A l'issue de mon stage de fin d'étude d'ingénieur auprès du centre de recherche et développement d'ArcelorMittal situé à Maizières-lès-Metz (France), j'ai eu pour missions : Etudier l'influence de la composition chimique et de la taille de grain austénitique sur la température de début de transformation martensitique (Ms) ainsi que sur sa cinétique pour des tôles laminées à chaud et à froid.

Après une analyse poussée de la bibliographie, il en ressort que l'équation proposée par Van Bohemen est la mieux adaptée pour décrire l'effet composition chimique de l'acier sur la température de début de transformation martensitique. Barbier a également proposé une équation qui prédit bien les résultats expérimentaux avec une incertitude étroite.

Pour ce qui est de la cinétique de transformation martensitique, il n'existe pas de réelle différence entre un acier laminé à chaud et à froid. Les deux évolutions de Ms en fonction de la taille de grain sont très similaires et peuvent être corrélées par une même courbe de tendance.

L'équation proposée dans cette étude prédisant la température Ms en fonction de la composition chimique et la taille de grain austénitique est de la forme: **Ms(°c) = Ms_VB-** $\boldsymbol{\alpha e^{-\beta * D}}$ avec Ms_VB: la Ms prédite par Van Bohemen. En choisissant $\alpha=46$ et $\beta=0{,}11$, on réussit à prédire les valeurs expérimentales de Ms avec une incertitude comprise dans 9°c.

Il est important de considérer la cinétique de transformation martensitique comme un procédé à deux étapes afin de pouvoir mettre en évidence l'effet taille de grain sur la cinétique de transformation. Le phénomène autocatalytique peut être considérer comme procédé au travers duquel se déroule la transformation mais n'est surement pas de premier ordre. Les équations proposées par Koistinen & Marburger et Yang & Bhadeshia prédisant la cinétique de transformation martensitique ne concordent pas exactement avec la réalité expérimentale.