QUENCH & PARTITIONING RESPONSE OF A MO-ALLOYED CMNSI STEEL

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Quenching & Partitioning (Q&P) has been recently proposed as a fundamentally new way of producing martensitic steels containing a considerable amount of retained austenite. It consists of a two step thermal treatment: after soaking, the steel is quenched to a predetermined temperature in the Ms-Mf range to produce a partially martensitic, partially austenitic microstructure. The second, so-called partitioning step, aims at carbon enrichment of the austenite by carbon depletion of the martensite and carbon transport to the austenite, in the absence of carbide formation. Thus, carbon stabilised austenite is retained in the microstructure after final quenching to room temperature.

Remarkably high strength/ductility combinations and significant volume fractions of retained austenite are obtained via Q&P processing of a Mo-alloyed CMnSi steel. The instantaneous strain hardening behavior shows a pronounced dependency on the partitioning temperature (PT) applied. Continuously decreasing n-values (with strain) are obtained at low partitioning temperatures where increasing the PT results in flattening of the strain hardening curves. Partitioning at 450℃ results in positive n-value vs strain behavior similar to TRIP steels. In addition, oscillations in the strain hardening curves are observed which have been hypothesized to be linked to a different dislocation substructure of the partitioned martensite. Linear arrays of straight screw dislocations are observed after partitioning at 450℃. The occurence of this dislocation substructure may be related to the retarding effect of Mo on dislocation mobility.

1.   Introduction

The Quenching and Partitioning (Q&P) process has been proposed as a fundamentally new way to produce a new type of advanced high strength steel [1]. The concept consists of a 2-step heat treatment where after soaking the steel is quenched to a pre-determined temperature (QT) which is lower than the martensite start temperature (M_s), but higher than the martensite finish temperature (M_f). Hence, the resulting microstructure at the QT consists of martensite and untransformed austenite. The second step aims at carbon enrichment of the untransformed austenite present at the QT by carbon depletion of the martensite laths, in order to decrease its M_s temperature so that thermally stable austenite is obtained at room temperature. In order to obtain the carbon-enriched austenite, the steel is either held at the QT for a longer partitioning time (Pt) or is brought to a higher, so-called partitioning temperature (PT, typically 350-450℃) and held, followed by final room temperature quenching. In this way, a martensitic microstructure containing a considerable amount of retained austenite is obtained. Alloying with Si, Al and/or P is employed to prevent carbide formation.

The amount of retained austenite depends on the partitioning temperature and time and also on the quench temperature applied, since this temperature determines the phase fractions and potential level of carbon enrichment. A methodology has been proposed to determine an "optimum" quench

temperature that assumes full carbon rejection from the martensite under constrained carbon equilibrium conditions in the absence of carbide formation [1,2,3,4,5,6,7,8].

Mechanical properties obtained by Q&P processing of a 0.19C-1.59Mn-1.63Si(wt%) steel grade reported by Clarke *et al.* indicated that Q&P is a viable way of producing high strength steels exhibiting appreciably high ductility levels [6,9]. Potential applications may be pillars, anti-intrusion bars, anti-theft components, racks, etc. [10]

The present contribution reports the mechanical properties obtained via Q&P processing after full austenitization of a Mo-containing CMnSi grade. The effect of Mo-alloying on retained austenite stabilization is also assessed.

2.   Experimental Procedure

The chemical composition of the Mo-alloyed CMnSi grade is given in Table 1. A (Mo-free) CMnSi steel (Table 1) was also included in this study to clarify the effect of Mo on the austenite stabilization. Both steels were received in the full hard cold rolled condition. Annealing was performed using salt baths. Soaking was done at 850℃ for 150s resultin g in full austenitization for both steel grades. The quench temperature was calculated according to the method proposed by Speer [1]. An optimum quench temperature of 240℃ was obtained for the Mo CMnSi grade and of 234℃ for the CMnSi grade. The austenite volume fractions calculated to be present at these temperatures are 21vol% for the MoCMnSi and 19vol% for the CMnSi grade. Partitioning was done at 350, 400 or 450℃ for partitioning times ranging from 10s to 300s. Retained austenite volume fractions were determined with magnetic saturation according to the method proposed by Wirthl *et al.* [11]. Tensile testing of the MoCMnSi Q&P heat treated samples was done on a screw driven INSTRON 5569 tensile test frame at a constant engineering strain rate of 5.6 10^{-4}/s. Tensile specimens, machined in the rolling direction, with 50mm gauge length were used. The instantaneous strain hardening (n-value) was calculated according to

$$n = \frac{\partial \ln \sigma}{\partial \ln \varepsilon} \approx \frac{\ln \sigma_2 - \ln \sigma_1}{\ln \varepsilon_2 - \ln \varepsilon_1}$$ [1]

with ε, true strain and σ, true stress. An average over 40 data points was made.

Table 1: Chemical composition (wt%), optimum QT (℃) and volume fraction of austenite present at the QT (vol%) for the MoCMnSi and CMnSi grades.

	C	Mn	Si	Mo	QT	fγ at QT
MoCMnSi	0.21	1.96	1.49	0.25	240	21
CMnSi	0.20	1.63	1.63	-	234	19

The Q&P microstructure was characterized using a JEOL JEM-2200FS TEM operating at 200 kV. Thin foils were prepared by first thinning to 70 μm using 400 grit SiC grinding paper. Discs of 3 mm diameter were cut from this thinned sheet and electropolished in a Struers Tenupol jet polisher using a solution of 95% acetic acid and 5% perchloric acid operating at 32 V and a temperature of 13℃.

3.   Mechanical Properties Obtained via Q&P Processing of a Mo-alloyed CMnSi grade

The mechanical properties obtained via Q&P following full austenitization at 850℃ are shown in Figure 1. Tensile strengths ranging from 1280 to 1510MPa and yield strengths from 1050 to 1195MPa are obtained in combination with uniform elongations in the range of 4-11% and total elongations in the range of 4-15%. In general, partitioning at a higher temperature results in lower strength levels

and higher elongations. Remarkably high ductility and strength combinations are obtained after partitioning at 450℃.

A summary diagram of the mechanical properties obtained is given in Figure 2, including comparison with commercially available cold rolled martensitic steel grades such as MartINsite [12] and Docol M [13]. Note that the elongation of the Docol M was reported for an A80 tensile test specimen. The specimen geometry used for the MartINsite was not reported. Mechanical properties obtained after full austenitization and Q&P heat treating of a 0.19C-1.59Mn-1.63Si(wt%) steel reported previously by Clarke *et al*. [6,9] are also shown in the graph. Sub-sized tensile specimens were used.

In general, higher ductility is exhibited by the Q&P microstructures compared to the commercial martensitic steel grades at similar strength levels. The MoCMnSi grade exhibits the highest ductility at tensile strength levels of 1300+/-50MPa corresponding to a partitioning temperature of 450℃.
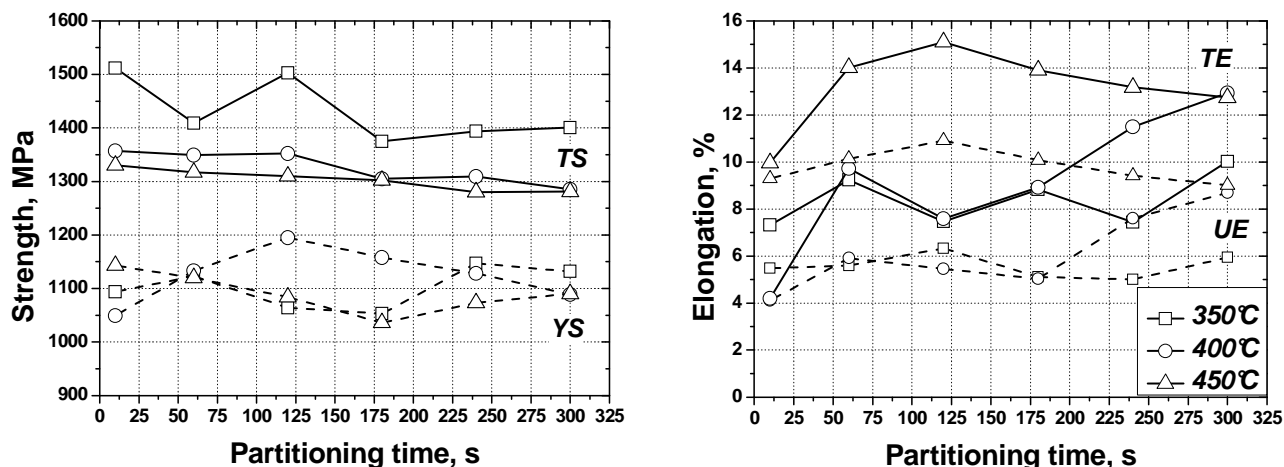

Figure 1: Mechanical properties obtained via Q&P heat treating after full austenitization of a MoCMnSi steel as function of partitioning time and temperature. Left: Tensile strength (TS) and 0.2% offset yield strength (YS). Right: uniform elongation (UE) and total elongation (TE).

4.   Strain Hardening Dependence on Partitioning Conditions

The stress-strain curves resulting from partitioning at different temperatures for a fixed partitioning time of 120s are given in Figure 3. Partitioning at 350℃ results in the highest tensile strength whereas partitioning at 450℃ gives the lowest tens ile strength and highest ductility. Instantaneous strain hardening (n-value) as function of true strain is also given in Figure 3. A clear dependence on the applied partitioning temperature is observed. Continuously decreasing instantaneous n-value vs. strain is obtained for PT=350℃. Partitioning at 4 00℃ flattens out the n-value curve. At 450℃ an upward slope of the n-value curve is obtained, similar to the strain hardening exhibited by TRIP steels.

Previous research has shown that the TRIP effect operates in Q&P steels, contributing to improved strain hardening and ductility [14]. The mechanical stability of the retained austenite is thought to depend on the partitioning conditions (time and temperature). For a fixed partitioning time of 60s, the highest austenite stability was obtained at a PT of 450℃, resulting in the most effective contribution of the TRIP effect to increased strain hardening [14]. In this study, the carbon content of the retained austenite has been shown to increase with increasing partitioning temperature for a Pt of 60s suggesting more effective decarburization of the martensite at a higher partitioning temperature resulting in lower strength levels. The softer martensite matrix may also yield a greater effectiveness of the TRIP contribution to strain hardening.

As shown in Figure 3, oscillations appear in the n-value curve at a partitioning temperature of 450℃, whereas this was not the case at lower parti tioning temperatures. A blow-up of the stress-strain curve (inset Figure 3) shows serrations for a PT=450℃ while continuous work hardening is seen for partitioning at 350℃ and 400℃. Serratio ns seem to appear on the stress-strain curve when

the TRIP effect is maximally contributing to the strain hardening. One might think that the serrations result from the austenite to martensite transformation. However, previous work on retained austenite stability [14] indicated that transformation of the austenite also occurs in microstructures partitioned at lower partitioning temperatures where smooth stress-strain curves were obtained. In addition, recent tensile testing at an elevated temperature (100°C) indicated an increased height of the serrations [15]. The austenite transformation slows down significantly at a higher temperature [16]. Thus, if the serrations were associated solely with martensite formation, a diminished effect might be expected at higher testing temperatures.   These serrations can hence not be ascribed solely to austenite transformation. Diffusion controlled mechanisms such as dynamic strain ageing, which are more likely to operate at elevated temperatures might also play a role.
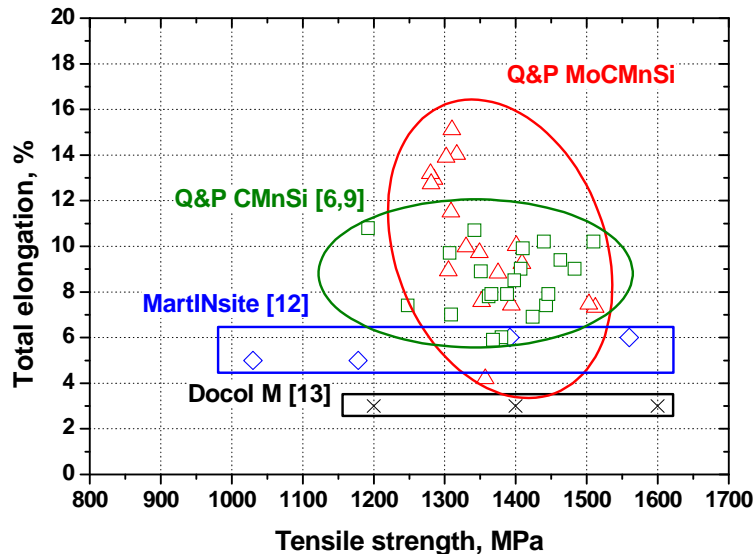

Figure 2: Summary of the mechanical properties obtained after full austenitization and Q&P heat treating of the 0.25Mo-0.21C-1.96Mn-1.49Si(wt%) grade along with commercially available cold rolled martensitic grades MartINsite [12] and Docol M [13]. Mechanical properties obtained by Clarke *et al.* [6,9] after full austenitization and Q&P processing of a 0.19C-1.59Mn-1.63Si(wt%) steel are also indicated in the graph.

The transition from serrated to non-serrated flow of low-carbon as-quenched martensite has been studied by Okamoto *et al.* [17]. A broad range of testing temperatures and strain rates were examined in this study. It was observed that serrated yielding occurred at elevated temperatures at certain ranges of strain rate. A detailed microscopic study was also carried out which showed that serrated and smooth yielding are associated with different dislocation substructures of the deformed samples. A very fine, well-developed dislocation cell structure is observed in the case of continuous yielding. Substructure exhibiting serrated yielding consists of uniform dislocation distributions characterized by linear arrays of screw dislocations, rather than distinct cell walls.

Figure 4 shows a TEM micrograph of an undeformed Q&P microstructure given a partitioning treatment at 450°C for 120s. Serrations on the str ess-strain curve were observed for this condition (Figure 3). The microstructure consists of martensite laths separated by retained austenite films. Arrays of straight screw dislocations are observed in the martensite matrix.

The dislocation substructure of the martensite observed after partitioning at 450°C for 120s is not necessarily anticipated to be the same as the one formed directly after quenching to QT. Dislocation annihilation and some recovery may take place during partitioning. Formation of low-angle dislocation cell walls resulting in the formation of low angle subgrains occurs during efficient recovery. Local solute mobility can affect the rate of recovery or dislocation annihilation [18]. Mo is known to retard recovery and recrystallization kinetics [19].   The microstructure in Figure 4 does not show cell

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formation. It has been suggested that the presence of straight screw dislocations rather than a recovered substructure, as observed here, can be ascribed to their lower mobility [20] providing evidence for solute segregation [21]. Pinning of dislocations has been ascribed to substitutional solutes such as Si and Mo even at temperatures where the substitutional solute is immobile in the lattice but mobile in the dislocation core [22].
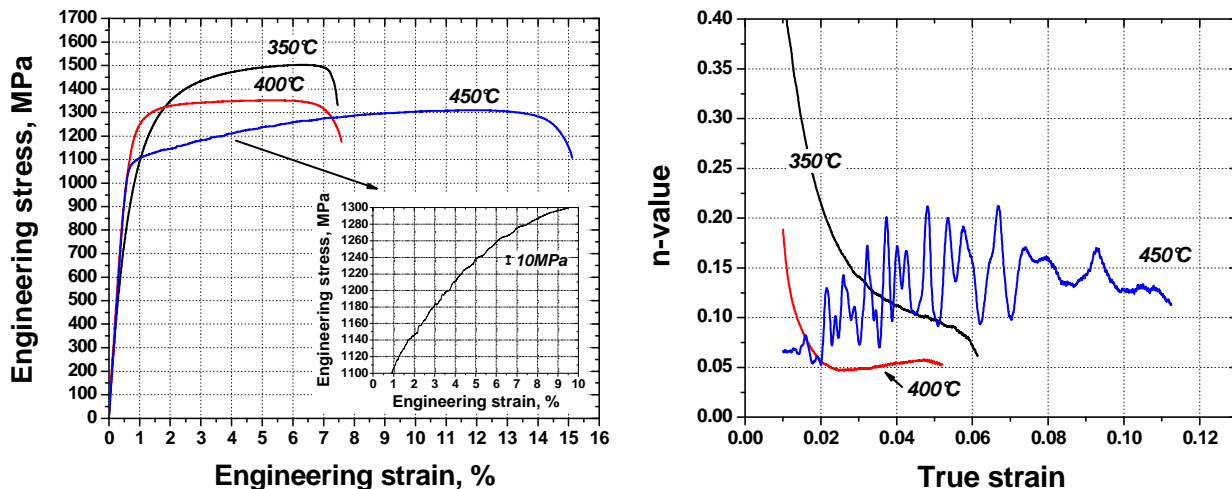

Figure 3: Stress strain (left) and instantaneous n-values (right) obtained for a fixed partitioning time of 120s and different partitioning temperatures.

Segregation of solute to dislocations may restrict cross-slip and development of serrated flow [17]. In addition, the pinning of dislocations may be enhanced by the strong affinity of Mo for carbon. Substitutional-interstitial Mo-C dipole interactions with dislocations in the serrated yielding region in a Fe-Mo-C alloy have been reported [23].

In addition to a different dislocation substructure, transition carbide precipitation has been observed at lower partitioning temperatures [24] whereas carbides were absent after Q&P at a higher PT. Swarr and Krauss [25] and Hornbogen [20] indicated that very fine precipitates may be effective in stopping dislocations in their slip planes and act as pinning points for dislocation generation, resulting in well-developed cell structures and smooth yielding. Further TEM characterization of deformed microstructures is ongoing and may provide additional insight.

It should be noted that serrated flow is usually associated with lower ductility [25]. However, recent work has suggested that Q&P steels exhibit a TRIP effect and that partitioning at 450℃ is associated with the highest austenite stability causing increasing strain hardening with increasing strain typical of TRIP steels. The highest elongation is hence obtained for this PT where serrated flow is observed.

5.   Retained Austenite Stabilized via Quenching & Partitioning

The retained austenite volume fractions stabilized via Q&P in the MoCMnSi steel are shown in Figure 5 (left). High volume fractions are obtained indicating the effectiveness of austenite stabilization via Q&P. The highest volume fractions are obtained after partitioning at 450℃. For comparison, the austenite volume fractions obtained via Q&P in the CMnSi steel (Table 1) are shown in Figure 5 (right). It should be noted that the steels differ only with respect to their Mo content. Soaking at 850℃ results in full austenitization for both grades and the quench temperatures and austenite volume fractions calculated to be present at the QT are similar (Table 1). When comparing the austenite fractions, higher amounts are retained in the Mo-alloyed grade via Q&P processing. In addition, different effects of prolonged partitioning on the austenite volume fraction are observed. Partitioning for longer than 10s results in decreasing fractions for the CMnSi steel for all partitioning temperatures

examined in this work. In contrast, the volume fractions obtained for the MoCMnSi steel appear to be much less sensitive to partitioning time. A systematic decrease with partitioning time is not observed for this grade for the partitioning times examined. Additionally, a different effect of partitioning temperature is observed. The highest austenite fractions are present at a partitioning temperature of 450℃ in the MoCMnSi grade, whereas short partition ing times (Pt<180s) results in the highest γ volume fractions after partitioning at 350℃ for th e CMnSi composition.
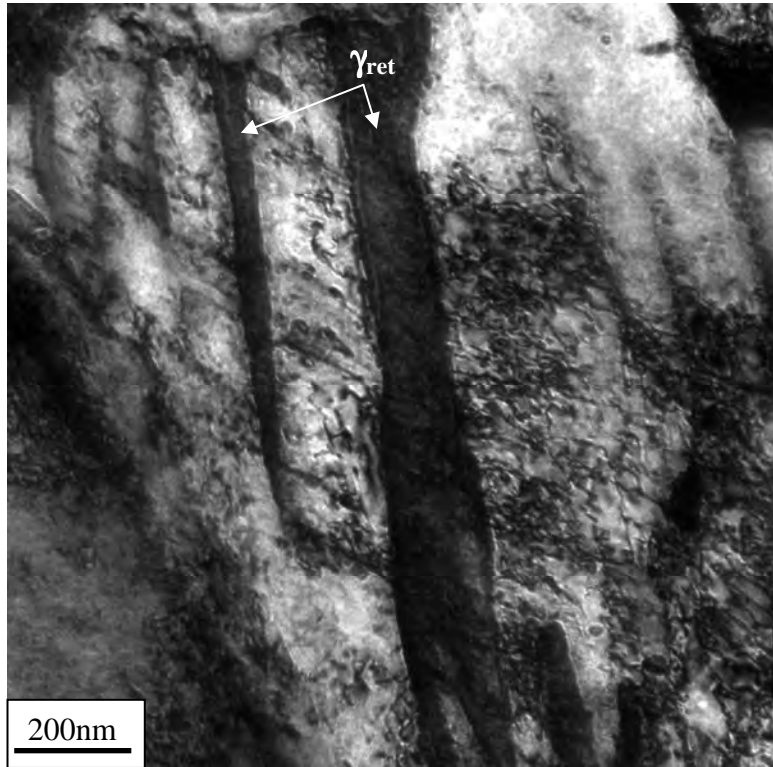

Figure 4: TEM micrograph of an undeformed MoCMnSi Q&P microstructure partitioned at 450℃ for 120s. Serrations were observed on the st ress/strain curve (Figure 3) for this partitioning condition. The retained austenite is present as thin films. Straight screw dislocations are present in the martensite crystals.

Partitioning for a longer time and/or at a higher temperature yields greater potential for carbon diffusion from martensite into austenite. Given the original assumptions of "ideal" Quench & Partitioning i.e. "full" partitioning of carbon, the absence of competing reactions such as carbide formation [1], etc., higher γ volume fractions are expected to be stabilized after partitioning for longer times and/or at higher temperatures (until the eventual onset of carbide formation). This is seen for the Mo-grade. However, this was not the case for the CMnSi steel where longer partitioning times and higher temperatures led to lower fractions. These lower fractions may be due to austenite decomposition as is suggested by the heat treatment results presented in the context of Figure 6. The CMnSi sample partitioned 10s at 350℃, containing t he highest austenite volume fraction, was taken from room temperature to 350℃ in a salt bath and h eld for 50s followed by water quenching. The austenite volume fraction was measured subsequently. The same austenite fraction was obtained as the one resulting from partitioning for 60s at 350°C. After the measurement, the test was continued via isothermal annealing at 350℃ for an additional 60s followed by water quenching and measurement of the austenite content. The treatments were continued in this way. Austenite contents corresponding to sequences of partitioning and then quenching, for a Pt of 120s, 180s, etc. respectively were measured. This suggests that the decreasing austenite volume fraction with

increasing partitioning time is due to the decomposition of austenite stabilized after a relatively short partitioning time of 10s.
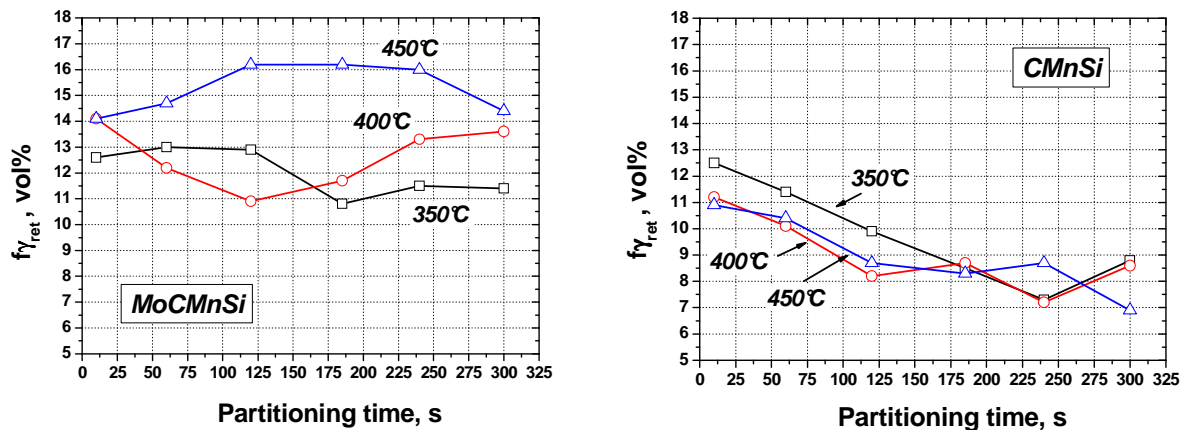

Figure 5: Austenite volume fractions retained via Q&P for a MoCMnSi (left) and a CMnSi steel (right) measured via magnetic saturation. Higher volume fractions are obtained for the Mo-alloyed grade. A higher partitioning temperature results in higher volume fractions for this composition. Decreasing volume fractions are observed with longer partitioning for the CMnSi grade.

Kim *et al.* [26] have recently suggested that austenite decomposition might be occurring during partitioning. The Q&P response of a 0.15C-1.51Mn-1.42Si(wt%) steel was studied in situ via dilatometry in their work. A volume expansion was measured during partitioning at the quench temperature (1-step Q&P) suggesting austenite decomposition. The exact mechanism involved remains unclear although the authors attributed this expansion to an isothermal martensite transformation which may proceed via autocatalysis or further growth of the pre-existing martensite.
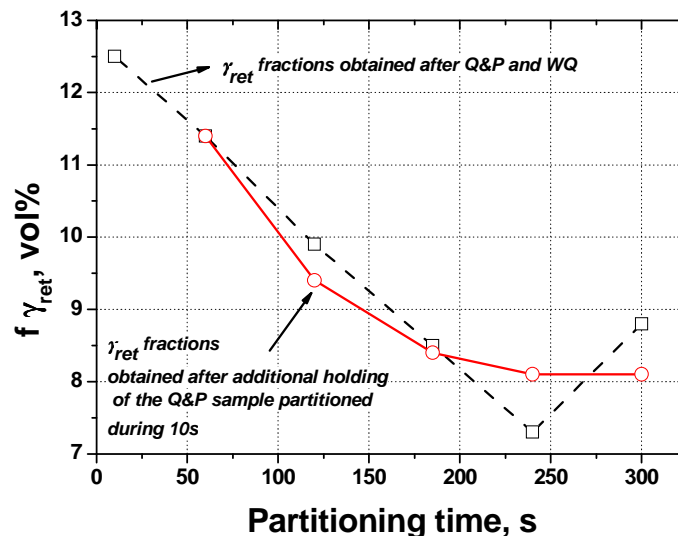

Figure 6: Austenite fractions obtained for the CMnSi grade after partitioning at 350°C (dashed line) and after reheating to 350°C and holding for similar times (solid line). The sample partitioned at 10s followed by water quenching was used for the latter heat treatment.

The present results obtained for the CMnSi grade suggest that more decomposition is occurring at a higher PT. At a higher PT, less driving force for martensite formation is available. On the other

hand, diffusion controlled processes may be activated such as bainite formation or further growth of martensite laths by interface migration [27].

A different trend is observed for the Mo-alloyed grade where the highest partitioning temperature results in the highest volume fractions of austenite. Hence, any diffusion controlled processes resulting in austenite decomposition seem to be retarded. This may be related to the solute drag-like effect (SDLE) Mo is known to have in the bainite transformation temperature region [28,29]. Mo slows down the pearlite and ferrite transformation, increasing hardenability, and to a lesser extend, the bainite transformation [30]. The effective suppression of ferrite and pearlite is primarily due to a solute drag mechanism. The austenite decomposition kinetics in the bainite region are carbon diffusion controlled in the austenite with a driving force that some investigators have suggested to be reduced by a so-called solute drag-like effect (SDLE). While it has been speculated here that Mo may influence the austenite amount in Q&P steels via solute effects on the transformation interface (e.g. bainite kinetics), further work would be needed to confirm this hypothesis directly.

6.   Conclusions

The Q&P response after full austenitization of a MoCMnSi steel has been assessed. Tensile strengths ranging from 1280MPa to 1510MPa are combined with total elongations up to 15%. A pronounced influence on partitioning conditions has been observed. Strain hardening shows a clear dependence on applied partitioning temperature for fixed partitioning times. Smooth yielding is observed after partitioning at lower temperatures, whereas serrations are observed in the stress-strain curves after partitioning at 450℃. This behavior may be associated with the observed dislocation substructure. The addition of Mo to a CMnSi composition resulted in higher retained austenite volume fractions and reduced sensitivity to partitioning time.

7.   Acknowledgements

8.   References

[1] J.G. Speer, D.K. Matlock, B.C. De Cooman and J.G. Schroth, *Acta Materialia*, 51, p.2611, 2003.
[2] M. Hillert and J. Ågren, *Scripta Materialia*, 50, p.697, 2004.
[3] J.G. Speer, D.K. Matlock, B.C. De Cooman and J.G. Schroth, *Scripta Materialia*, 52, Issue 1, p.83, 2005.
[4] M. Hillert and J. Ågren, *Scripta Materialia*, 52, Issue 1, p.87, 2005.
[5] J.G. Speer, A.M. Streicher, D.K. Matlock, F. Rizzo and G. Krauss, *Proc. of Austenite Formation and Decomposition,* Chicago, Illinois, USA, p.522, Nov. 9-12, 2003.
[6] A.M. Streicher, J.G. Speer, D.K. Matlock and B.C. De Cooman, *Proc. of the Int. Conf. Advanced High-Strength Sheet Steels for Automotive Applications*, Warrendale, PA, USA, p. 62, June 6-9 2004.
[7] J.G. Speer, D.V. Edmonds, F.C. Rizzo and D.K. Matlock, *Current Opinions in Solid State and Materials Science*, 8, p.219, 2004.
[8] J.G. Speer, F.C. Rizzo, D.K. Matlock and D.V. Edmonds, *Proc. of the 59th Annual Congress of ABM*, Sao Paulo, Brazil, p. 4824, July 19-22, 2004.
[9] A. Clarke, *PhD thesis*, Colorado School of Mines, Golden, CO, 2006.
[10] B.C. De Cooman and J.G. Speer, *Steel Research Intl.77*, No. 9-10, p.634, 2006.

[11] E.Wirthl, A. Pichler, R. Angerer, P. Stiaszny, K. Hauzenberger, Y.F. Titovets and M. Hackl, *Proc. of the Int. Conf. on TRIP-Aided High Strength Ferrous Alloys*, Ghent, Belgium, p.61, June 19-21 2002.

[12] www.mittalsteel.com/Products/Automotive+Applications/Martensitic+Steels/

[13] www.ssabdirekt.com/upload/dokument/Datasheets/GB/Docol/GB8207Docol.pdf

[14] E. De Moor, S. Lacroix, A.J. Clarke, J. Penning and J.G. Speer, *submitted to Met Trans.*

[15] E. De Moor, *unpublished work*, 2007.

[16] L. Samek, E. De Moor, J. Penning and B.C. De Cooman, *Metall. Trans. A*, Vol. 37A, p.109, 2006.

[17] S. Okamoto, D.K. Matlock and G. Krauss, *Scripta Met. et Mat.*, Vol. 25, p.39, 1991.

[18] J.D. Embury, *Strengthening Methods in Crystals*, A. Kelly and R.B. Nicholson eds., John Wiley & Sons, NY, p.331, 1971.

[19] S. Yamamoto, T. Sakiyama and C. Ouchi, *Transactions ISIJ*, Vol. 27, p.446, 1987.

[20] E. Hornbogen, *Trans. ASM*, Vol. 57, p.120 ,1964.

[21] J.P. Hirth, *Mechanical Properties of BCC Metals*, M. Meshii ed., TMS-AIME, Warrendale, Pennsylvania, p.181, 1983.

[22] L.J. Cuddy and W.C. Leslie, *Acta Met.*, Vol.20, p.1157, 1972.

[23] J.D. Baird and A. Jamieson, *Journal of the Iron and Steel Institute*, Vol. 210, p.841, 1972.

[24] E. De Moor, S. Lacroix, L. Samek, J.Penning and J.G. Speer, *Proc. of the 3rd Int. Conf. on Advanced Structural Steels*, Gyeongju, Korea, Aug. 22-24, p.873, 2006.

[25] T. Swarr and G. Krauss, *Metall. Trans. A*, Vol. 7A, p.41, 1976.

[26] S.J. Kim, Han S. Kim and B.C. De Cooman, *Proc. of Materials Science & Technology (MS&T)*, Detroit, USA, p.73, Sep. 16-20 2007.

[27] J.G Speer, R.E. Hackenberg, B.C. De Cooman and D.K. Matlock, *Phil. Mag. Letters*, Vol. 87, No.6, p.379, 2007.

[28] G.J. Shiflet ant H.I. Aaronson, *Metall. Trans. A*, Vol.21A, p.1413, 1990.

[29] K.R. Kinsman and H.I. Aaronson, *Proc. of Transformation and Hardenability in Steels*, Climax Molybdenum Co., Ann Harbor, MI USA, p.39, 1967.

[30] Steven and Haynes, *J. Iron Steel Inst.*, Vol.183, p.349, 1956.