#### REVIEW OF MICROALLOYED STRUCTURAL PLATE METALLURGY -

ALLOYING, ROLLING, HEAT TREATMENT

Heinrich Baumgardt\*, Harald F. de Boer\*, Friedrich Heisterkamp\*\*

\*Thyssen AG. - Forschung Kaiser-Wilhelm-Strasse 100 41 Duisburg 11 Hamborn West Germany

\*\*Niobium Products Company Limited Wagnerstrasse 4 D-4000 Duesseldorf West Germany

### Abstract

The historical development of structural steels and their main requirements are presented. The reduction of the carbon content and the use of microalloying and alloying elements for grain refinement as well as for precipitation and solid solution hardening led to HSLA steel grades with good toughness and weldability. Modern technologies in steelmaking, hot rolling and heat treatment in combination with the chemical composition are used for an economical production of plates with special requirements. The rules and recommendations for fabrication are mentioned. Cumulative frequencies of mechanical properties and some examples of completed structures show the successful application of microalloyed steels.

#### Introduction

At the present time high strength low alloyed (HSLA) steels are readily available. These steels have good resistance to brittle fracture and a favorable behavior during manufacture. This review outlines the development of these steels by pointing to the importance of alloying, rolling and heat treatment. The transfer of fundamental physical metallurgical knowledge into the production of hot rolled microalloyed steels is discussed. This transfer takes place by means of modern steel making and rolling procedures and it is shown which level of properties **can** be achieved in large scale production. The behavior during manufacturing is illustrated by some characteristic examples.

#### Historical Development

The main requirements for structural steels are high strength, brittle fracture resistance and favorable processing behavior. This combination of properties has only recently been achieved; but the development of structural steel started in 1845, when puddle steel replaced cast iron for the first time (Figure 1). The application of welding in construction together with the basic knowledge that was gained by the investigation of metal failures have determined the development of structural steels to a large extent leading to a restriction of carbon content, the fixing of soluble nitrogen and the refinement of microstructure.

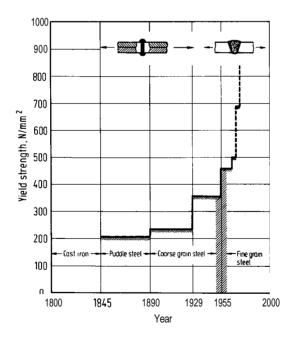


Figure 1. Historical development of structural steel plate.

Well-known failures have occured to bridges and in ships; the bridge at the Station Zoo in Berlin collapsed in 1936 and even in 1962 heavy damage was reported at a bridge in Melbourne, Australia. In the years 1942-1949 cracked Liberty - ships revealed inadequate weldability and poor toughness of the selected steel (1, 2). These experiences and findings led in Germany to the development of the steel St 52-3 which has a minimum yield strength of 355  $N/mn^2$ . The weldability of this steel was mainly obtained by the restriction of carbon to about 0.20 percent. The toughness was improved by the addition of about 0.030 percent Al which gave grain refinement by AlN-particles. Similar developments led e.g. in the United Kingdom to microalloyed steels (3 - 5) which finally resulted in steel grade 50 D of BS 4360 (6). This corresponds in France to NFA 35-501, E 36, and so on. The steel St 52-3 was the starting point of the development of microalloyed steels. Their yield points and impact transition temperatures are schematically (7) shown in Figure 2. The following section deals with the influence of alloying elements and impurities on the properties of structural steels.

#### Alloying and Metallurgical Treatment

Carbon was, at the beginning of the development of structural steels, the most important alloying element required to achieve the tensile properties. However, increasing the carbon content means a higher proportion of pearlite in the microstructure and this affects considerably the formability and the toughness of a steel (Figure 3) (8). Therefore, the carbon content must be reduced as far as possible to reach a high degree of toughness. Obtaining strength without affecting the toughness is possible by alloying with elements such as manganese, nickel and silicon. They substitute iron in the solid solution which is the basis of the steel. The favorable influence on strength and toughness of an increased manganese content at constant carbon concentration is shown in Figures 4 and 5 (9). Within the range of 05 to 1.5 percent manganese the increment of yield strength by the addition of 1 percent manganese amounts to about 50  $N/mm^2$ . Additionally, these Figures show the influence of grain size on the toughness characteristics. The fine grain steel reveals a much better impact transition temperature  $T_{27}$ ; compared

to the coarse grain steel, the difference is about 50. Besides, this fine grain size increases the yield strength by about 20  $N/{\rm mm}^2$ , whereas the tensile strength is not altered significantly.

An improvement of the toughness behavior at constant strength is also possible by lowering the carbon content and the subsequent loss of strength can be balanced largely by increasing the manganese content. The influence of the manganese to carbon ratio on the mechanical properties is evident from Figures 6 and 7 (10). It must be emphasized that above 2 percent manganese, even with low carbon contents, both the yield strength and the impact transition temperature deteriorate. This is caused by the precipitation of cementite on the grain boundaries.

For large scale production, a ratio of 1.75 percent manganese to 0.10 percent carbon may be applied. A content of 0.03 percent niobium will give intensive grain refinement. Such a steel has a minimum yield strength of  $355 \, \text{N/mm}^2$ . However, compared to conventional steels of this strength level, its toughness and weldability are remarkably better.

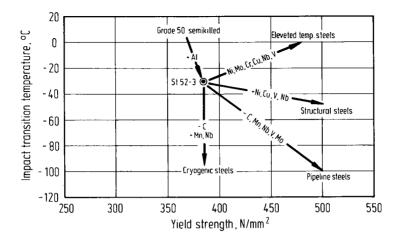


Figure 2. Development of structural steels (schematically).

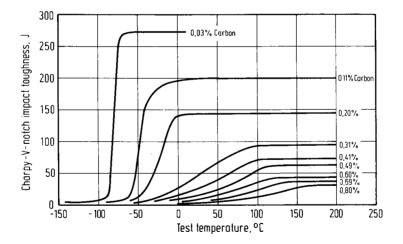


Figure 3. Effect of carbon and hence the pearlite content on impact-transition temperature curves of ferritepearlite steels.

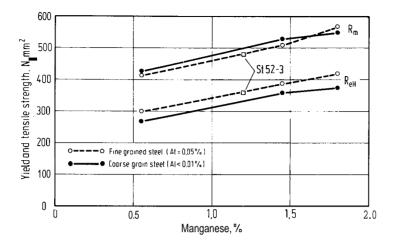


Figure 4. Effect of manganese content on yield and tensile strength, normalized 0,17% C; 0,35% Si; 0,006% N.

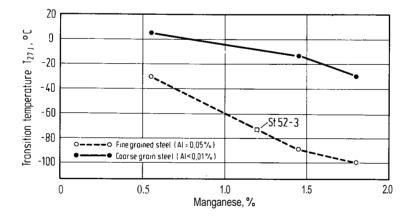


Figure 5. Effect of manganese content on impact transition temperature, normalized 0,17% C; 0,35% Si; 0,006% N.

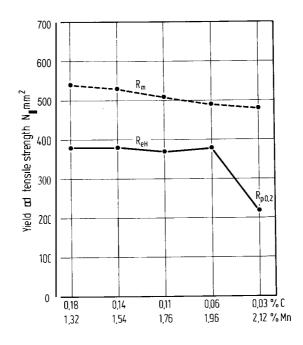


Figure 6. Effect of the Mn/C-ratio on yield and tensile strength.

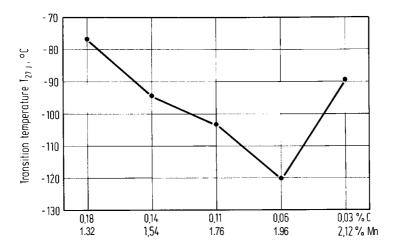


Figure 7. Effect of the Mn/C-ratio on the impact transition temperature.

From time-temperature-transformation diagrams it is known that nickel retards the transformation of austenite even more than manganese. Therefore, the  $\gamma$  /a transformation after normalizing takes place at a lower temperature. This causes a certain grain refinement of the microstructure and consequently the yield strength and the toughness are improved. This consideration applies for nickel concentrations up to about  $0.5\,$  percent. The strengthening by solid solution of nickel is negligible. Due to influence of nickel on the transformation behavior, the microstructure of steels containing about  $0.6\,$  percent nickel contains a substantial portion of bainite produced during air cooling from the normalizing temperature. This applies mainly for relatively light plates of about 10 mm thickness which cool fairly rapidly. They may then have to be annealed to obtain favorable properties.

Good characteristics are achieved by the combined alloying of copper and nickel. The copper content should be balanced by an equal quantity of nickel to avoid hot shortness. The influence of copper on the yield strength is shown in Figure 8 (11). Copper gives precipitation hardening and this is most effective in the range of 0.4 to 1 percent copper. Sometimes, after normalizing, the copper will not be precipitated totally. In these cases the full increment of yield strength will only be achieved after annealing at about 450 C. An advantage of strengthening by copper instead of carbon is the fact that copper contributes only slightly to the hardness of the heat affected zone during welding. Finally, it must be mentioned that copper increases the yield strength at elevated temperature as well.

The alloying elements chromium and molybdenum play an important role especially with regard to the transformation behavior and the formation of alloy carbides. This means that chromium and molybdenum additions up to about 05 percent increase the tensile properties of normalized steels. They improve substantially the yield strength at elevated temperatures. The combined application of these alloying elements makes it possible to achieve, in the normalized condition, a yield strength up to about 500 N/mm<sup>2</sup> at ambient temperature and up to about 255 N/mm<sup>2</sup> at 400 C. This cannot be done without microalloying elements (Figure 9) (11). The range of yield strength indicated for normalized steels in this Figure, covers the field within which this type of steel attains optimum properties concerning strength, toughness and behavior during manufacture. This limitation applies accordingly to steel types which are normalized and tempered or quenched and tempered.

The so-called ferritic-pearlitic steels which contain such elements as chromium, molybdenum or nickel, have a significant amount of bainite within their microstructures. They are, therefore, usually tempered between 600 and 700 C after normalizing. Since copper, like chromium and molybdenum, improves the yield strength at elevated temperatures, it can be used to restrict the contents of chromium and molybdenum in normalized plus tempered steels. This substitution favors the toughness behavior and the weldability of these steels.

The microalloying elements niobium, vanadium and titanium which precipitate in fine dispersions of carbides, nitrides or carbonitrides increase the strength. This is unfortunately accompanied by a corresponding toughness reduction. The amount of strengthening depends on the quantity, size and distribution of precipitated particles. Microelements are most effective in thermomechanically treated steels. This is discussed in other papers of this book in detail (12, 13).

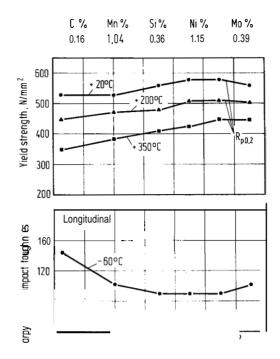


Figure 8. Effect of copper on the yield strength and impact properties.

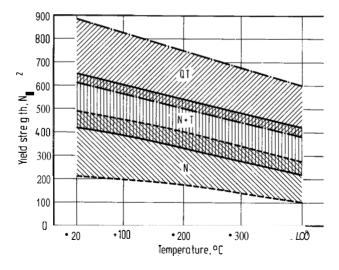


Figure 9. Range of strength covered by normalized (N), norm + temp. (N+T) and quenched + temp. (QT) steels.

During the transformation from  $\gamma$  - to  $\alpha$  -iron the dispersion of precipitated carbides and nitrides leads, through nucleation, to the formation of a fine grained microstructure and retards grain growth during following heat treatments. The correlation between the concentrations of the microalloying elements and the grain size in the normalized condition is shown in Figure 10 (14). Niobium is most effective, whereas vanadium does not give grain refinement in normalized steels. Titanium gives a fine grain, but nowadays contents of more than 0.03 percent are used only with steels for cold formed parts such as truck frames. The main reason why titanium is not used in higher concentrations in structural steels, is the difficulty to maintain the narrow range of normalizing conditions to get good toughness properties. If the normalizing temperature is exceeded, titanium carbides are dissolved and thus grain growth is not retarded. During the subsequent cooling the precipitation of titanium carbides causes an intense hardening. The formation of coarse grains and precipitation hardening result in poor toughness properties.

In contrast to high titanium concentrations, lower contents of about 0.03 percent are favorable with regard to behavior during manufacture. At such low titanium concentrations very few titanium carbides exist but mainly very small titanium nitrides are formed. They are able to retard effectively grain growth at high temperatures. Thereby the formation of coarse grain in the heat affected zone during high heat input welding is largely surpressed, a situation which gives good toughness properties (15). The influence of niobium and vanadium on the mechanical properties of C-Mn-steels, rolled and normalized 12 mm thick plates, is indicated in Figure 11 (16). Through the addition of 0.15 percent vanadium the yield and tensile strength increase is about  $100 \text{ N/mm}^2$ , while the impact energy at -20 C is deteriorated to 50 percent of the value of the plain C-Mn-steel. It can be seen that precipitation hardening by vanadium is very effective in a light plate thickness of 12 mm even in the normalized condition. Alloying with 0.06 percent niobium increases the yield and tensile strength by about 50  $N/mm^2$ , but the impact energy is only slightly affected. This is because niobium acts in normalized steels mainly through grain refinement and much less through precipitation hardening. The combination of 0.15 percent vanadium and 0.06 percent niobium results in tensile properties which correspond to the values of the vanadium alloyed steel, but due to grain refinement through niobium the impact energy is far higher than with the steel alloyed only with vanadium. Besides this example, there are further data available on the influence of microalloying elements on the mechanical properties of high strength low alloyed steels (17-21)

#### Sulfide, Oxide and Hydrogen Control

An important process for improving the toughness of a steel is the removal of nonmetallic inclusions. To achieve low sulfur contents, to control the shape of sulfides and to improve deoxidation, there are several different metallurgical procedures.

The desulfurization of large quantities of hot metal can take place in torpedo-ladles or other ladles through injection of mixtures of calcium carbide and gas producing agents (22). This results usually in sulfur contents between 0.010 and 0.020 percent, but it is possible to achieve even lower sulfur contents. Desulfurization can also be done effectively by stirring calcium carbide or limestone into the hot metal. The sulfur content can then be reduced easily below 0.005 percent. However, the capacity of stirring installations is lower than that of injection plants.

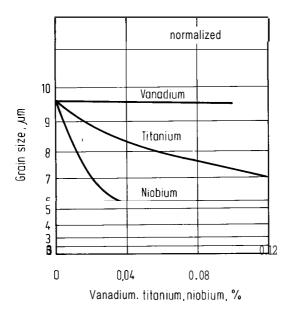


Figure 10. Effect of vanadium, titanium and niobium on the grain size.

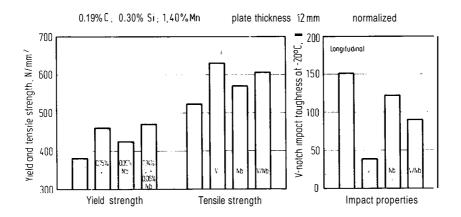


Figure 11. Effect of vanadium and niobium on the mechanical properties.

The injection treatment of steel has been developed at Thyssen-Niederrhein AG (23). Starting from usual sulfur contents, concentration as low as 0.002 percent can be attained. After teeming, calcium or magnesium compounds are injected into the steel within the ladle. Besides desulfurization and deoxidation, this process supplies another positive effect; the element calcium increases the hardness of any remaining sulfides, so that, during hot rolling, no elongated sulfide bands occur. In this way the anisotropy of mechanical properties of the rolled products is reduced.

Vacuum degassing removes the hydrogen. The treatment according to the RH-process (24) makes the temperature and the chemical composition within the steel ladle homogenous and improves the removal of nonmetallic inclusions.

The influence of various sulfur contents on the toughness of about 20 mm thick plates of the shipbuilding steel EH36 is shown in Figure 12 (25). The heat for the plate with the very low sulfur content was calcium treated by means of the TN-process. The difference between transverse and longitudinal impact energy values is only slight. The ratio of transverse to longitudinal values amounts to 50 percent only even for sulfur contents of 0.018 percent. Desulfurization to concentrations about 0.010 percent sulfur without any sulfide shape control leads undoubtedly to an improvement in toughness, but it is not at all as effective as the TN-treatment.

The behavior of plates during loading in the through-thickness direction can be evaluated by the reduction of area of tensile specimens, taken perpendicularly to the plate surface. The reduction of area in the through-thickness direction that is required to void lamellar tearing, depends on the occurring stresses (26). The influence of the sulfur content of plates on their reduction of area in the through thickness direction is shown in Figure 13. As it is with the toughness, the best values are from those steels that are TN-processed.

### Plate Rolling and Heat Treatment

Besides alloying, rolling and heat treatment play the most important roles regarding optimization of structural plate properties.

In the early years of plate production, the rolling process has been exclusively used to break down ingots or slabs to the desired form and dimension of the finished plate. However, it soon became rather obvious that the deformation process itself had a certain effect on microstructure and therefore on plate properties. Today, basically three rolling procedures are applied in practice, having in common that they take increased advantage of the influence of time, temperature and deformation on the recrystallization process transformation and precipitation behavior of steel. The basic objective is to achieve a high degree of grain refinement combined with a controlled amount of precipitation strengthening (27). In all three procedures, niobium plays an important role mainly as a grain refiner.

The behavior of the austenite grains during three rolling procedures is schematically shown in Figure 14, with the time-temperature correlation shown in Figure 15. The three different rolling processes can be described as follows:

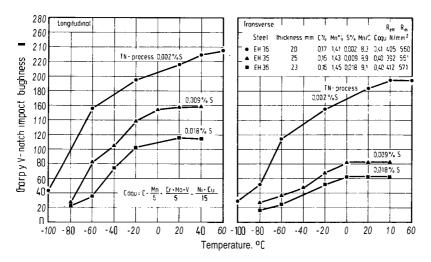


Figure 12. Effect of sulfur content and calcium treatment by TN-process on the Charpy-impact properties of steel EH 36.

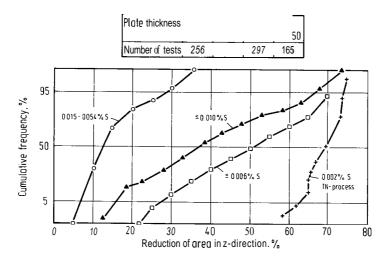


Figure 13. Influence of sulfur content and sulfide shape control on the reduction of area in the z-direction of StE 36 plates.

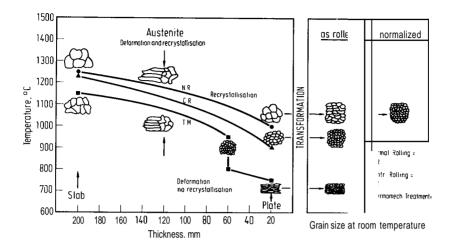


Figure 14. Change of size and shape of grains during plate rolling.

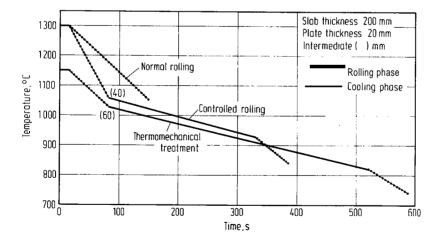


Figure 15. Time-Temperature-Development during various rolling procedures for 20 mm plate.

## Normal Rolling (NR)

NR is characterized by high rolling temperatures with corresponding low resistance to straining of the material. This results in short rolling times and therefore high mill productivity. The starting austenite grain size is coarse, deformation is followed by immediate recrystallization and grain growth. The final microstructure is a coarse ferrite/pearlite Widmannstatten structure which is improved by a normalizing treatment to refine the grain structure.

#### Controlled Rolling (CR)

In our consideration CR or rolling with controlled temperature is thought as a replacement of the normalizing process giving equivalent mechanical properties and a better plate surface. The procedure is characterized by a certain amount of deformation just above the  $\[Ar_3]$  austenite/ferrite transformation temperature.

#### Thermomechanical Treatment (TM)

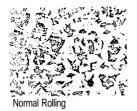
TM is generally characterized by a high amount of deformation (3 to 5 times the final plate thickness) below the recrystallization temperature of austenite. As a result of such a low finishing temperature the fine austenite grains are heavily strained and therefore transform into an exceptionally fine ferrite/pearlite microstructure. In this context niobium plays an important role, since it retards the recrystallization effectively and at small additions.

Due to the low rolling temperatures, the time necessary to produce plate  $\mathbf{is}$  even longer than for controlled rolling. For the steel grades considered here, thermomechanically treated plate is not yet widely applied. However, the process is widely used in combination with normalizing to improve properties of normalized steel grades as will be demonstrated later.

The resulting microstructure, when applying the described rolling procedures and after normalizing, are shown in Figure 16. The change from Widmannstatten structure to the very fine grained microstructure after thermomechanical treatment is obvious. The normalized microstructure and the ferrite grains are more uniform.

It has been known for a long time, that repeated normalizing further improves structural steel properties, in particular toughness. In this context the importance of microstructure such as grain size, dislocation density and state of precipitation prior to heat treatment becomes obvious. With the introduction of controlled rolling or thermomechanical treatment a tool has been provided to influence this austenite structure. Even though it is correct that it is principally applicable also for aluminum killed, not microalloyed steels, its advantage becomes more pronounced in the presence of niobium with its strong influence on the as rolled microstructure and its high amount of precipitation in the austenite.

To what extent a proper austenite conditioning prior to normalizing can influence microstructure and related properties of the finished product is shown in Figure 17 (28). A medium C-Mn-Nb-steel of the type StE 355 has been rolled to various rolling schedules and then normalized. The results show that with increasing rolling severity (lowering of finishing temperature) the properties are improved.



وحاجر فالمرجوع المجريد 21.11.1 

Controlled Rolling

-----NR and normalizing ne se anno 1930 an A Anno 1930 ann an Anno 1930 an Anno Anno 1930 an Anno 19 and a second \* Panetor anten since and the low مان مراجع معادم من المراجع الم المراجع AND AND AND

Charles Mary Street CR and normalizing

مربيه فتقامه معالم مسترفية والم Thermomechanicol Treatment

ومالقعته والبناء والاسترماع

IM and normalizing

100 Jum

The microstructure of 30 mm plate after various Figure 16. rolling procedures and in combination with normalizing 0.15% C; 0.25% Si, 1.35 Mn; 0.040% Nb.

Even though the normalizing eliminates precipitation hardening, the yield strength increases from 360 to more than  $400 \text{ N/m}^2$  due to extra grain refinement, partially inherited from the as rolled microstructure and partially caused by control of the austenite grain size due to niobium carbide precipitation during the normalizing process.

By the same token, both the 50 percent FAT-Temperature and the N11-Ductility-Transition-Temperature (NDT) are improved. As will be shown later, this production route is a suitable way for fabrication of LPG-steels.

Not only in the case of steels for low temperature service, but also for improvement of hot strength, niobium is a suitable alloying element. This is demonstrated by a comparison of early British data (29) referring to silicon killed, aluminum killed and niobium treated steels, upper part of Figure 18. However, a remarkable further improvement of elevated temperature strength was reported recently (30) in the case of applying controlled rolled steels rather than normalized ones, other things being equal. Even at 400 C, normally the upper limit for applying microalloyed steels, the strength of thermomechanically treated medium C-Mn-Nb steel is still higher than that of a low C-Mn-Nb steel in the normalized condition. Naturally, the latter steel in the same condition (TM-treated) has, at about 500 C, still the same strength level as the former steel at 400 C. The same considerations apply to the creep strength of both steels in both conditions.

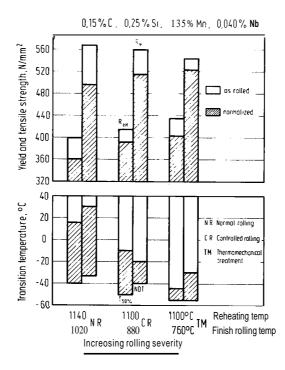


Figure 17. Correlation between various rolling schedules, nprmalizing and mechanical properties of 30 mm plates for structural application.

Since most specifications do not yet allow application of such steels in the thermomechanical treated condition, the obvious advantage of the combination of niobium alloying plus rolling can be used only in non-certified structures. In this context, niobium alloyed steels have been used with great success for instance for BOF vessels, where the maximum allowable shell temperature was increased to 350 C without running the risk of shell deformation. The advantage was a longer operating period of the vessel due to allowable lower minimum refractory wall thickness.

As far as the mechanism for the improved strength at high temperature is concerned, it is thought that the incomplete precipitation of niobium carbide in the as rolled condition leads to further precipitation on dislocations during operation at high temperature and related creep strengthening.

To support the tendency towards applying steels in the as rolled condition, data have been established to demonstrate the correlation between

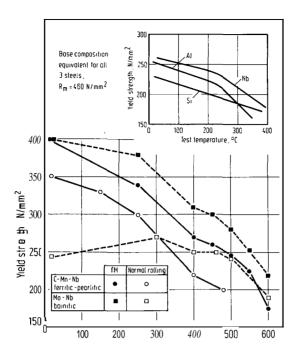


Figure 18. Influence of niobium content on elevated temperature yield strength in the TM and normalized condition.

alloying concepts and necessary rolling schedules (31). As Figure 19 shows, the maximum strength by niobium is reached at around 0.03/0.04 percent Nb for the given rolling conditions, a fact that is well known. Lowering of finishing temperature gives only a marginal strength increase independent of niobium content.

Concerning toughness improvement the situation is somewhat different. To achieve equivalent transition temperature e.g. FATT = -60 C, there exists a choice between a very low niobium content (0.008%) and low finish rolling temperature (750 C) or rather high niobium values (0.12% Nb) and no or very limited controlled rolling (920 C) and other possibilities between these extremes.

A further method of improving structural steel properties is the introduction of accelerated cooling after rolling (32). The correlation between steel plate properties, rolling and cooling conditions and alloy design are shown in Figure 20. Also, austenite conditioning, enhanced by niobium additions prior to cooling remarkably increases strength without impairing toughness at all. Recent developments in this field have led to the installation of on line accelerated cooling devices in Japan (33).

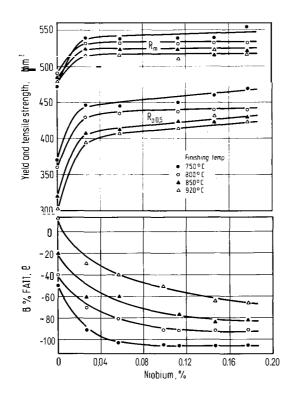
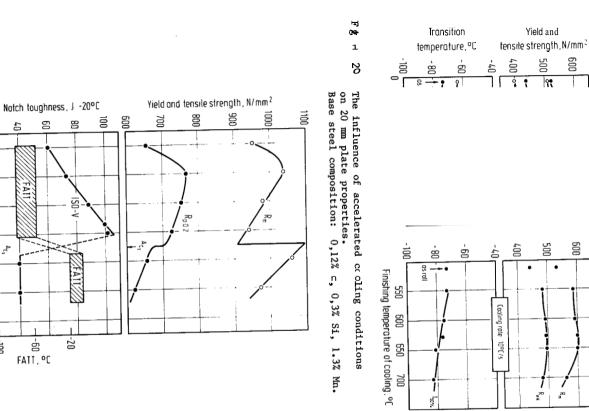


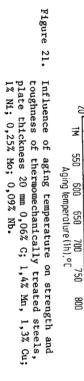
Figure 19. Correlation between niobium content and rolling conditions on 20 mm plate properties. Base composition: 0,08% C, 0,3% Si, 1,55% Mn.

A further measure to improve the strength of structural, microalloyed steels is tempering or aging after rolling or normalizing. This is in particular known in Mo-Nb or V-steels (34, 35), where the influence of molybdenum on austenite/ferrite transformation suppresses coarse precipitation during transformation. A subsequent tempering at around 600 C leads to a remarkable strengthening effect due to precipitation hardening and annealing of low transformation temperature products. The effect is more pronounced in the thermomechanically treated plus tempered than in the normalized plus tempered condition. A consequent pursuing of this behavior and taking advantage as well of the influence of copper precipitation has led to the development of Nicuage steels (36). Their response to aging treatment is shown in Figure 21. It is interesting to note that aging of the thermomechanically treated material between 550 C and 650 C, one hour, improves yield strength with no influence on the transition temperature. However, the Charpy-V-Notch energy is even improved in this range by annealing of the bainite-martensite constituent. Higher aging temperatures lead to a "dualphase" structure with the occurrence of untempered martensite areas causing deterioration of toughness and yield strength.



٠

C - Mn - 0,03 Nb



60

40

FAIT

e FATT,⁰C

F.

20

Ħ

550

750

800

-100

106

## Applications

Steel structures are exposed to different loads and service conditions. This requires a variety of steel grades to find, for a particular application, the optimum economic and technological justification.

#### Structural Steels

For structural purposes plain C-Mn-steels with 235 to 355 N/mm<sup>2</sup> minimum yield strength are usually applied. These steel grades are standardized in many countries. They have proven their usefulness for more than 30 years (Table 1). Plates, wide flats, flanged beams and other profiles of these steels are produced. Fine grained, normalized steels are applied for structures such as pressure vessels, fixed or mobile storage tanks, pen stocks, bridges, dolphins, masts and derricks as well. as complete offshore structures.

The fine grained steels reveal some advantages compared to plain C-Mnsteels. The restriction of the carbon content of these steels results in good toughness and weldability. The microalloying elements make it possible to achieve a yield strength around 500 N/mm<sup>2</sup>, without exceeding a carbon level of about 0.20 percent. Plates of these steels allow a relatively light structural design that reduces the internal stresses of welded joints and increases the resistance against brittle fracture. The simultaneously obtained weight savings are most advantageous for mobile structures. The normalized fine grained steels cover the range of minimum yield strength from 255 to 500 N/mm<sup>2</sup> and they can be used for service temperatures from about -20 C to 400 C. The steel grades StE 355 and StE 460 according to German standard or the corresponding steel grades in other countries, respectively, are the most important normalized fine grain steels (Table 1) (37).

The steel grade StE 355 can be produced without microalloying element, but small additions of niobium improve the microstructure and thus the specified tensile and toughness properties are more easily achieved. The niobium alloyed steel is particularly suitable for the type of controlled rolling that is equivalent to the normalizing treatment. Intensive controlled rolling on the other hand is a thermomechanical treatment such as is applied for rolling steels for large diameter pipes. Controlled rolling that substitutes normalizing can be done with plates of the mentioned steel in thickness up to about 60 mm. Figure 22 shows the mechanical properties of up to 50 mm thick plates. A node manufactured of this steel grade with high through thickness properties is shown in Figure 23.

To achieve a minimum yield strength of 460 N/mm<sup>2</sup> the steel is nickel and vanadium alloyed and the carbon content must not exceed 0.20 percent with regard to the weldability. The aluminum content is limited to 0.020 percent and nitrogen is increased to about 0.015 percent to get full advantage of the precipitation hardening through vanadium. There is another variety of a steel grade with 460 N/mm<sup>2</sup> minimum yield strength; this steel has a reduced carbon content of max. 0.15 percent. The carbon reduction is balanced by around 0.60 percent copper which gives precipitation hardening. The vanadium content is kept below 0.10 percent by means of an addition of about 0.03 percent niobium. This copper-nickel-microalloyed steel reveals essentially better toughness and weldability than the only nickel-vanadium alloyed StE 460. Figure 24 shows mechanical properties of plates made of this improved steel. A 800 t floating derrick of this steel grade is shown in Figure 25. A special pressure vessel of a HSLA steel with 500 N/mm<sup>2</sup> yield strength appears in Figure 26.

|   | Steel                           | Chemical composition %<br>(Ladle analysis) |               |                       |       |               |              | Mechanical properties <sup>1)</sup> |                  |    |                   |     |                               | Rules                             |                  |
|---|---------------------------------|--|---------------|-----------------------|-------|---------------|--------------|-------------------------------------|------------------|----|-------------------|-----|-------------------------------|-----------------------------------|------------------|
|   |                                 | с  | Si            | Mn                    | Ni    | Nb            |              | R.                                  | m R              | A  | n⊂<br>At20<br>ule | ŢZ  | Germany                       | France                            | Grect Britain    |
| • |                                 |  |               |                       |       |               |              |                                     |                  |    |                   |     |                               |                                   |                  |
|   | St 37-3                         | <b>∍ 0,17</b>                              |               |                       | ÷.,   |               |              | 225                                 | 340 - 470        | 24 | 27                | -20 | DIN 17100                     | NFA 35-501                        | BS 4360          |
|   | St 52-3                         | <b>≈0,20</b>                               | = Q55         | <del>=</del> 1,60     |       |               |              | 345                                 | 490 - 630        | 20 | 27                | -20 | DIN 17100                     | NFA 35 - 501                      | BS 4360,968      |
|   |                                 | High Strength Low Alloy Steels             |               |                       |       |               |              |                                     |                  |    |                   |     |                               |                                   |                  |
|   | St E 355                        | =0,20                                      | 0,10/<br>0,50 | 0,90/<br>1,60         | -     | ≠0,05         |              | 355                                 | 490 - 630        | 22 | 27                | -20 | SEW 089<br>(draft DIN 17102)  | NFA 36 - 201 - 205 -<br>208 - 506 | BS4360,1501,968, |
|   | St E 460                        | ¤ Q15                                      | 0,10/<br>0,50 | 110/<br>150           | 0,60  | ≠Q03          | 0,60Cu 0,12V | 450                                 | 560 - 730        | 17 | 27                | -20 | SEW 089<br>(droft DIN 17 102) | NFA 36 - 201                      | BS 4360          |
|   |                                 | Shipbuilding Steels                        |               |                       |       |               |              |                                     |                  |    |                   |     |                               |                                   |                  |
|   | Grade A                         | +Q.23                                      | ≠Q35          | •2,5×C                | -     | -             |              | 235                                 | 400 - 490        | 22 | -                 | -   |                               | draft IACS                        |                  |
|   | EH 36                           | ⊐ Q,18                                     | 010/<br>050   | 090/<br>160           | -     | 0.02/<br>0,05 |              | 355                                 | 490 - 620        | 21 | -40°C             | -   |                               |                                   |                  |
|   |                                 | Cryogenic Steels                           |               |                       |       |               |              |                                     |                  |    |                   |     |                               |                                   |                  |
|   | 11 Mn 5                         | <del>-</del> 014                           | 0,15/<br>0,50 | 070/<br>1,60          | ≠0,30 | ± 0,05        |              | 255                                 | 400 - 490        | 24 | -                 | -55 |                               | NFA 36 -208                       |                  |
|   | 13 Mn 6                         | = Q15                                      | 015/<br>0,50  | 0 <i>7</i> 0/<br>1,60 | = Q30 | ¤ 0,05        |              | 325                                 | 490 - 570        | 21 | -                 | -55 |                               | NFA 36-208                        |                  |
| ÷ | Steels For Elevated Temperature |  |               |                       |       |               |              |                                     |                  |    |                   |     |                               |                                   |                  |
| 1 | 19 Mn 6                         | 015/<br>023                                | 0,40<br>0,60  | 10-15                 | -     | -             | -            | 345                                 | 510 - <b>650</b> | 20 | <b>±0°C</b><br>31 | -   | draft DIN17155                | NFA 36 - 205                      | <b>BS</b> 1501   |
|   | 15NiCuMoNb 5                    |  |               |                       |       | l .           | Q70Cu Q30Mo  |                                     | 610 - 760        | 16 | 31                | -   | VDTÜV                         | <del></del>                       | <b>BS</b> 1501   |
|   | 9CrMoNiNb 9 10                  | ± 0,10                                     | 0,15/<br>0,50 | 0,4- O <b>B</b>       | 080   | -10-%C        | 1,0Mo 2,2Cr  | 295                                 | 470 - 610        | 18 | 31                | •   | SEW 640                       |                                   |                  |

Table I. Data of typical structural steels.

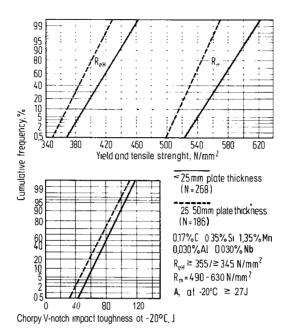


Figure 22. Cumulative fequencies of mechanical properties of structural microalloyed plates.

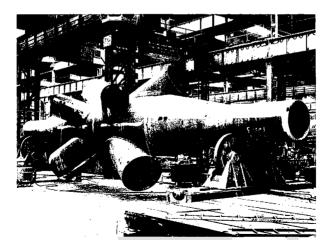


Figure 23. Node for offshore platform of HSLA steel with 355 N/mm<sup>2</sup> yield strength and high through thickness properties.

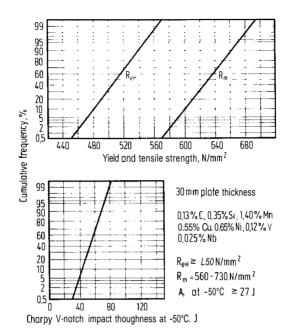


Figure 24. Cumulative frequencies of mechanical properties of microalloyed plates for constructions and pressure vessels.

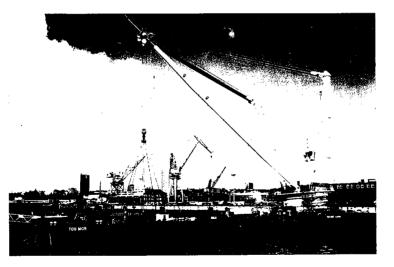


Figure 25. 800 t floating derrick. Stulckenmast is manufactured of HSLA steel FG 47CT Manufacturer Blohm + Voss.

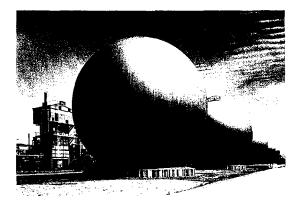


Figure 26. Spherical pressure vessel of HSLA steel with 500 N/mm<sup>2</sup> yield strength.

#### Shipbuilding Steels

The normal strength shipbuilding steels which are not microalloyed have a minimum yield strength of  $235 \text{ N/mm}^2$  (Table 1).

The high strength shipbuilding steels may contain up to 0.05 percent niobium and/or up to 0.10 percent vanadium. Normally these steels are niobium alloyed. For weldability the carbon content is limited to max. 0.18 percent. Generally these steels are normalized. The approval to substitute normalizing by controlled rolling is given by some Classification Societies under certain conditions.

## Cryogenic Steels

Low temperature ferrite/pearlite structure steels can be applied at service temperatures down to -55 C. Their yield strength is in the range of 235 to 355 N/mm<sup>2</sup>. They are mainly used for tanks to transport or to store liquefied petroleum gas (LPG). The steels may contain up to 0.70 percent nickel. Lower service temperatures such as for liquefied natural gas (LNG) require steels with more nickel.

Steel grades with a minimum yield strength of  $265 \text{ N/mm}^2$  respectively, for use down to -55 C service temperatures may contain on average 0.10 percent C, 0.25 percent Si, 1.5 percent Mn and 0.040 percent Al. Depending on the required strength level and the plate thickness additions up to 0.30 percent nickel and up to 0.03 percent niobium are applied (Table 1). The extremely fine grained microstructure, that gives the desired toughness, is achieved by the combination of controlled rolling and subsequent normalizing. The mechanical properties of plates that have been produced in that way are given in Figure 27 (38). The main feature of these steels is the low NDT-temperature of -60 C that was determined according to ASIM E 208. Similar steel grades have been developed elsewhere (39). Figure 28 shows a twin vessel for an IFG tanker of a fine grained steel grade.

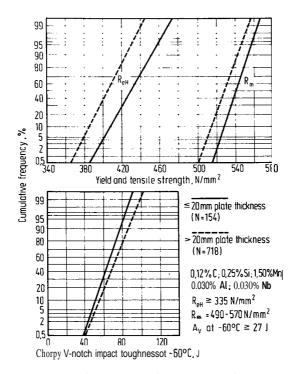


Figure 27. Cumulative frequencies of mechanical properties of plates of HSLA steel for cryogenic applications.

### Steels for Elevated Temperature

Low alloyed steels are used for vessels in the chemical industry as well as for boilers and pressure vessels of power plants. These steels which are in service at elevated temperatures, have usually a yield strength at 350 C of up to 350 N/mm<sup>2</sup>. The chemical composition has been adjusted to the applied heat treatment which may be normalizing plus annealing or quenching in water or oil plus subsequent tempering. In the following, the properties of three niobium alloyed steels for elevated temperature are described.

Heavy plates of the steel grade 13 Mn Ni Mo 54 are rolled in thickness up to 150 mn and subsequently normalized plus annealed. The high yield strength at elevated temperatures is based on the combination of the alloying elements Ni-Mo-Cr. A further addition of 0.01 percent niobium supports the formation of a fine microstructure even in the center of very heavy plates. Thus, the differences of the mechanical properties between the surface and the center are negligible (40).

The properties at elevated temperatures of the steel grade 15 Ni Cu Mo Nb 5 are achieved through the combination of Ni-Cu-Mo. This steel does not contain chromium, but about 0.02 percent niobium. The mechanical properties of 50 to 120 mm thick plates are presented in Figure 29.



# Figure 28. Twin vessel for LPG - tanker of fine grain steel.

A prerequisite with regard to the application of ferritic steels in contact with austenite steels in sodium cooled nuclear power plants, is the avoidance of carbon transportation from ferritic to austenitic parts. Systematic investigations about the carbon diffusion between niobium alloyed steels which are based on the grade 10 Cr Mb 9 10, and austenitic steels showed that the diffusion can be stopped. This occurs when the niobium addition is sufficient to trap the carbon and the nitrogen of the steel completely, that means niobium contents up to about 1 percent (41). The toughness which would have been decreased with a sole niobium addition is restored by the addition of 0.6 percent nickel. The steel grade 8 Cr Mb Ni Nb 9 10 is used for example for parts in the primary circulation system of nuclear power plants. The service temperature may rise up to 590 C.

# Fabrication

The most important processes during manufacturing of structural steels are hot and cold forming, cutting, machining and welding. Recommendations for the manufacture of these steels are given e.g. in Stahl-Eisen-Werkstoffblatt 088, Technische Regeln fuer Dampfkessel (TRD), Technische Regeln fuer Druckbehaelter (AD), Technische Regeln fuer Druckgasverordnung, ISO and ASME Boiler and Pressure Vessel Code, British Standard 1501 and GAPAVE Service des Mines.

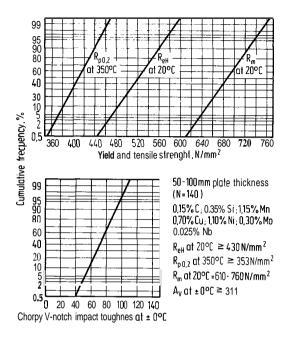


Figure 29. Cumulative frequencies of mechanical properties of plates of HSLA steel for pressure vessels at elevated temperature.

Some important facts from these rules and recommendations are mentioned in the following.

#### Hot Forming

For hot forming, the plates should not be heated above 1050 C to avoid heavy grain growth. Depending on the plate thickness, hot forming can be done in several steps. Before the final step of hot forming takes place, the plate should not be reheated above 980 C. The hot forming shall be finished above 750 C. In case of a deformation less than 5 percent within the final forming process, the finishing temperature may drop to 700 C. This consideration excludes straightening and smoothing of the formed part.

A preheating before welding is necessary if the plate temperature drops below +5 C. If the indicated plate thickness is exceeded, even at temperatures above +5 C a preheating is recommended. It can be seen that the limit of the plate thickness decreases with increasing yield strength.

| Minimum Yield Strength (N/mm <sup>2</sup> )                     | Limit of Plate Thickness (mm) |
|---|-------------------------------|
| <pre>     355     355 to 420     420 to 590     &gt; 590 </pre> | 30<br>20<br>12<br>8           |

The preheating temperature for tack welding and welding is between 80 C and 200 C. If a strong susceptibility to cold cracking is indicated, it is recommended to anneal the joints at 250 C immediately after welding. More details about welding are given in another paper (42) in this book.

## Cold Forming

Forming below recrystallization temperature is called cold forming. The main processes for cold forming are bending, chamfering and dishing. Cold forming should be performed below the highest allowable stress relief temperature, because higher temperatures may cause deterioration of mechanical properties.

Depending on the degree of deformation, cold forming changes the mechanical properties (Figure 30). Small degrees of deformation lead to a loss of yield strength, if stressing is carried out in the opposite direction to the cold forming process (Bauschinger-effect). Higher degrees of deformation increase the tensile properties. The toughness is decreased at any degree of deformation. After heavy cold forming the strength increment is released and the toughness is restored by a stress relief treatment. This will give back, nearly restore, but not completely, the original mechanical properties (Figure 30). The rules demand therefore in certain cases a new normalizing or quenching and tempering treatment.

#### Torch Cutting

During manufacturing, plates have to be thermally cut or edges have to be prepared for welding by the thermal cutting. Preheating for plate temperatures above  $\pm 10$  C is not necessary. At temperatures below  $\pm 10$  C a zone of 100 mm width along the edge should be preheated. If the edges will be cold formed, a zone of 100 mm width along the cold formed edge should be preheated to 120 - 200 C, even at temperatures above  $\pm 10$  C. If the edge becomes a part of the structure, a preheating is recommended. If dynamic loads are envisaged at the edges, they must be machined.

## Welding

The steels which are discussed in this paper are weldable by application of any of the usual welding processes, using good procedures. The mechanical properties in the heat affected zone of welded joints are mainly influenced by the chemical composition of the steel as well as the time-temperature cycle during welding. Good toughness properties in the heat affected zone can be achieved above all through restriction of the welding heat input.

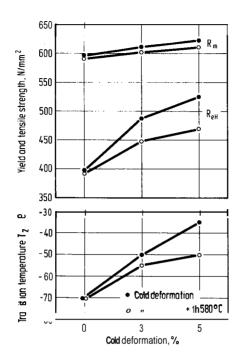


Figure 30. Effect of cold deformation on the mechanical properties of HSLA steel with min, yield strength of 355 N/mm<sup>2</sup> 0,18% C; 0,44% Si; 1,46% Mm, 0,050% Nb.

## Stress Relieving

Stress relief heat treatment after welding is recommended, if the type of structure and/or the envisaged service loads make a relief of welding stresses advisable due to lower residual stresses of the welded structure. It is used mainly with plates thicker than 100 mm.

Along with the stress relieving treatment, it has to be considered that a deterioration of the mechanical properties of the welded joint and the base metal may occur. The reheating up to the determined annealing temperature has to take place slowly. Figure 31 shows the influence of stress relieving on the characteristics of steel grade 3tE 355 (43). During pressure vessel fabrication, involving very heavy plates, the total duration of stress relief annealing may amount to more than 50 hours. For steel development this must be taken into account to avoid degeneration of properties.

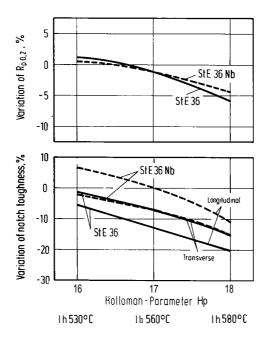


Figure 31. Mechanical properties of steel StE 36 after variable stress relief annealing treatments.

#### Conclusions

A review **has** been presented of the role of niobium in structural plate steels with a historical appreciation of the development and metallurgy of structural steels. It is shown that grain refinement and precipitation mechanisms can be promoted by niobium in C-Mn steels and that the addition of other alloying elements such as Ti, V, Ni, Cu, Cr and Mo can give additional beneficial properties. Related development, in desulfurization and inclusion shape control are described.

A detailed account of the physical metallurgy of plate rolling and heat treatment is given, differentiating between conventional rolling, controlled rolling and thermomechanical processing. The effects of these processes on grain structure and mechanical properties is discussed. Considerable emphasis is placed on the optimization of mechanical properties by balancing steel composition against steel processing and heat treatment variables.

A section devoted to steel applications has reviewed a wide range of product applications including general structural components, ship plate and low and high temperature steels. Finally some details of fabrication procedures and process with respect to HSLA plate are presented which include hot and cold forming, flame cutting, welding and stress relieving.

#### References

- F. Bruhl, and H. Adrian; "The Development of the High Strength Weldable Steels and for Steel Structures, their Use and Processing", Stahl und Eisen 86 (1966) No. 11, pp. 645-62.
- A. Mahadevan, and M. Thiele; "The New Edition of DIN 17100 Steels for General Structural Purposes", Stahl und Eisen 101 (1981) No. 2, pp. 111-15.
- 3. W. B. Morrison; Personal Information on First Trials with Niobium Newport Iron Works, Dorman Long Ltd., 1960.
- W. B. Morrison; "The Influence of Small Niobium Additions on the Mechanical Properties of Commercial Mild Steels", J. Iron and Steel Inst. 201 (1963) No. 1, pp. 43-46.
- W. B. Morrison; "The Influence of Small Niobium Additions on the Properties of Carbon-Manganese Steels", J. Iron and Steel Inst. 201 (1963) No. 4, pp. 317-25.
- J. A. Chapman, A. Clark, and Ph. P. Kirkwood; "Steels for North Sea structures", Metal Construction 6 (1974) No. 11, pp. 342-47.
- L. Meyer, and H. de Boer; "General Outline of High-Strength Low Alloy Steels", Thyssen Techn. Ber. 9 (1977) No. 1, pp. 20-29.
- F. B. Pickering; "High-Strength, Low-Alloy Steels A Decade of Progress", pp. 9-31 in: Microalloying 75, Union Carbide Corp., ed., New York, N. Y., 1977.
- K. Born; "Neuzeitliche Feinkornstaehle Kritische Betrachtung ihrer Schweiß eignung", pp. 1-8 in: Fachbuchreihe Schweiß technik No. 23, Deutscher Verlag für Schweiß technik, Duesseldorf, 1962.
- E. Biener, and W. Lauprecht; "Investigations of the Influence of the Manganese Carbon Ratio on Brittle Fracture Behavior and Weldability of High Strength Fine Grained Structural Steel", Stahl und Eisen 96 (1976) no. 21, pp. 1044-50.
- K. Born, and K. Haarmann; "Richtlinien und Grenzen in der Entwicklung warmfester Staehle fuer den Dampferzeugerbau bis zu Betriebstemperaturen von etwa 400°C, VGB Mitt. (1965) No. 98, pp. 311-21.
- A. J. De Ardo, J. M. Gray, and L. Meyer; "Fundamental Metallurgy of Niobium in Steel", paper presented at the Intern. Symp. "Niobium 81", San Francisco, Ca., Nov. 1981.
- H. Gondoh and T. Osuka; "Ferrite Pearlite Steels for Line Pipe and Plate", paper presented at the Intern. Symp. "Niobium 81", San Francisco, Ca., Nov. 1981.
- L. Meyer, H. E. Buehler and F. Heisterkamp; "Metallurgical and Technological Basis for the Development and Production of Pearlite Reduced Structural Steels", Thyssen Forsch. 3 (1971) No. 1/2, pp. 8-43.
- 15. Kanazawa et al., IIW Document IS/IIW-952-76.

- H. Adrian; "Beitrag zur Kenntnis der Wirkung von Legierungszussetzen auf die Festigkeitseigenschaften von hochfesten schweiß baren Baustaehlen", Dr.-Ing.-Diss. RWTH Aachen, 1968.
- 17. J. N. Cordea; "Niobium and Vanadium-Containing Steels for Pressure Vessel Service", WRC Bulletin 203 (1975), p. 319-s.
- Ch. Lanner; "Finkornstillsatsers Kvaeve Bindande Effekt", Jernkont, Ann. 153 (1969) No. 6, pp. 277-85.
- K. J. Irvine and F. B. Pickering; "Low-Carbon Steels with Ferrite-Perlite Structures", J. Iron Steel Inst. 201 (1963) No. 11, pp. 944-59.
- A. W. Pense; "Twenty Years of Pressure Vessel Steel Research", Weld. J. 59 (1980) No. 11, pp. 311-s/25-s.
- L. Meyer, F. Heisterkamp, and W. Mueschenborn; "Columbium, Titanium, and Vanadium in Normalized, Thermo-Mechanically Treated and Cold-Rolled Steels" pp. 153-67 in: Microalloying 75, Union Carbide Corp., ed., New York, N.Y., 1977.
- H. P. Haastert, W. Meichsner, H. Rellermeyer and K. H. Peters; "Desulphurisation of Pig Iron through the Injection of Carbide Mixtures by Means of Injection Lances", Thyssen Techn. Ber. 7 No. 1, pp. 1-7.
- E. Foerster, W. Klapdar, H. Richter, H. W. Rommerswinkel, E. Spetzler, J. Wendorf; "Desoxidation and Desulphurisation by Blowing of Calcium Compounds into Molten Steel and its Effects on the Mechanical Properties of Heavy Plates", Stahl und Eisen 94 (1974) No. 11, pp. 474-85.
- 24. H. Maas and M. Wahlster; "Use of the Vacuum Circulation Process in Steel Plants with a Mixed Production Program", Stahl und Eisen 90 (1970) No. 22, pp. 1196-1201.
- H. Baumgardt, H. de Boer, G. Tritthart; "Higher-Strength Shipbuilding Heavy Plate Made of Micro-Alloyed Steels Having Special Toughness Properties", Thyssen Techn. Ber. 10 (1978) No. 1, pp. 1-7.
- J. C. M. Farra and R. E. Dolby; "Lamellar Tearing in Welded Steel Fabrication", The Welding Institute, Abington, U. K. 1972.
- K. Lorenz, W. M. Hof, K. Hulka, H. Litzke and U. Schrape; "Thermomechanical and Temperature-Controlled Rolling of Plate and Hot Strip", Stahl und Eisen 101 (1981) No. 9, pp. 593-600.
- H. Baumgardt, A. De Vito, and F. Heisterkamp; "Einflugunterschledlicher Walzbedingungen auf die Eigenschaften eines nioblegierten Baustahles im normalgegluehten Zustand", Internal Report, Thyssen AG, Italsider, CBMM, Sept. 1978.
- J. M. Mackenzie; "Niobium Treated Carbon Steels", pp. 30-35 in: ISI 81 (Spec. Rep. 81), London, 1963.
- G. Bernard, R. Bruyere, M. Grumbach; "Evaluation of Steels with High Elastic Limit for Use in Boilermaking", Rev. Metallurg. 77 (1980) No. 4, pp. 327-40.

- F. Heisterkamp, B. Bergmann, H. Stuart, and L. Chaussy; Developments in Niobium Steels for Linepipe Applications", paper presented at the Intern. Conference on Steels for Line Pipe and Pipe-Line Fittings, London, U. K., Oct. 1981.
- 32. Ch. Ouchi, J. Tanaka, I. Kozasu and K. Tsukada; "Control of Microstructure by the Processing Parameters and Chemistry in the Arctic Line Pipe Steels", ASTM Special Technical Publication 672, presented at the Conference Micon 1978.
- Nippon Kokan Technical Bulletin 1981, OLAC-Process, On-Line-Accelerated-Cooling on Plate Rolling.
- 34. W. E. Lauprecht, T. Wada, P. Boussel; "Trends in Steel and Consumables for Welding", pp. 555-68, paper presented at the Welding Inst. Conference London, U. K., 1978.
- A. Massip and L. Meyer; "Heavy Plate and Hot Rolled Strip of Bainitic Steels with very Low Carbon Content", Stahl und Eisen 98 (1978) No. 19, pp. 989-96.
- A. G. Haynes; "High Strength Structural Steels Nicuage Type 1 and Nicuage IN-787", INCO Ltd., London, U K., 1975.
- W. P. Carter; "Microalloyed Steels for Storage Tanks and Pressure Vessels Operating at Low Temperatures", pp. 716-23 in: Microalloying 75, Union Carbide Corp., ed., New York, N. Y., 1977.
- 38. W Janzon and H. Baumgardt; "Steels for Storage and Transportation of Liquefied Gases at Temperature as Low as -55°C", Thyssen Techn. Ber. 12 (1980) No. 1, pp. 24-29.
- **39.** H. C. Entrekin, C. R. Roper, A. D. Wilson; "Heat Treated Columbium Steel Plate for Low Temperature Applications", paper presented at the AIME Annual Meeting Atlanta, Ga., March **1977**.
- 40. G. von Reumont; "Stand der Entwicklung bei Staehlen mit guter Schweißeignung fuer warmgluehende Druckbehaelter in Dampfkraft- und Kernenergienanlagen", pp. 27-54, paper presented at VGB - Werkstofftagung, Duesseldorf, 1973.
- K. Lorenz, E. Kranz, H. Fabritius; "Ein ferritischer Cr-MO-Stahl mit Niobzusatz fuer den Einsatz beim Bau natriumgekuehlter Kernreaktoren", Klepzig Fachberichte 78 (1970) No. 10, pp. 564-68.
- R. Ph. Kirkwood; "Welding of Niobium Containing Microalloyed Steels", paper presented at the Intern. Symp. "Niobium 81", San Francisco, Ca., Nov. 1981.
- F. Heisterkamp, L. Meyer, and Ch. Straßburger; "Tendencies in the Development of Steels with Improved Weldability for Offshore Structures", Stahl und Eisen 97 (1977) No. 15, pp. 203-08.