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Effects of Niobium Microalloying on Microstructure and Properties of Hot-Dip Galvanized Sheet

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Niobium microalloying is effective in hot-rolled and cold-rolled steels by providing a fine-grained microstructure resulting in increased strength. To optimize the strengthening effect, alloy design and hot-rolling conditions have to be adapted. As a key issue the dissolution and precipitation characteristics of Nb are discussed in particular with regard to the run-out table conditions. It is then considered how the hot-rolled microstructure and the solute state of Nb interact with the hot-dip galvanizing cycle. The adjusted conditions allow controlling the morphology and distribution of phases in the cold-rolled annealed material. Additional precipitation hardening can be achieved as well. The derived options can be readily applied to produce conventional HSLA and IF high strength steels as well as to modern multiphase steels. It will be explained how important application properties such as strength, elongation, bendability, weldability and delayed cracking resistance can be influenced in a controlled and favorable way. Examples of practical relevance and experience are given.

Keywords *: microalloying, strength, galvanizing, delayed cracking, weldability*

1. Introduction

The quest for high strength automotive steel sheet with adequate formability has led to the development of different steel types characterized by various microstructures delivering a typical property profile. The microstructure is adjusted by the chemical composition of the steel on the one hand side and by thermo-mechanical processing on the other side. Due to economic reasons as well as weldability issues the alloying content is kept low in automotive sheet steel. The actual strength is made up by a combination of solid solution hardening, grain refinement, precipitation hardening and transformation hardening. While carbon, manganese, silicon, and aluminum make up the base alloying concept small amounts of niobium, titanium, vanadium, chrome and molybdenum (Fig. 1) are being added to either improve the steel's property profile or to widen the processing window. The additional alloying costs caused by the use of microalloying elements principally have to be weighted against the processing benefits and added value they provide.

Niobium microalloying offers the largest variety of beneficial metallurgical effects as shown in Fig. 1. The amount

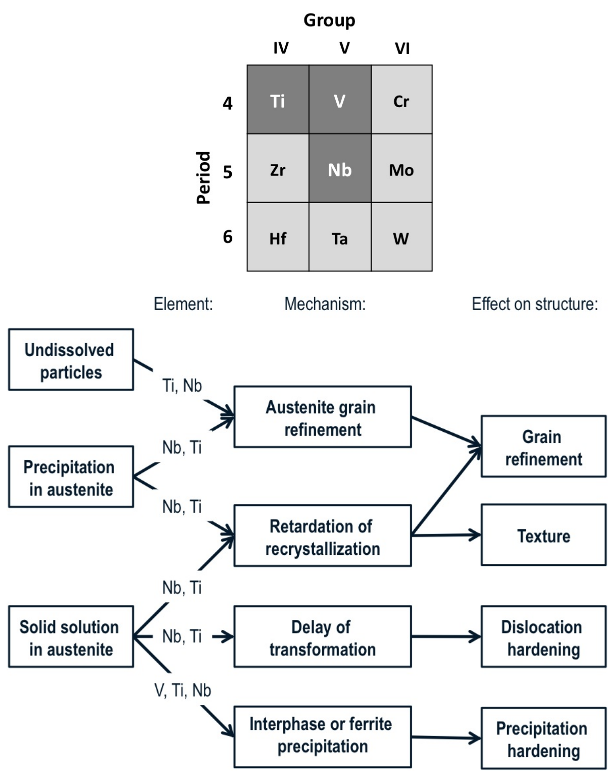

Fig. 1. Transition metals for special alloying purposes and metallurgical effects of microalloying elements (Nb, Ti, V).

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of niobium necessary to achieve these effects and thus the involved alloying cost is also quite small. It is well established that niobium is the most efficient alloying element in providing grain refinement. Besides of that, niobium also supports transformation hardening and precipitation strengthening under suitable processing conditions. The optimum use of these niobium related effects requires a careful design of the alloy as well as the consideration of the entire processing chain in the steel mill. All the necessary knowledge and know-how has been generated over 40 years of intensive niobium microalloying research.[1)]

2. Niobium effects during hot rolling process

2.1 Effects of niobium during reheating

Since Nb is a strong carbide and nitride former its solubility decreases with increasing carbon and nitrogen content in the steel melt (Fig. 2a). The nitrogen content in blast furnace steel is low and the carbon content of today's automotive steel sheet usually does not exceed 0.25%. Thus at least 0.03% Nb can be brought into solution at a typical hot strip mill slab reheating temperature of 1250 °C. This amount of Nb is sufficient to effectively provide grain size control. Most of the automotive sheet material however contains carbon levels not higher than 0.1% allowing the addition of soluble Nb to be raised to a level of 0.06 to 0.1%. Such an increased amount of Nb can provide additional effects like transformation delay or precipitation hardening. Any Nb added above the solubility limit will not dissolve during reheating and remain in form of small particles. Such non-dissolved particles can have two functions. One is to restrict austenite grain coarsening during slab reheating; the other is to provide hydrogen traps in applications where hydrogen induced cracking is a problem. Austenite grain size control during reheating is however mostly done by a sub-stoichiometric (referring to nitrogen) addition of Ti (Fig. 2b). Over-stoichiometric Ti addition leads to very coarse TiN particles that form already in the liquid steel and therefore have no pinning effect. A refined reheat austenite grain structure principally leads to a finer grain size in the final product since all grain-refining mechanisms further reduce the initial reheat grain size.

2.2 Effects of niobium during austenite conditioning

Niobium that has been dissolved during reheating has the potential to re-precipitate as fine Nb(C,N) particles during austenite conditioning. As the temperature drops during rolling the solubility of Nb is reduced as indicated in Fig. 2a. However, the kinetics of Nb re-precipitation is rather sluggish so that Nb can remain in solid solution even beyond the amount postulated by the solubility limit under thermodynamic equilibrium conditions. Both, precipitate and solute Nb retard the recrystallization of deformed austenite by either particle pinning or solute drag on the austenite grain boundaries. Niobium being in solid solution after finish rolling has the potential to delay the phase transformation and to form strengthening precipitates during or after the phase transformation.[2)] There are different ways of retaining Nb in solid solution after hot rolling. Austenite conditioning has to occur above the temperature of maximum precipitation. The time between reduction passes has to be short (usually the case in a hot strip mill). Increased levels of Mn or Mo generally retard

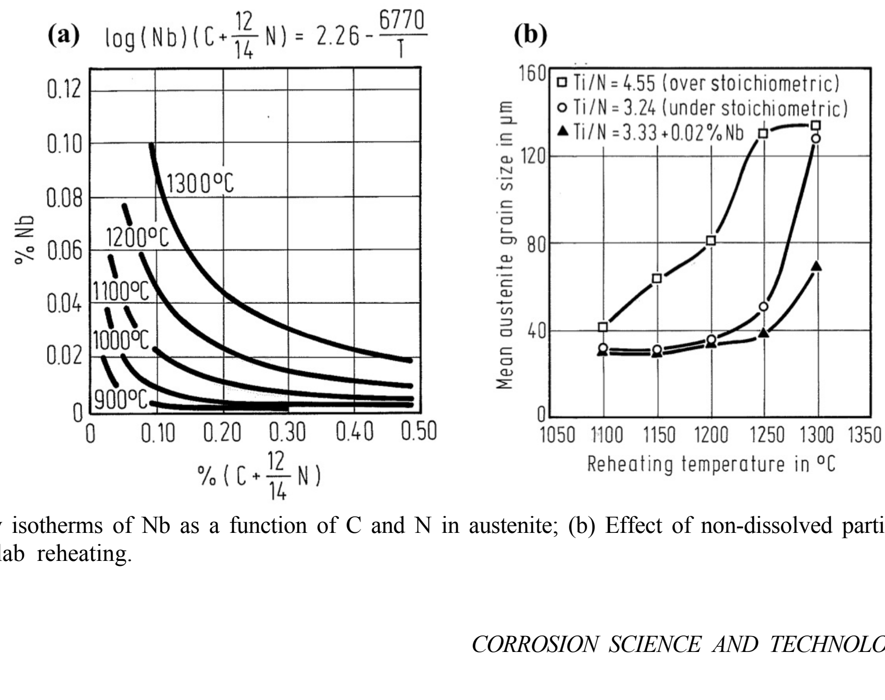

Fig. 2. (a) Solubility isotherms of Nb as a function of C and N in austenite; (b) Effect of non-dissolved particles on the austenite grain size during slab reheating.

the precipitation start.[3),4)] Since an increased level of Nb also raises the recrystallization-stop-temperature controlled rolling with austenite pancaking can be performed even at elevated finish rolling temperature.[5)] Experiments have revealed that under such conditions a significant share of Nb can be kept in solution especially when the carbon content is on a low level.

2.3 Effects of niobium during cooling & coiling

When a significant amount of Nb is in solution in austenite at the transformation temperature, has an important effect on the CCT diagram and subsequent transformation during continuous cooling. This manifests itself in a lower transformation start temperature as well as in an increased tendency to form non-polygonal ferrite microstructures. This trend is becoming more pronounced if the cooling is accelerated. Fig. 3a demonstrates that these effects are strongest for solute Nb, while Ti and especially V are similarly effective only when present in much larger amount.[6)]

The reduced transformation temperature due to solute Nb results in an increased nucleation rate of ferrite grains, hence the grain size will be smaller. This grain size refinement adds to what has already been achieved by austenite conditioning. Experience with thin automotive hot strip has shown that the combination of both grain-refining effects can result in a ferrite grain size of ASTM 15 even when the cooling rate is moderate and the coiling temperature is at around 600 °C.[7)] On the other hand solute Nb provides grain refinement even if austenite pancaking is not possible, for instance when rolling high strength IF steel.

Under increased cooling speed a higher share of non-polygonal microstructure is formed. This can be Widmannstatten ferrite, acicular ferrite, bainite or martensite in that order with increasing cooling speed and decreasing coiling temperature, respectively.[8)] These microstructures are fine grained and dislocation hardened.

Regarding the precipitation behavior of Nb under these circumstances, Fig. 3b indicates the influence of coiling temperature and isothermal holding time.[9)] It is evident that the higher the coiling temperature, the faster precipitation occurs. However, also Ostwald ripening is occurring efficiently at higher temperatures and longer times so that an increased share of the precipitates will be incoherent with the matrix. Such precipitates make only little contribution to yield strength. At a coiling temperature of around 600 °C optimum conditions prevail to have a large fraction of solute Nb precipitating and Ostwald ripening is slow to leave most precipitates coherent and thus effective for hardening. At lower coiling temperature towards 500 °C precipitation kinetics becomes slower so that an increasing share of Nb remains in solid solution. This share of Nb is available for secondary precipitation hardening during later heat treatment cycles.

3. Niobium effects during hot dip galvanizing process

Hot-dip galvanizing can be applied to hot rolled steel as well as cold rolled steel. In the first case hot rolled

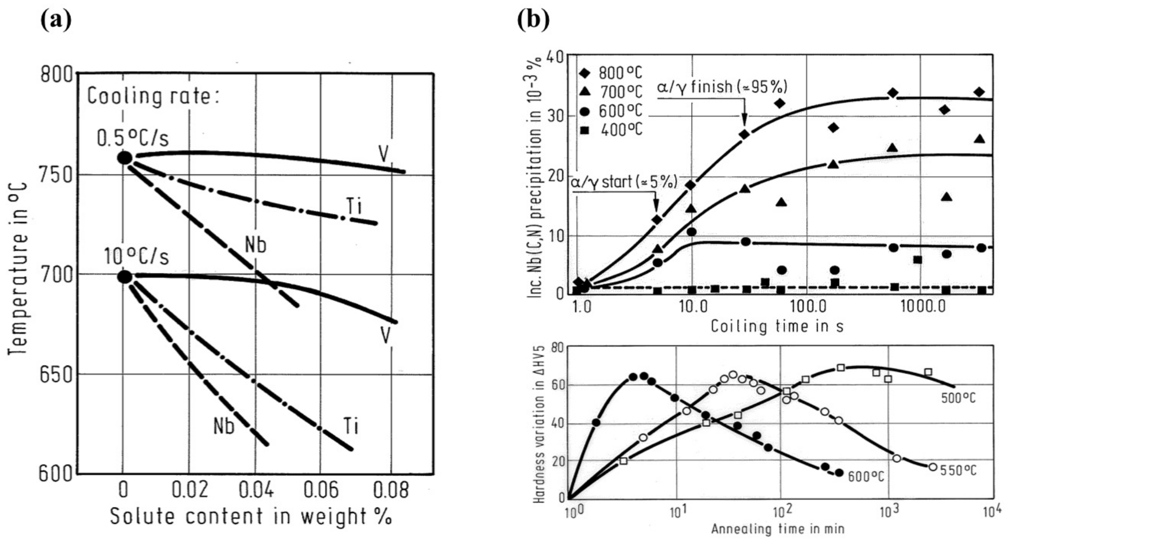

Fig. 3. (a) Dependency of A_{r3} temperatures on solute microalloying content in 0.1%C-1.5%Mn steel with standard austenite grain size of 100 µm; (b) Effect of isothermal holding on Nb precipitation in 0.04%C-0.5%Mn-0.04%Nb steel.

strip is heated to a temperature above the zinc pot temperature. In the second case recrystallization annealing is necessary to reset the heavily deformed cold rolled microstructure. The annealing temperature is below A_{r1} for ferritic steel grades and between A_{r1} and A_{r3} for multiphase steels. During this temperature cycle Nb can cause important effects that have impact on the microstructure and properties of the final material.

3.1 Effects of niobium during galvanizing of hot strip material

Under conventional hot dip galvanizing conditions for hot rolled strip the treatment temperature is too low to cause a change in the state of Nb. Typically the yield and tensile stress increase by 15-20% and 5-10%, respectively, after galvanizing of pearlite-reduced or pearlite-free steel due to ageing by interstitials.[10] This behavior is independent of the type of microalloying element used in the alloy.

If the hot strip material has been processed to contain solute Nb as described above it is possible to precipitate this Nb by adjusting a suitable time-temperature schedule before the galvanizing treatment. The aim is precipitating the solute Nb but keeping the precipitates small in size to obtain a maximum strength increase. Due to the shortness of the heat-treating cycle in continuous galvanizing line, the peak temperature needs to be rather high for achieving a substantial amount of precipitation. Experience has shown that precipitation leading to a strength increase starts at around 625 °C. Maximum strengthening occurs in the range of 675 to 725 °C and particle coarsening due to overaging is noticed at higher temperature leading to a strength decrease. The yield strength increase was often found to be in the range of 100 to 200 MPa for steel with low carbon (<0.08%) and elevated Nb (0.05-0.1%) content whereas the increase of the tensile strength is somewhat smaller.[11),12)]

Fig. 4 exemplarily demonstrates the processing-property relationship for Nb precipitation hardening in low-carbon high-niobium steel. This alloying concept is characterized by a particularly high non-recrystallization temperature and can hence enter the finishing train of the hot rolling mill between 1000 and 950 °C. The finish rolling temperature is between 870 and 850 °C. Accelerated cooling on the run-out table and coiling at temperatures below 550 °C result in a fully non-polygonal ferritic microstructure and a high share of solute Nb after down cooling. Some Nb however is being precipitated - in this case around 0.02% (Fig 4a) - during austenite conditioning. Post coiling annealing treatment can then bring the remaining solute Nb to precipitate as indicated in Fig. 4a. Indeed at temperatures around 700 °C the kinetics is fast enough to let all solute Nb precipitate within a time frame that is typical for a continuous hot dip galvanizing line. Size measurement by SANS revealed that even at longer annealing times the particles have an average diameter below 2 nanometers (Fig. 4b). At higher annealing temperatures, like 800 °C, particle coarsening occurs quite quickly. The average particle size and the amount of particles determine the yield strength increase as shown in Fig. 4c. The nomograph confirms that under optimum conditions a yield strength increase of 150 to 200 MPa is feasible.

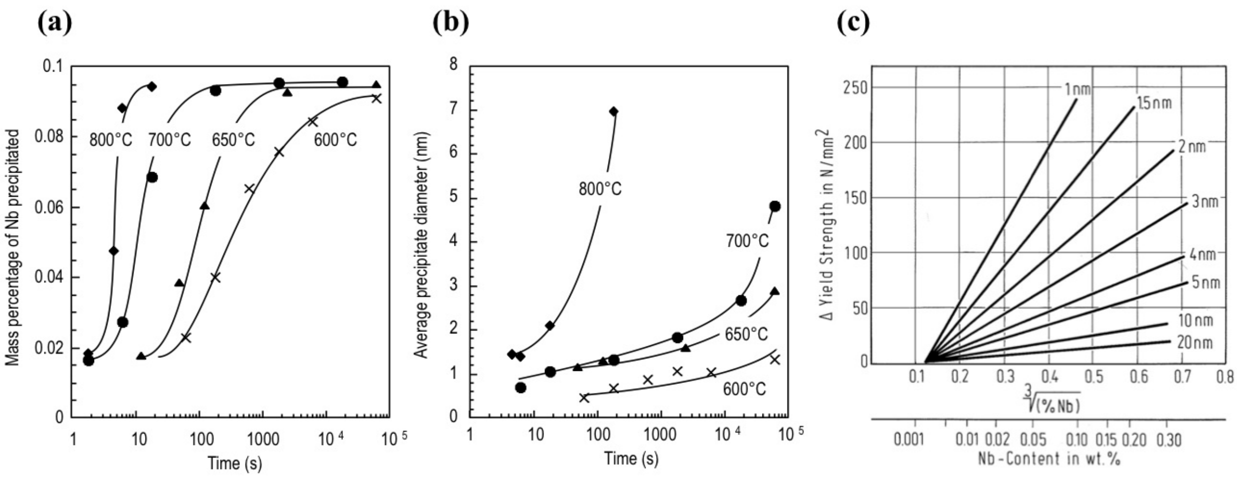

Fig. 4. Precipitation behavior of hot rolled strip with 0.03%C-1.7%Mn-0.1%Nb after low temperature coiling; (a) Fraction of precipitated solute Nb after annealing treatment at various temperatures and times; (b) Coarsening behavior of NbC precipitate depending on annealing temperature and duration; (c) Influence of NbC precipitate amount and average size on yield strength increase.

Production trials have shown that low-carbon high-niobium steel can provide yield strength of up to 650 MPa when coiling is done at low temperatures around 500 °C. Under this condition the microstructure non-polygonal and very fine-grained providing excellent hole expansion behavior. Due to the low coiling temperature, however, precipitation strengthening is suppressed. When such steel is then treated in a continuous hot dip galvanizing line, solute Nb can precipitate and add to the already present high strength level. By this way yield strength in the order of 800 MPa is achievable with a very lean alloying concept.

3.1 Effects of niobium during recrystallization annealing of cold rolled material

Nb atoms dissolved in ferrite significantly delay the recrystallization of steel after cold rolling. The presence of each 0.01% solute Nb raises the recrystallization temperature by 15-20 °C.[13] This effect was found to saturate at 0.05% dissolved Nb. The C-content is a measure for the amount of precipitates when Nb alloying is over-stoichiometric to C, i.e., in IF steel. Lower C-content results then in fewer NbC precipitates and hence lower recrystallization temperature.

The grain size in cold rolled microalloyed steels is mainly controlled by the amount of precipitates. The mass product Nb×C has a direct influence on the grain size of the annealed steel. The larger this product the smaller is the final grain size and hence the higher is the yield stress of the steel after annealing. Furthermore, a fine distribution of precipitates limits the grain size scattering and thus contributes to microstructural homogeneity. A large Nb×C mass product provides vey fine grain size even at high annealing temperature. High annealing temperatures on the other hand lead to fast Ostwald ripening and hence precipitation strengthening is reduced.

Another controlling parameter for recrystallization is the cold rolling reduction. A higher degree of reduction promotes recrystallization. Microalloyed HSLA steels require a cold reduction of at least 60% to yield a sufficient fraction of recrystallized ferrite. Nb microalloying results in smaller final grain size than Ti microalloying after continuous annealing of highly cold rolling reduced steel, which is beneficial for yield strength.

In IF steel a strong retardation of recrystallization is observed compared to unalloyed Al-killed steel.[14] The activation energy for recrystallization of Nb stabilized IF steel is marginally higher than that for Ti stabilized IF steel. In IF steel Nb only forms carbides whereas Ti forms nitrides, carbosulfides, phosphides and carbides. The Nb carbides are smaller and more homogeneously distributed than the Ti based precipitates. Therefore Nb stabilized IF steels exhibit typically a finer grain size and a small effect of precipitation hardening. Besides solid solution strengthening by P is more effective. Hence Nb stabilization is the optimum route for the production of high strength IF steel.

A more advanced design of high strength IF steel is based on an increased carbon level stabilized by an increased over-stoichiometric Nb addition.[15] A significantly refined grain size and an increased amount of precipitates characterize this alloy design thus providing a strength increase. The recrystallization temperature is also raised compared to a standard Nb based IF steel design, as expected. During annealing the new alloy design develops a higher volume fraction of grains having a <111>//ND orientation. This is related to a smaller grain size in the prior hot rolled strip providing more grain boundary area, which is considered to be a favorable nucleation site for <111>//ND grains. The volume fraction of <111>//ND grains in the annealed steel is strongly related to the mean r-value. Indeed an improved mean r-value is being observed at simultaneously fine grain size. This not only provides excellent deep drawing properties at high strength but also reduced "orange-peel" on highly deformed outer surface panels. Another interesting effect is the generation of precipitate depleted-zones during recrystallization annealing. This is related to higher diffusivity in the grain boundary leading to Ostwald ripening of the fine NbC precipitates. As the grain boundary migrates this precipitate coarsening mechanism occurs similarly in the area passed by the boundary. The precipitate-depleted zone has lower yield strength than the core of the grain containing finer precipitates. Yielding occurs at a lower stress in the precipitate-depleted zone but the precipitation hardened grain core controls tensile strength. Thus the yielding range is increased providing an improved n-value.

Another innovative approach for high strength IF steel alloy design is based on dual addition of over-stoichiometric Ti and Nb.[16] This alloy design leaves a large fraction of Nb in solid solution. As explained before, a non-polygonal ferritic structure is formed when such steel is coiled at low temperature after hot rolling. This hot band shows a quite strong fiber texture similar as in a cold rolled material. Thus the development of a recrystallized texture leading to a good r-value is enhanced. Solute Nb in such steel segregates to the grain boundary and delays recrystallization even at a temperature close to A_{r1} compared to Ti-only stabilized steel. This behavior has an important practical implication as grain coarsening and consequently softening in the heat affected zone of spot and laser welds is avoided. Another beneficial practical effect of grain refinement and Nb segregation to grain boundaries is the

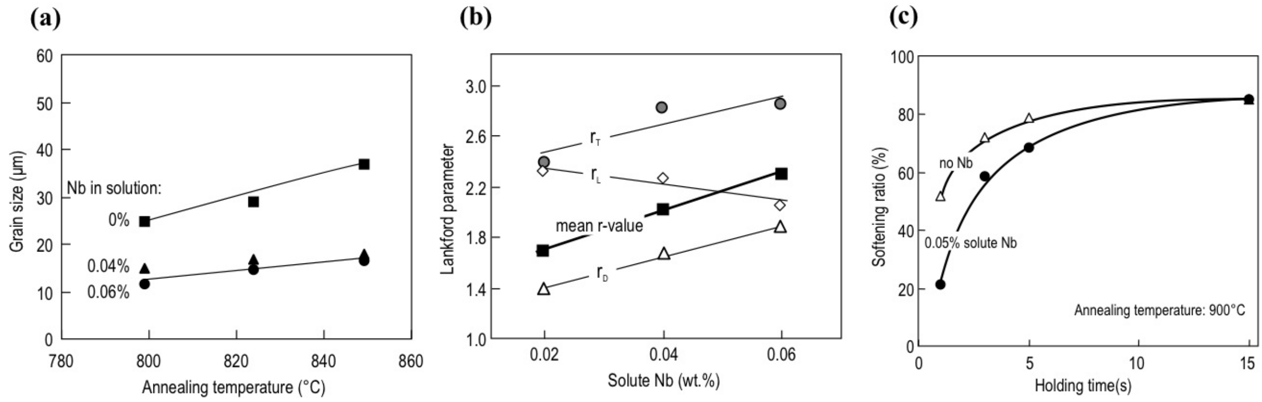

Fig. 5. Effects of adding Nb to a Ti-stabilizes IF high strength steel (0.003%C-0.002%N-0.07%Ti-Mn-P); (a) Evolution of final grain size in function of annealing temperature at various solute Nb levels; (b) Evolution of r-value in function of the solute Nb level; (c) Softening behavior for annealing close to the A_{r1} temperature.

strongly reduced temperature below which secondary work embrittlement occurs. In conventional (Ti stabilized) IF steel SWE can be only avoided by adding a small amount of boron to the alloy, which however is detrimental to the r-value.

3.1 Effects of niobium during intercritical annealing

The production of modern multiphase high strength steels relies on intercritical annealing after cold rolling. In this process the cold deformed material is heated into the two-phase region between A_{r1} and A_{r3}. In this way a defined amount of austenite is established, which is transformed into either martensite, bainite or retained austenite by fast cooling.

The microstructure of the prior hot strip has an important influence on the transformation behavior of the cold rolled material during intercritical annealing. It is standard procedure to coil the hot band in the range of 600-650 °C into a ferritic-pearlitic microstructure as this relatively soft structure is facilitates cold rolling. The grain size is quite coarse and pearlite can form bands in the strip center. Correspondingly the annealed microstructure will be quite coarse and inhomogeneous. Pearlite bands can transform into martensite lines, which are detrimental to bending and profiling operations.

Adding Nb to such steel leads to a finer grained hot band structure particularly when combined with a lower coiling temperature. The fine-grained structure has two important effects with regard to intercritical annealing. The phase transformation from ferrite to austenite and vice versa is accelerated due to the larger total grain boundary area being and effective nucleation site. Newly formed austenite islands are smaller and isolated so that carbon enrichment is higher and more homogeneous. This leads to more stable and harder martensite or retained austenite islands. In this way it becomes possible to produce low-carbon dual phase steel with elevated strength (Fig. 6a).[17] The strength in such steel is built up by the second phase, grain refinement and precipitation hardening. At lower annealing temperature also a share of non-recrystallized ferrite can be present in the microstructure. At higher annealing temperature traces of bainite may form as an additional phase raising particularly the yield strength. The presence of bainite in a DP microstructure however reduces the total elongation but improves the hole expansion behavior.

A refined microstructure with deglomerated hard phases shows a clearly improved bending and hole expansion behavior (Fig. 6b).[18] The bake-hardening effect also becomes more pronounced since free carbon residing in the grain boundaries has a shorter diffusion distance into the refined ferrite grain structure to pin mobile dislocations.[19]

In TRIP steel the increased ferrite formation kinetics and corresponding higher carbon content in the austenite in Nb-alloyed grain refined material result in a markedly increased yield and tensile strength. Furthermore, the properties of the Nb microalloyed variant are less sensitive to the bainitic holding time (Fig. 6c), which is a considerable advantage when producing TRIP steel on galvanizing lines equipped only with a short overaging section.[18]

Precipitation engineering allows fine-tuning of particular properties in multiphase steels. Strengthening is only possible by Nb that is solute after coiling and precipitates during the annealing cycle. This allows the production of high yield strength multiphase steel.[20] Precipitates already present in the hot band will not dissolve during high temperature annealing but experience some coarsening due to Ostwald ripening. Such particles have potential to act as deep traps for hydrogen and are a potential remedy to de-

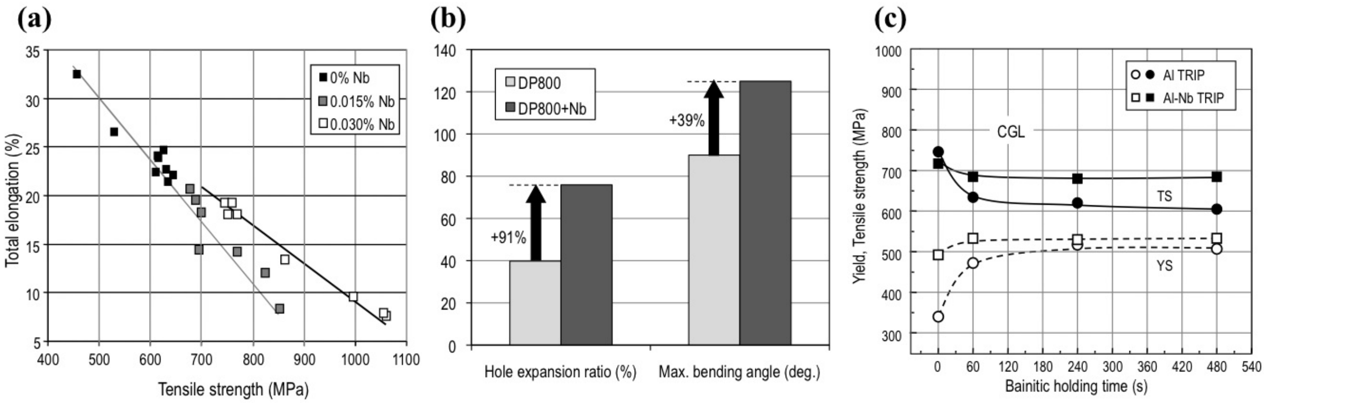

Fig. 6. (a) Effect of Nb addition on property balance in low-carbon DP800 steel (0.08%C-2.0%Mn-0.5%Cr); (b) Effect of Nb induced grain refinement on hole expansion and bending behavior in DP800 steel; (c) Property balance in TRIP steel (0.2%C-1.5%Mn-2.0%Al-0.045%Nb) in function of bainitic holding.

layed cracking observed in multiphase steel of the highest strength level.[21)]

4. Conclusions

Niobium microalloying offers a unique combination of beneficial effects to optimize the strength-property balance in automotive sheet steel. It takes a holistic approach of simultaneously considering alloy design, processing route and application demands to achieve the optimum solution in terms of microstructure and mechanical properties. Although Nb microalloying due to the low alloy content is already cost attractive as such, it is recommended performing a cost-benefit analysis considering processing and application advantages to fully appreciate the added value of Nb.

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