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RESEARCH ARTICLE

Development of advanced high strength steels using hydrogen quench continuous annealing technology

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Abstract: By using hydrogen quench continuous annealing technology, Stelco Inc. has developed a suite of Advanced High Strength Steel (AHSS) grades with tensile strength greater than 1000 MPa to meet standard automotive specifications and for unique customer requirements. These grades were optimized by correlating chemical composition and processing parameters with microstructures and mechanical properties. Dual-Phase 980 (Stelco trademarked STELMAX^{TM} 980 DP), Multi-Phase 1180 (STELMAX^{TM} 1180 MP), Martensitic Steel 1300 (STELMAX^{TM} 1300 M) and 1500 (STELMAX^{TM} 1500 M) products met strength and formability requirements with excellent flatness and surface quality. Hydrogen quench continuous annealing technology not only ensures all developed AHSS grades have consistent mechanical properties across the entire strip length (from strip head to tail) and width (from edge to edge), but also produces high product yield compared with other continuous annealing processes.

Keywords: advanced high strength steels, hydrogen quenching, continuous annealing, microstructure, mechanical properties

1 Introduction

To meet stringent passenger-safety and fuel consumption requirements, Advanced High Strength Steels (AHSS) with a better balance of mechanical properties, light weight, durability and crash energy absorption have been applied extensively to the body-in-white starting in the early 2000's. There are several classes of AHSS: Dual-Phase (DP) steel, Transformation-Induced-Plasticity (TRIP) steel, Multiphase Phase (MP) steel, Twinned-Induced-Plasticity (TWIP) steel, Ferritic-Bainitic (FB) and Martensitic Steel (MS)[1,2]. Their excellent mechanical properties are the result of their unique chemistry, processing control and microstructure. These AHSS steel grades can be manufactured by controlling cooling rate from austenite or austenite plus ferrite, either on the run out table of the hot strip mill, in the hot rolled coil, or in the cooling section of the continuous annealing line for hot dip coated or continuously annealed products.

The essential difference of modern continuous annealing lines is the cooling medium used to affect the cooling rate from the annealing temperature to the designed quenching temperature. The cooling medium and associated cooling rate has an important impact on mechanical property uniformity, flatness, surface quality and productivity. Currently, most continuous annealing lines are using one of the following cooling media: rapid gas jet cooling, gas-water spray cooling and cold or hot water quenching[3]. Whereas, this paper will discuss the recent development of different AHSS grades produced on a continuous annealing line with hydrogen quench technology[4]. Grades developed were Dual-Phase 980 (Stelco trademarked STELMAX^{TM} 980 DP), Multiphase 1180 (STELMAX^{TM} 1180 MP), Martensitic 1300 (STELMAX^{TM} 1300 M) and 1500 (STELMAX^{TM} 1500 M). A correlation between chemical composition and processing parameters from the hot strip mill through to the cold mill and continuous annealing line will be presented.

2 Chemistry design

The chemistry design of AHSS is essential to meet the required strength levels while balancing formability and weldability. The annealing profile, *i.e.* critical hydrogen quench cooling rate, annealing time and temperature at maximum line speed, for each given cross section also has to be taken in consideration. A comparison of the

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Table 1. AHSS chemical composition (wt.%)

Grade	C	Mn	P	Si	S	Cr + Mo	Ti + Nb
STELMAX^{TM} 980 DP	0.10-0.20	1.50-2.00	< 0.025	0.20-0.80	< 0.005	0.10-0.30	0.02-0.04
STELMAX^{TM} 1180 MP	0.10-0.20	1.50-2.00	< 0.025	0.20-0.80	< 0.005	0.30-0.50	0.02-0.04
STELMAX^{TM} 1300 M	0.20-0.30	0.50-1.00	< 0.025	—	< 0.010	0.20-0.50	0.02-0.05
STELMAX^{TM} 1500 M	0.25-0.35	0.50-1.50	< 0.025	0.40-1.20	< 0.010	0.20-0.60	0.02-0.05

chemistries for different AHSS grades developed at Stelco Inc. is listed in Table 1. Control of phase transformation is required to promote the coexistence of different microstructural constituents. Their individual mechanical behaviour and mutual interaction develop the desired strength-ductility balance. Proper control of these multiphase microstructures is accomplished through chemistry design and processing control.

DP steel is composed of a soft ferrite matrix and 10-70% of hard martensite islands depending on the DP grade. To achieve the unique combination of mechanical properties for DP steel, carbon is restricted from 0.10 to 0.20% plus 0.3-0.7% Si and 1.0-2.0% Mn are added. Up to 0.4% Cr and/or Mo is used to stabilize austenite and strengthen the ferrite. In some cases, Nb, Ti and V are used to refine the microstructure and promote ferrite formation[5]. The presence of soft and hard phases in the dual phase microstructure results in a high sensitivity to edge fracture, *i.e.* low edge stretchability. To overcome low edge stretchability, STELMAX^{TM} 1180 MP is designed to reduce the differences between soft and hard constituents. Thus, Cr and Mo are added to suppress ferrite formation.

Martensitic steels are the hardest type of AHSS and have high tensile strength plus a high yield to tensile strength ratio. The strength of STELMAX^{TM} 1300 M and 1500 M is controlled mostly by carbon content, however, other alloying elements such as Mn, Cr, Si and Mo can be added to achieve the required strength, ductility, bendability and weldability[6,7].

3 Processing parameters

3.1 Steelmaking, casting and hot rolling

Stelco's AHSS grades are manufactured using 275 ton basic oxygen furnaces. Hot-Metal-Rotary-Lance-Desulphurization technology is used to reduce sulphur concentration before the molten iron is transferred to the basic oxygen furnace vessel[8]. This hot metal treatment practice can keep sulphur under 0.005%, which is important to reduce the volume of sulphide inclusions, as well as improve slab internal quality[9]. Stelco's steelmaking facility has both a RHOB Vacuum Degasser and a Ladle Treatment Station to ensure temperature and chemical homogeneity. Hydrogen concentration is controlled under 0.0002% to reduce the risk of hydrogen embrittlement.

The steel is cast in a curved mould, twin strand continuous caster after the liquid metal treatment. Stelco's slab caster is capable of casting all AHSS grades due to its split roll design from segments 4 to 14 and air mist cooling capacity. Slabs are torch cut to length based on customer requirements. All AHSS slabs are stack cooled indoors to reduce the cooling rate and avoid slab cracking. If needed, scarfing is used to remove superficial slab defects before hot rolling.

The first step of the hot rolling process is to reheat the slab to the desired temperature. Reheating time and temperature are set to balance the dissolution of microalloy particles formed during solidification with control of austenite grain coarsening at high temperature. To prevent excessive austenite coarsening during reheating, Ti is added to retard austenite grain growth[8]. The slab is fed into a reversing rougher mill after reheating where it is reduced from the original slab thickness (240 mm) to a predetermined transfer bar thickness depending on final thickness. The Stelco hot strip mill has a coil box between the roughing and finishing mills. The coil box promotes a homogeneous austenitic microstructure and uniform temperature profile from head to tail and from edge to edge before entering the finishing mill. The six-stand finishing mill further reduces the strip to the desired hot band gauge. Controlling finishing and coiling temperatures within-coil and from coil to coil is also important to ensure consistent mechanical properties prior to downstream processing. To assist with modeling the cold rolling process, samples were collected from hot bands for the different grades. Typical hot band mechanical properties are displayed in Table 2.

3.2 Pickling and cold rolling

During hot rolling, oxide scale forms on the surface of the hot rolled coils. Stelco uses push-pull hydrochloric acid pickle lines to remove the scale from AHSS grades. Speed on the lines is controlled to avoid grain boundary oxidation on Si-added AHSS grades. Oil is applied just before recoiling to provide lubricant in the first pass of

Table 2. Typical Hot band AHSS mechanical properties

Grade	YS (MPa)	TS (MPa)	EL (%)
STELMAX^{TM} 980 DP	825	925	11
STELMAX^{TM} 1180 MP	825	925	11
STELMAX^{TM} 1300 M	450	600	22
STELMAX^{TM} 1500 M	515	735	20

subsequent cold reduction operations.

Cold rolling is carried out at a 4-stand tandem mill to further reduce the strip thickness, introduce work hardening, and improve thickness tolerance and surface flatness. The total reduction achieved by cold rolling for AHSS grades generally varies from 50 to 75%. The reduction in each stand is distributed uniformly through the mill except for the final stand where lower reduction is used to impart control of flatness, gauge and surface finishes. During the cold rolling operation, most of the energy expended in cold work dissipates in the form of heat and only a small fraction (<10%) is stored in the reduced strip as strain energy[10]. The release of this stored energy provides the driving force for recovery and recrystallization during the subsequent annealing process[11].

3.3 Hydrogen quench-continuous annealing

The annealing process consists of heating to a soaking temperature, holding at that temperature, and then quenching and aging/tempering. Figure 1 shows the schematic of the annealing process for different AHSS grades. The annealing schedule varies by grade. The heat treatment is defined based on the peak annealing temperature, along with the soaking time which is controlled by line speed and the critical cooling rate that can be achieved at the quench section. Supercritical annealing close to Ac3 is selected for STELMAX^{TM} 980 DP, followed by slow cooling to the intercritical region to form ferrite, then rapid cooling and overaging to promote martensite tempering and carbide precipitation. However, for STELMAX^{TM} 1180 MP, overaging is selected to promote martensite tempering to improve elongation. Both STELMAX^{TM} 1300 M and STELMAX^{TM} 1500 M are reheated to full austenitezation annealing temperature, followed by rapid cooling to promote martensite formation. Tempering occurs in the transformation zone as the strip cools inside the furnace or it can be heated in the transformation zone for tempering to increase the formability.

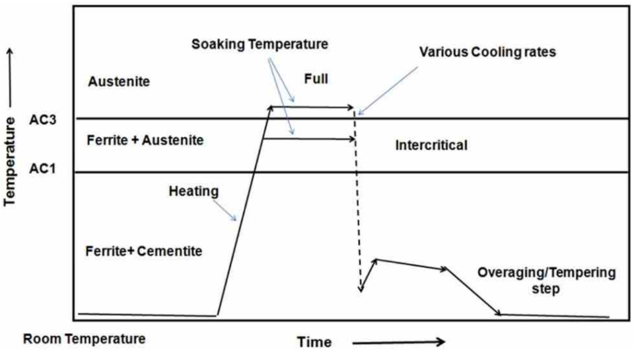


Figure 1. Schematic representation of annealing process for different AHSS grades

A schematic of the continuous annealing with hydrogen quenching process is shown in Figure 2[12]. The furnace starts with a standard sealed roll system, and there is no segregation of the furnace atmosphere (80% Hydrogen and 20% Nitrogen) from the entry seal rolls through the exit seal rolls. The reheating furnace has five zones which can be controlled independently. The reheating temperature can be set from a maximum of 980°C to a minimum of 780°C. Following the reheating furnace section is a slow cool section. There are two independently controlled zones where the temperature can be set in a range of 500°C to 980°C. The hydrogen quenching section is just after the slow cool section. Hydrogen flow, distance of nozzles from the strip, and open length of the distribution system are all adjustable. The open length of the distribution system is controlled by a movable curtain which can block passage of the chilled furnace atmosphere. This curtain is part of the control system and can independently adjust the quench rate and quench end temperature. The cooling rate setup is determined by the strip thickness and steel grade, as well as the quench end temperature which can be varied from 500°C to the system temperature of 200°C or less. Following the hydrogen quench section there is a hot leveler that was designed to eliminate the crossbow introduced during the hydrogen quench. The temperature within the hot leveler can be adjusted from 80 to 550°C to ensure that enough austenite phase is retained to effectively correct the shape. A transformation section is right after the hot leveler. The transformation section temperature can be controlled in a range of 80 to 550°C. Following the transformation section, there is a final cooling section that can reduce the strip temperature below the oxidation temperature before delivery to the atmosphere[12].

Hydrogen quenching technology allows for infinitely adjustable cooling control resulting in consistent mechanical properties across the entire strip width and length. In addition, the jet cooler in the quenching section offers very intensive and symmetrical cooling on both sides of the strip which promotes excellent flatness. A hot leveler located immediately after the hydrogen quench zone ensures the strip has superior temperature uniformity and flatness[12]. A comparison of martensitic grade flatness

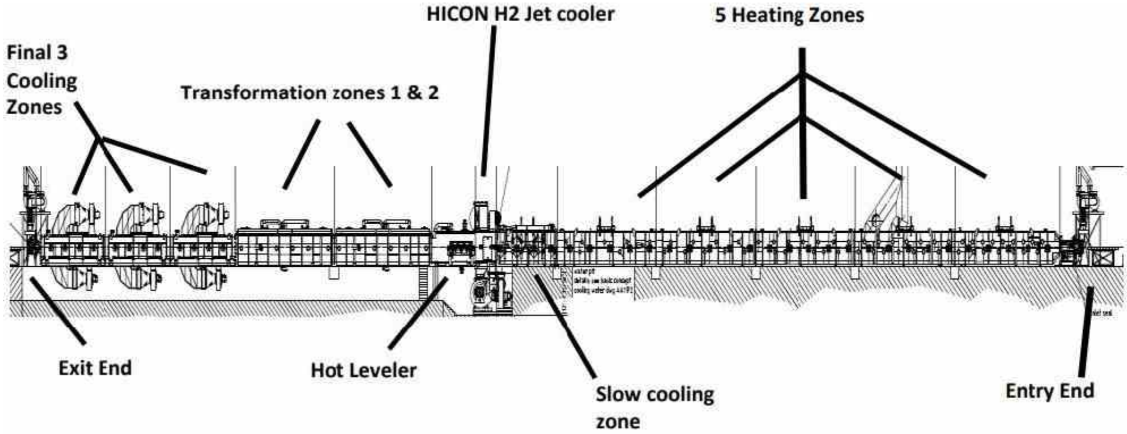


Figure 2. Schematic layout of continuous annealing with hydrogen quenching process (strip transport is from right to left on the page)

between water and hydrogen quench continuous annealing lines is shown in Figure 3. The water quenched strip shows edge wave, center buckle with poor flatness and has to be temper rolled to correct the shape; while the hydrogen quenched strip has excellent flatness and can save processing cost by avoiding temper rolling. Comparison of martensitic grade surface quality of both water and hydrogen quenched strips is shown in Figure 4. Water quenched strip has an oxide layer with steam pockets and off flat errors[13]. While hydrogen quenched strip has a flat and clean surface owing to no water being used, and there is no need to re-pickle after quenching.

Figure 3. Comparison of martensitic grade flatness by (a) water quenched with edge wave and center buckle, and (b) hydrogen quenched strip with excellent flatness (courtesy HyCAL, a Ferrous Metal Processing HyCAL facility of Ferragon Corporation in Gibraltar, MI, USA)

Even with the additional process steps of temper rolling and re-pickling, the rejection rate of water quenched strip is higher than 30%, however, the rejection rate using hydrogen quench technology is as low as 3% throughout the product range[13]. In addition, the hydrogen quench can be interrupted to produce the tailored microstructures needed for third generation AHSS grades such as Quench and Partition (Q & P), TRIP Bainite (TRIPB) and Carbide Free Bainite (CFB).

(a)

(b)

Figure 4. Comparison of martensitic grade surface quality (a) water quenched strip with an oxide layer, steam pockets & off flat errors, and (b) hydrogen quenched strip with clean surface

4 Microstructure

The typical microstructure of AHSS grades after hydrogen quench continuous annealing is shown in Figure 5. The AHSS samples were prepared by standard metallographic techniques with 2% Nital solution etching to reveal the microstructure.

The STELMAX^{TM} 980 DP microstructure (Figure 5(a)) consists of a soft ferrite phase (dark contrast), a high percentage of hard martensite phase (grey contrast) added to improve the strength, and a small percentage of bainite phase. During hydrogen quench continuous annealing, the strip is annealed in the intercritical region (ferrite + austenite) for a certain time followed by hydrogen quenching to below the martensite start temperature in Figure 1. This transforms the high carbon austenite to martensitic plates/islands (second phase) within a soft ferrite matrix. The cooling rate affects the amount of martensite produced. The strength of DP steels is mainly dependent

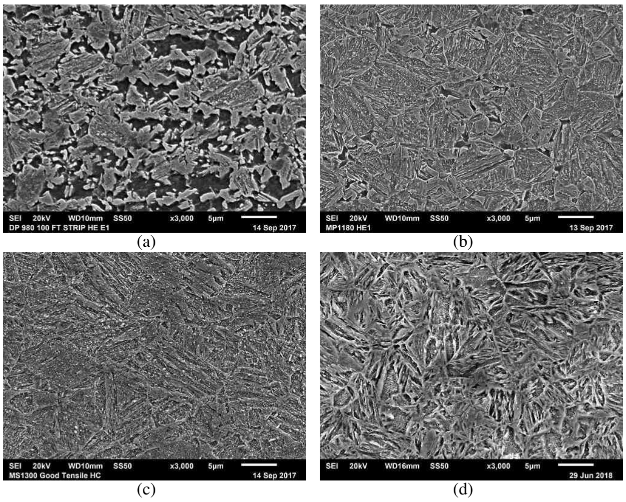
Table 3. Stelco developed AHSS grades mechanical properties

Grade	Gauge	Head			Tail		
	(mm)	YS (MPa)	TS (MPa)	EL (%)	YS (MPa)	TS (MPa)	EL (%)
STELMAX^{TM} 980 DP	1.60	631	1134	12	589	1119	12
STELMAX^{TM} 1180 MP	1.46	1010	1215	7	981	1283	7
STELMAX^{TM} 1300 M	0.50	1143	1322	4	1140	1308	5
STELMAX^{TM} 1300 M	2.00	1065	1380	7	1104	1364	7
STELMAX^{TM} 1500 M	1.40	1304	1549	7	1285	1544	7
STELMAX^{TM} 1500 M	1.60	1310	1547	7	1299	1542	7

on the relative hardness and volume fraction of the secondary phase[14]. With the combination of ferrite phase providing excellent formability, and martensitic phase providing improved ultimate tensile strength, DP steels are increasingly used in safety-critical auto body structural components owing to their superior energy absorption versus conventional high strength steels.

The microstructure of STELMAX^{TM} 1180 MP (Figure 5(b)) is characterized by a mixture of hard phases, *i.e.* a high percentage of lath-shaped martensite plate, bainite, and maybe retained austenite, in a relatively soft ferrite matrix. STELMAX^{TM} 1180 MP produced by hydrogen quench continuous annealing is designed to have increasing amounts of martensite in a ferrite matrix, in which the strength of the steel is proportional to the amount of martensite present. This leads to a high degree of work-hardening which is beneficial for both forming and edge stretching.

The chemistry and annealing process for martensitic STELMAX^{TM} 1300 M and STELMAX^{TM} 1500 M are designed to suppress ferrite transformation during hydrogen quenching to a temperature below the martensite start region. Isothermal holding at this temperature allows complete microstructure transformation to martensite. This is seen in the microstructures of STELMAX^{TM} 1300 M (Figure 5(c)) and STELMAX^{TM} 1500 M (Figure 5(d)), the latter of which has finer and interlinked martensitic grains. Very fine carbides were also observed in the microstructure of developed AHSS steels inside individual martensitic and bainitic laths (Figure 5(a-d)).



(a) (b) (c) (d)

Figure 5. SEM images showing the microstructure of AHSS (a) STELMAX^{TM} 980 DP, (b) STELMAX^{TM} 1180 MP, (c) STELMAX^{TM} 1300 M, and (d) STELMAX^{TM} 1500 M

5 Mechanical properties

Typical mechanical properties for the developed AHSS grades at Stelco Inc. are summarized in Table 3. From Table 3 it can be seen that STELMAX^{TM} 1180 MP, STELMAX^{TM} 1300 M, and STELMAX^{TM} 1500 M met GMW3399 MP1180, MS1300 and MS1500 respectively. STELMAX^{TM} 980 DP tensile strength of 1134 MPa is just above the GMW3399 maximum of 1130 MPa, however, it met both Toyota and Honda DP980 specifications. Elongation of all AHSS grades listed in Table 3 is much higher than the specified minimum requirement. The higher elongation indicates that AHSS developed at Stelco has better ductility and formability. In addition, the strip head and tail testing results demonstrated that the hydrogen quenching technology can achieve consistent mechanical properties across the entire strip length.

Table 4 shows the tensile test results for a 1.60 mm STELMAX^{TM} 1500 M at edge, center and edge locations. The continuous annealing line with hydrogen quench technology has high consistency in mechanical properties across the strip width.

Stelco's recently developed STELMAX^{TM} 980 DP, STELMAX^{TM} 1180 MP, STELMAX^{TM} 1300 M and STELMAX^{TM} 1500 M with improved and consistent mechanical properties have been extensively utilised in automotive body structure, recreation vehicle frame and safety shoe plate replacing stainless steel. These successful developments will be used as a guide to develop even

Table 4. Mechanical property variation

	Head			Tail		
	YS (MPa)	TS (MPa)	EL (%)	YS (MPa)	TS (MPa)	EL (%)
Edge	1309	1543	7	1287	1531	7
Center	1310	1547	7	1299	1542	7
Edge	1302	1542	7	1283	1529	7
μ±σ	1307 ± 4	1544 ± 3	7 ± 0	1290 ± 8	1534 ± 7	7 ± 0

higher strength AHSS grades (*i.e.* STELMAX^{TM} 1700 M) and the third generation AHSS such as Quench and Partition (Q & P), TRIP Bainite (TRIPB) and Carbide Free Bainite (CFB) grades.

6 Conclusion

(1) AHSS grades developed at Stelco were optimized by chemistry design and process parameter control including: steelmaking, hot rolling, cold reduction and hydrogen quench continuous annealing.

(2) STELMAX^{TM} 980 DP, STELMAX^{TM} 1180 MP, STELMAX^{TM} 1300 M and 1500 M products with unique microstructures and mechanical properties met standard automotive specifications with high ductility and formability.

(3) All AHSS grades showed excellent flatness and consistent mechanical properties across the entire strip length and width by using hydrogen quench continuous annealing technology.

(4) Hydrogen quench continuous annealing technology has better strip surface quality, low steel production and processing cost, as well as high productivity.

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