

# AHSS Coating Issues and Concerns

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## Introduction

- Compared to HSS, AHSS grades use higher amounts of alloys such as Mn, Si, Mo, and C - many of which have a higher affinity for O than Fe
- Achieving good zinc adherence using traditional continuous annealing furnace practices is an ongoing issue with higher alloy steel due to the difficulty in reducing their more stable oxides
- Considerable research is underway that focuses on modified furnace conditions from those used for low carbon and HSLA steels
- Some producers are looking at other methods of avoiding zinc adherence problems

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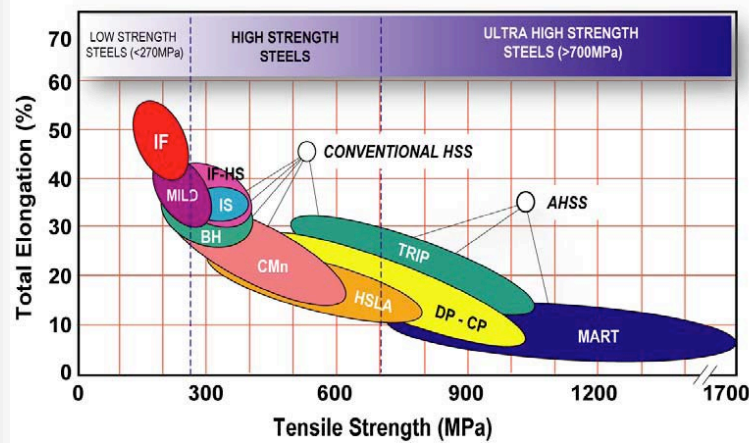
## Topics of Discussion

- Review of AHSS steel grades and metallurgy
- Selective Oxidation during annealing
- Internal oxidation
- Control of oxidation/reduction
- Other methods to avoid selective oxidation

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## The Family of Coated Sheet Steels



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## AHSS Mechanical Properties

Steel Grade	YS (MPa)	UTS (MPa)	Tot. EL (%)
HSLA 350/450	350	450	23-27
DP 300/500	300	500	30-34
DP 350/600	350	600	24-30
TRIP 450/800	450	800	26-32
DP 500/800	500	800	14-20
CP 700/800	700	800	10-15
DP 700/1000	700	1000	12-17
MS 1250/1520	1250	1520	4-6

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## AHSS Chemistries

**Table 1** Overview of the Alloy Basis, the Applied Hardening Mechanism and the Resulting Steel Grades

Steel Grade	Alloy Basis	Hardening Mechanism	Main Alloying Addition
Microalloyed grades	LC	precipitation, grain refinement, solid solution	Ti, Nb and/or V, Mn
Rephosphorized LC grades	LC	solid solution, grain refinement	P, Mn, Si
BS IF grades	IF (Ti, Nb or Ti + Nb)	solid solution, grain refinement, precipitation	P, Mn, Si, B
BH grades (LC)	LC	solid solution, grain refinement	P, Mn, Si
BH grades (ULC)	ULC (Ti, Nb, V)	solid solution, grain refinement	P, Mn
DP/MP grades	LC	transformation	C, Mn, Cr, Mo
TRIP grades	LC	transformation	C, Mn, Si, Al, P

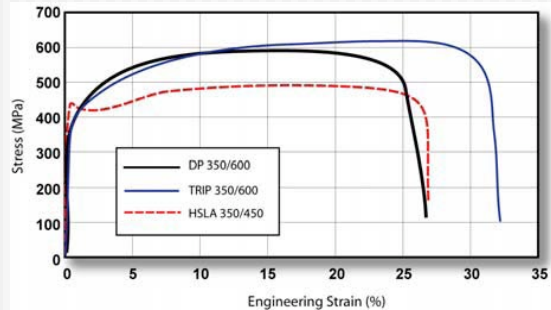
- For both DP and TRIP
  - C level of 0.1 to 0.4%, but as low as possible for good weldability
  - Mn level of 1.0 - 2.5%
  - Cr & Mo up to 1.2% (together)
  - Si level of 1.0 - 2.5%, and/or Al level of 1.0 - 2.5%
  - Often micro-alloyed with Nb, V, or Ti for grain refining and precipitation hardening

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## Stress-strain Behavior

- The high work hardening rate and good elongation of DP steels give them much higher UTS than conventional HSS of similar YS
- TRIP steels have a lower initial work hardening rate than DP steels, but the hardening rate persists at higher strains. This gives an advantage over DP in the most severe stretch forming applications



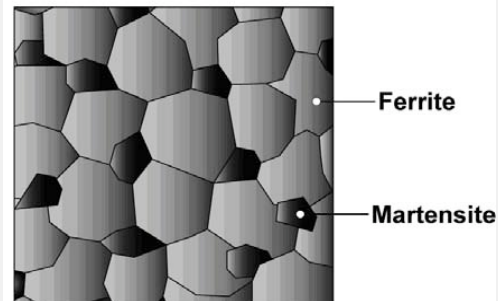
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## Dual Phase Steels

- Ferritic matrix containing a hard martensitic second phase in the form of islands
- Higher volume fraction of second phase generally increases strength
- For coated products DP is produced by controlled cooling from the two-phase ferrite plus austenite phase to transform some austenite to ferrite before controlled cooling to transform the remaining austenite to martensite

### Ferrite-Martensite DP



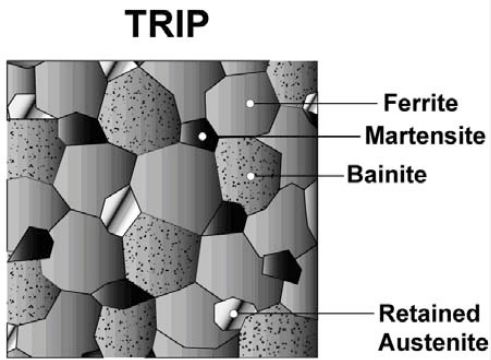
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## TRIP Steels

(Transformation Induced Plasticity)

- Retained austenite embedded in a primary matrix of ferrite, with varying amounts of martensite and bainite
- Requires the use of an isothermal hold at an intermediate temperature which produces the bainite
- Higher C and Si content results in the significant volume fractions of retained austenite
- During deformation retained austenite progressively transforms to martensite with increasing strain thereby increasing the work hardening rate at higher strain levels



The micrograph shows a complex microstructure with large, light-colored polygonal grains of ferrite. Interspersed among these are smaller, darker regions of martensite and bainite. Small, dark, irregularly shaped particles of retained austenite are also visible within the ferrite matrix. Labels with leader lines point to these four distinct phases: Ferrite, Martensite, Bainite, and Retained Austenite.

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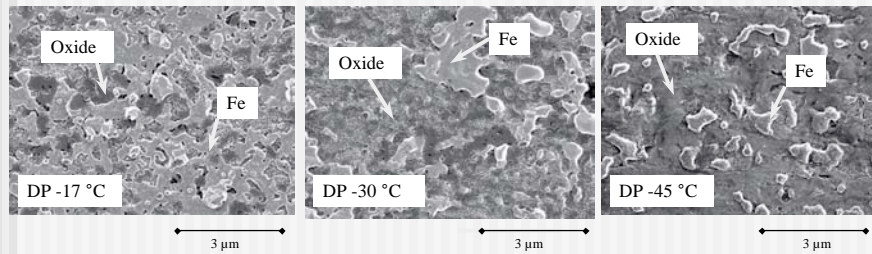
## Oxide Formation During Annealing

- Despite protective atmospheres oxides of elements with a higher affinity for O than Fe form on the steel surface and cannot be reduced under normal conditions
- These oxides cause zinc adhesion failure or interfere with the galvanneal reaction
- In CA furnaces very low dew points have been used to control oxides.
- Research on highly alloyed AHSS steels has shown that ultra-thin oxide layers can form over large areas of the surface at very low dew points - often referred to a Selective Oxidation
- At higher dew points there tends to be selective accumulation of alloying elements along the grain boundaries, resulting in increased Fe content near the surface

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## Selective Oxidation



Annealed AHSS surfaces after heat treatment at 800 °C at various dew points

Source: Galvatech 07 Proceedings - B. Schuhmacher paper

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## Selective Oxidation

- At the AHSS production level, it has been found that mere addition of moisture to the incoming gas will not ensure effective stabilization of the dew point in the furnace, sufficient to avoid selective oxidation

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## Oxidation/Reduction

- ThyssenKrupp have found that a better way to achieve good zinc wetting on AHSS is to use an oxidation/reduction technique
- Iron-based alloy surfaces exposed to an oxidizing atmosphere will primarily form a Fe oxide layer that completely covers the surface
- Unlike the oxides of Mn, Si, Cr, and Al, Fe oxide can easily be reduced by hydrogen downstream in the furnace

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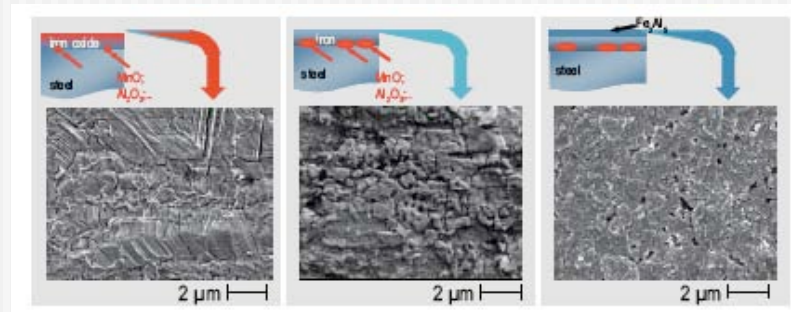
## Internal Oxidation

- The water vapor formed during the oxidation/reduction process prevents formation of harmful oxides on the surface and embeds the stable alloy oxides, keeping them from interfering with the Fe-Zn reaction
- The name used to describe this process is "Internal Oxidation"
- The best method of accomplishing it is to directly preheat the strip using a direct-fired furnace (DFF)
- Many new lines built to produce AHSS have only radiant tube (RT) furnaces, so accomplishing internal oxidation is a huge challenge

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## Internal Oxidation



SEM scans of the various stages of the oxidation/reduction technique

Source: Galvatech 07 Proceedings - B. Schuhmacher paper

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## Control of Oxidation/Reduction

- Using oxidation/reduction requires that it be closely controlled by being able to measure the thickness of the oxide layer formed
  - Furnace sensors based on reflectance work well for homogeneous oxide layers
  - At temperatures above 700°C, use infrared pyrometry just downstream from the oxygen feed-in point
- The above techniques are being used successfully in Europe to produce coated AHSS

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## Control of Oxidation/Reduction

- Recent research had shown that reducing Si and increasing Al improves the reactive wetting of TRIP steels at  $-30^{\circ}\text{C}$
- While Mn does selectively oxidize, it has been found that at levels as high as 1.5% it does not adversely affect reactive wetting - the reason being that MnO is reduced by the Al in the zinc bath. This suggests that routine zinc pot analysis should include Mn - at least when running high Mn steels

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## Other Methods to Avoid Selective Oxidation

- Heat and soak sheet at  $850 - 1000^{\circ}\text{C}$  to cause reduction of  $\text{SiO}_2$  by C from the steel. Still a lab procedure and is energy intensive
- Use Mo as it does not selectively oxidize - very expensive
- Treat hot band at  $720^{\circ}\text{C}$  prior to pickling to segregate Si and P oxides at grain boundaries about 10 microns below surface. May be a viable added process to avoid retrofitting galvanize lines with a DFF

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## ASTM Specifications for AHSS

- Currently no ASTM standard(s) for AHSS
- Europe has prEN 10336 (Dec 2006) describing the technical delivery conditions for HD and EG sheet metal of multi-phase steels with respect to formability