MICROALLOYING ELEMENTS IN STEEL

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ABSTRACT

Microalloying elements can be differentiated from classic alloying elements in the steel not only by their relatively low concentration but also by their effects. They bind tramp elements and form second phases in the matrix. In this sense the metals aluminium, niobium, titanium, vanadium and zirconium are discussed. There are three non-metals, boron, phosphorus and tellurium, which alter the steel properties by means of other mechanisms, but could still be included among the microalloying elements.

The microalloying metals are characterized by the limited solubility of their compounds with oxygen, sulfur, nitrogen and carbon. Effective binding of these elements and the deliberate use of dissolution and precipitation processes thus becomes possible in particular in connection with hot forming and heat treatment.

The microstructural effects of precipitate dispersions and sulfide shape control influence production processes and also material properties by affecting hot formability, the kinetics of recrystallisation, austenite transformation, grain refinement, precipitation hardening, texture formation, aging behaviour and cold formability.

Short descriptions are given of the special characteristics of each individual microalloying element. Alumium, for example, is characterized by its dual function as a deoxidizer and nitride former. Niobium is the most effective element with regard to grain refinement and precipitation hardening. Titanium is almost as effective but can also be used for very stable nitrogen binding and sulfide shape control. Vanadium is characterized by its greater solubility and corresponding flexibility. Zirconium binds nitrogen and sulfur without producing fine dispersions. Of the three non-metals, boron increases hardenability, and phosphorus the ferrite matrix strength in sheet steel. Tellurium can reduce sulfide elongation during hot rolling.

A further positive development of the microalloying elements could be assured if problems connected with the alloying and casting operations, the optimization of alloy combinations, the obtainment of more data on steel properties, and the development of new steel grades and products could be solved to the advantage of microalloying.

good problems of a fundamental nature emerge from this area of activity - nice theses for Wedepohl's students.

INTRODUCTION

Microalloying elements, as their name suggests, are used in small concentrations in steel. Therefore, only minor quantities are necessary for the production of steel. This can be illustrated through a comparison with the classical alloying element chromium. More than two million tons of chromium are produced per year, while the production of all microalloying elements together is less than one-tenth of this amount. But since these elements have become very important as a result of the strong influence that they exert in steel, it is quite justified that a general survey on all aspects of these alloying elements should be given here, which includes not only their specific characteristics but also their common aspects.

CLASSIFICATION OF ALLOYING ELEMENTS

There has so far been no unequivocal definition of the term "microalloying elements". It is therefore practical to discuss the characteristics of microalloying elements and differentiate them from other alloying and treatment elements.

Steel is an iron matrix in which foreign atoms are either substitutionally or interstitially dissolved and in which second phases are embedded. The elements accompanying the iron and the second phases can have either a detrimental or a beneficial effect on the properties of the final product. Alloying elements are those elements which are added to the steel with the objective of altering certain properties in a desired direction. This can be achieved by changing the matrix, by binding detrimental tramp elements into less harmful or even useful compounds, or by producing additional second phases. A characteristic of alloying elements is that a precisely predetermined percentage and the obtainment of the highest possible yield is sought. Specific elements are also used in steel production to purify the liquid steel of undesired tramp elements such as oxygen and sulfur. The aim of a treatment of this sort is to deoxidize or desulfurize the steel as completely as possible. A particular characteristic of such treatments is the obtainment of the highest possible treatment-metal utilization to eliminate the reaction product so that only a low residual content is left in the solidified steel. An excessive alloy content of these elements is generally undesirable. These elements, which include calcium and rare-earth metals, should not be regarded as alloying elements and will not be discussed in detail in this paper. One exception is aluminium, which is not only the most important

treatment element as deoxidiser but is also indispensable as a microalloying element.

Microalloying elements could be differentiated from the other alloying elements in the steel simply by means of the alloy content, which could be given as ranging from 10^{-3} to 10^{-1} %. The upper limit of the concentration would then correspond to a few tenths of a percent. This is also approximately the lower limit for the classic alloying elements. A less formal, yet functional differentiation can be made between microalloying elements and classic alloying elements when their effects are considered. Whereas the microalloying elements are effective through their binding of tramp elements or as second phase precipitates in the iron matrix, the classic alloying elements alter the steel properties mainly by changing the steel's matrix. The very intensive effect of microalloying elements becomes clear when one realizes that the desired effects are achieved by using just one alloying atom among 1000 iron atoms. In the case of boron the ratio is even as low as 1 : 20. 000. In contrast, the atomic ratios of the classic alloying elements contained in the steel matrix range from 1 : 100 to 1 : 5. By differentiating in this way it would be possible to name eight microalloying elements, i. e. the metals aluminium, niobium, titanium, vanadium and zirconium and the non-metals boron, phosphorus and tellurium. This group of greatly differing elements cannot, however, be termed as "microalloying elements" in the conventional sense of the word. Also, this differentiation should not be understood as a new definition, otherwise all aluminium-killed steels, for example, would have to be classified as "microalloyed". In this paper, these eight elements will nevertheless be included in the classification of "microalloying elements". It should not go unmentioned that many of these elements are also used in certain steel grades in larger concentrations as "classic" alloying elements.

The search for the microalloying elements and the optimization of their application came about for different reasons: saving of expensive alloying elements, avoidance of supply bottle-necks and above all, improvement of steel properties. Fig. 1 shows the history of the application of microalloying elements in structural steels. The precise date of their introduction is not easy to give. It does, however, become clear that during the past 40 years or so the spectrum of microalloying elements has become very broad. As a complement, two important agents used for deoxidation and desulfurization are also shown, namely calcium and rare-earth metals. Even though the histories of the application of these eight microalloying elements are not uniform and quite varying quantities of the elements are nowadays added, all of the aforementioned elements are regularly used in the production of steel.

GENERAL SURVEY OF THE MICROALLOYING ELEMENTS

The non-metals boron, phosphorus and tellurium each have a specific and well differentiated function as alloying elements in the various steel grades. But the microalloying metals have in contrast to the non-metals many common properties, which can be understood from their proximity to one another within the periodic table of elements (Fig. 2). Each metal shows, in common with its neighbours, a marked tendency to form carbides and nitrides. They are, however, differentiated by their ability to cause precipitation hardening through these compounds. Only the metals titanium, vanadium and niobium are able to do this.

The metals aluminium, titanium and zirconium show a great affinity to oxygen, with the two latter metals also showing a great affinity to sulfur. Of particular importance is the use of microalloying elements to bind nitrogen and carbon. Apart from very stable compounds such as TiN and ZrN, which are practically insoluble in the solid phase, there are those which are of limited solubility. Fig. 3 shows the solubility isotherm at 1000°C for the most important of these combinations (1). It can be seen that the compounds are located in the region about the solubility limit when usual percentages of carbon or nitrogen and of an alloying metal are present. Heat treatment, in particular in combination with hot forming, can be used to control the process of dissolving and precipitating the compounds in such a way that the steel structure and mechanical properties are decisively altered. Aluminium can also drastically influence the steel's properties by way of nitride formation, even if precipitation hardening does not result through AlN. The effect produced by zirconium is based on the very stable binding of nitrogen and also, when its content is sufficiently high, on additional sulfide shape control.

In the following, a general picture will be given of the microstructural effects of the microalloying elements and also of the macroscopic effects on the steel properties. The mechanisms and property changes can here only be described in a general and qualitative way since in a particular case the characteristics of a microalloying element, its alloy content, the basic composition and the treatment of the steel would have to be taken into consideration. The literature contains a great abundance of data in this connection (2...5).

Microscopic effects of the microalloying elements

The influence that the microalloying elements have on the steel's microstructure is attributable to a few basic processes which are caused by the alloying elements in a dissolved form or in a precipitated condition. If the microalloying elements are in solid solution, they bring about a reduction in the thermodynamic activity of

the carbon and nitrogen atoms through their strong affinity to the metalloids. They also retard all diffusion processes in the iron matrix.

The most important property of the metallic microalloying elements is their tendency to form carbides and nitrides, as already mentioned. The formation of precipitates and their effects on the macroscopic properties thus play a dominant role, as illustrated in Fig. 4, which shows the effects of the microalloying elements. The compounds are all of an identical structural type and are characterized by the chemical composition MX. M represents various metals because of the isomorphism of the compounds, and the metalloid X can represent both carbon and nitrogen (6). One characteristic of the compounds is their very high hardness. Dislocations can therefore only penetrate such precipitates if they have extremely small dimensions.

The size, arrangement, and, above all, effects of the precipitates vary considerably, depending on the time and the temperature of their formation. Fig. 5 shows the broad spectrum of differing forms of precipitates. Whereas coarse precipitates of the type MX, which can also be seen as inclusions, do not exert any notable influence on the mechanical properties, the specific effect of the precipitates increases as the dispersion becomes finer. The carconitrides, which are predominantly precipitated on the boundaries of grains, sub-grains and twins, cause within the austenite temperature range a blockage of the microstructure and promote the nucleation of transformation processes. Dislocations caused by hot deformation considerably accelerate the precipitation process in the austenite (7). The C-curve, which is characteristic of precipitation kinetics, is thus strongly shifted towards shorter times. The very low degree of solubility in the ferrite leads to accelerated precipitation within this temperature range. Considerable supercooling and favourable nucleation conditions produce very finely dispersed precipitates in the ferrite. Coherency stresses and the prevention of dislocation movement by such fine precipitates and clusters are the cause of a high degree of precipitation hardening.

Three of the microalloying elements influence the shape of the sulfides in the steel (Fig. 6). While titanium and zirconium greatly strengthen the sulfide phase as a result of the sulfur binding in the carbosulfides of the type $M_4C_2S_2$, alloying of the manganese sulfides with tellurium makes the inclusions less formable. Boron only forms fine nitride precipitations if the nitrogen is not combined with stronger nitride forming elements. Boron-nitride formation is undesirable, if the purpose of boron is the retardation of the austenite transformation.

Macroscopic effects of microalloying elements

The effects of the microalloying elements on steel properties are very varied, depending on the different states of dissolution and precipitation. Some important effects are listed and evaluated in Fig. 4. A short explanation of these effects is based on the sequence of properties that occurs as the temperature decreases. It is for this reason that the properties, which are important for the processing of the steel, are discussed first, followed by the material properties, which are important for the end product.

Dissolved microalloying elements can bring about an increase in the hot strength of the austenite, though only a small one. This, however, is hardly of importance during hot forming. The precipitation of carbides or nitrides on austenite grain boundaries can, especially within the lower temperature range of the austenite zone, cause intercrystalline failure and thus considerable deterioration in the hot formability if the strain rate is low, for example, when a cast strand is subjected to bending (8...10). Fig. 7 shows a schematic diagram of how, in particular, aluminium and niobium can contribute to a weakening of the austenite grain boundaries. A small addition of titanium can partially reverse this process by stable binding the nitrogen in the steel.

One of the most important effects caused by the microalloying elements is the retardation of recrystallization during hot forming (7). Fig. 8 shows schematically that the effect is not caused so much by the dissolved metal atoms but rather by fine strain-induced carbonitride precipitates. Niobium raises the recrystallization threshold to a particularly high level, whereas titanium only shows a similar effect when relatively high alloy contents are involved. In contrast, vanadium produces only a mild retardation of recrystallization (11...13). Fig. 9 shows the effect of the three microalloying elements. Under normal hot forming conditions recrystallization takes place in the area above each of the curves, while below the curves recrystallization is prevented.

The influence of the microalloying elements on the transformation is particularly dependent on their state in the austenite. Whereas dissolved atoms cause austenite transformation to decelerate, fine precipitates can produce an acceleration through the nucleation effect. Fig. 10 illustrates this effect in a niobium-alloyed steel which, compared with an unalloyed steel, shows accelerated or retarded ferrite formation, depending on whether niobium is precipitated or dissolved.

The prevention of recrystallization in microalloyed steels leads to the obtainment, during subsequent cooling, of a deformed, not yet recrystallized austenite prior to transformation. The high dislocation density in the austenite causes a considerable increase in the transformation temperature. The strain-induced precipitation of the microalloying elements also contributes to this effect.

Fig. 11 shows that, as the deformation temperature decreases, it is possible to raise the ferrite formation start by more than 100° C (14). In spite of a very high solution temperature, the transformation temperature then corresponds to that typical for a normalizing treatment.

The ferrite formation resulting from a deformed austenite leads to a considerable degree of grain refinement. Among the precipitating microalloying elements, this is particularly pronounced in the case of niobium and least pronounced in the case of vanadium. Grain refinement increases the yield strength and improves the brittle fracture transition temperature. Precipitation hardening can take place in the ferrite in a temperature range about 600° C, thereby producing a further increase in yield strength, but this influences the brittle fracture transition temperature unfavourably. Fig. 12 illustrates these relations in schematic form for the three microalloying elements niobium, titanium and vanadium (6). The contribution of grain refinement and precipitation hardening to the total yield-strength increase and to the effects upon the transition temperature can be broadly influenced by the choice of deformation temperature since a decrease in the final deformation temperature encourages the grain refinement and reduces the precipitation hardening potential.

The precipitation of microalloying elements can be used to advantage not only in conjunction with thermo-mechanical treatment but also with conventional heat treatments. Examples of this are grain refinement after normalizing, and precipitation hardening after quenching and tempering.

A particular feature of many microalloyed steels is the development of a specific ferrite crystal texture that is dependent upon the thermal history of the final product. Fig. 13 shows the textures that occur in the case of hot or cold-rolled products and the effects on the mechanical properties. In the case of thermomechanically treated plate or strip the transformation from deformed austenite produces a texture that shows pronounced yield strength anisotropy. The increase in yield strength measured in the transverse direction, compared with the longitudinal yield strength, can, under certain conditions, be used as a means of texture strengthening. In cold-rolled and annealed sheet, textures can develop that are characterized by a "cube-on-corner" orientation. The deep drawability of the sheet is improved by this texture as a result of the high r_m value. The conditions for such textures are particularly favourable in steels with titanium or niobium contents which are over-stoichiometric compared with the carbon and nitrogen contents.

The metals included among the microalloying elements are, as a result of their nitrogen binding tendency, able to extensively reduce or eliminate the susceptibility of steel to aging.

The precipitation of titanium nitrides can be controlled to form a very fine dispersion of nevertheless stable precipitates so that the grain growth in the upper austenite range is inhibited (15). Structural

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steels containing such titanium nitride dispersion can be welded using a high heat input, without an undesirably large grain size being obtained in the heat-affected zone (Fig. 14).

In steel sheet for cold forming, an extremely soft condition can be achieved, which improves the formability, by adding a percentage of microalloying elements that is overstoichiometrical in respect to the carbon and nitrogen contained in the steel (6). The condition of this ferrite, which is free of interstitially dissolved atoms, is called "interstitial-free" and is characterized by the absence of a pronounced yield point, by resistance to aging, by a high plastic anisotropy and by a considerable strain hardening potential.

The already mentioned possibility of sulfide shape control, which can be achieved by using the elements titanium, zirconium or tellurium, macroscopically reduces the anisotropy of toughness properties which is typical of many flat rolled structural steels (2). The characteristic values for elongation, reduction of area and notch toughness transverse to the main rolling direction, can be approximated to the respective longitudinal values by means of sulfide shape control. It is also thus possible, in the case of plate intended for use in highly stressed structures, to increase the resistance to lamellar tearing that occurs due to tensile stresses in through-thickness direction. Fig. 15 shows schematically the possibilities for improving the toughness parameters. This includes sulfide shape control, a combination of sulfide shape control and additional desulfurization, and desulfurization only. It can be seen that the joint effect of desulfurization and sulfide shape control, as optimally achieved when using calcium, improves the mechanical properties most effectively.

SPECIAL CHARACTERISTICS OF THE INDIVIDUAL MICRO-ALLOYING ELEMENTS

A description is given in the following of the microalloying elements' special characteristics and main applications. The metals are first of all discussed, followed by the non-metals.

Aluminium (16)

Of the elements under discussion here, aluminium is the only one that is used both as a deoxidizing agent and as a microalloying element. The grades usually designated as special-killed or aluminium-killed steels generally contain at least 0.020 % metallic aluminium. This aluminium, designated as Al soluble, is used as a microalloying element to bind the nitrogen contained in the steel.

After solidification of the steel, the reduced solubility within the austenite temperature range causes aluminium nitride precipitation to occur. Finely dispersed aluminium nitrides impede the grain growth in the austenite. During the γ/α-transformation they act as nuclei and in this way accelerate the austenite transformation. The hardenability of a steel containing aluminium is thus reduced when compared with an aluminium-free steel of identical basic composition. The most important effect of the aluminium nitrides is the ferrite grain refinement and the achievement of aging resistance. The last mentioned properties are very important quality characteristics for weldable structural steels.

The controlled precipitation of aluminium nitrides in cold-rolled sheet produces a favourable texture that improves the deep drawability of the sheet by means of increased plastic anisotropy (r-value). A distinguishing feature, when studied microscopically, of correctly controlled recrystallization annealing is the formation of a pancake ferrite structure.

Niobium (17)

The outstanding characteristic of niobium, and the decisive one with regard to the element's application, is the interplay of dissolution and precipitation of niobium carbonitrides that takes place during the hot forming and heat treatment of steel. Very low niobium contents - one niobium atom to 10.000 iron atoms - have a very great effect due to their very fine dispersion. The thermomechanical treatment of niobium-alloyed steels produces a very small grain size and causes precipitation hardening of the ferrite. The strong retardation of recrystallization during hot forming, however, requires a considerable increase in the rolling force within the lower hot forming temperature range.

Niobium carbonitrides in the austenite are able to retard the grain growth. As the niobium content increases, so does the limiting temperature for the grain growth also increase. In normalized steels the carbonitride precipitates cause the formation of fine-grained ferrite, but no significant precipitation hardening takes place.

The strengthening effect of niobium in cold-rolled and recrystallization-annealed sheet is clearly smaller than in hot-rolled products because of the coarsening of the prcipitates caused by annealing. If the niobium content in the steel is overstoichiometric in respect to the carbon and nitrogen contents, an "interstitial-free" steel is obtained which is characterized by its extraordinarily good forming properties.

Titanium (18)

Because of the thermodynamical and physical similarity of titanium carbide to niobium carbonitride, the behaviour of these two microalloying elements in structural steels is to a great extent identical. The specific effectiveness of titanium, expressed in terms of atom percentages, is, however, only one-tenth as great as that of niobium. However, since no flattening of the concentration influence but rather a proportional strengthening occurs, titanium can also be used to obtain very considerable strength increases. The relation of precipitation hardening to grain refinement hardening is higher in the case of titanium. It is possible to take advantage of the sluggish recrystallization of titaniumalloyed steels used for cold-rolled sheet to produce partially recrystallized sheet with a correspondingly high strength (19).

Its very great affinity to nitrogen brings about a stable nitrogen binding at high temperatures. This improves the hot formability at low rates of deformation. A stable titanium nitride dispersion can be used to improve the properties within the heat-affected zone of welded joints where a high heat input is applied (see also Fig. 14). Even small contents of titanium make the steel largely ageresistant.

Titanium's tendency to form compounds with sulfur can be used for sulfide shape control. Complete binding of the sulfur in carbosulfides of the type $Ti_4C_2S_2$, however, requires an adjustment of the sulfur, manganese and titanium contents.

The strong deoxidizing effect of titanium also involves the risk of unwanted titanium fade during the casting of the steel. This is a reason for certain property scattering.

Vanadium (20)

Vanadium is more soluble in steel than the already mentioned microalloying metals. Since the nitride is less soluble than the carbide, the dissolution and precipitation behaviour of vanadium can be broadly controlled by correspondingly adjusting the steel's basic composition, above all by increasing the nitrogen content (21, 22). In general, however, the effect of the vanadium precipitates is less than that of niobium and titanium precipitates. The mild retardation of recrystallization, on the other hand, has hardly any effect on the required rolling forces during hot forming.

In low-carbon weldable steels, vanadium is generally in solid solution, even within the lower austenite temperature range. In this state, vanadium retards the transformation process, and for this reason it is also taken into account in the various carbon equivalent formulae. Vanadium's relatively high solubility, on the other hand, may be advantageous because it can cause precipitation hardening even after normalizing treatment. The strength can also be increased in quenched and tempered steels containing medium

carbon percentages by means of vanadium carbide dissolution and precipitation. A typical example of this is the use of 49 MnVS 3 steel for forged car crank-shafts (23).

Zirconium (24)

Zirconium is used as a microalloying element to bind the nitrogen and/or as a means of sulfide shape control. The zirconium nitrides are relatively coarse inclusions and do not exert any influence on the mechanical properties of the steel. Other microalloying elements which require nitrogen to achieve precipitation, such as aluminium and vanadium, should therefore not be combined with zirconium. Normalizing an aluminium-killed steel containing zirconium coarsens the ferrite structure because no finely dispersed AlN particles are able to form. This function can, however, be accomplished by NbC or TiC. Similar to titanium, zirconium forms carbo-sulfides if the alloy surplus is larger than the quantity required for nitrogen fixation. The great affinity of zirconium to oxygen makes its use in the steelmaking shop problematical.

Boron (25)

Boron is characterized by the extreme retarding effect that it has on the austenite transformation into ferrite. By using just a few ppm the beginning of the ferrite transformation can be considerably retarded. Boron is therefore used to improve the hardenability of quenched and tempered steels. Its effect, which increases as the carbon content decreases, is nowadays also used to obtain a bainitic structure in low-carbon weldable structural steels.

Since nitrogen binding induced by boron would eliminate the effect on the transformation process, boron has to be prevented from forming nitrides. It is for this reason that in boron-alloyed steels the nitrogen is effectively bound to zirconium or titanium.

Nitrogen binding using boron can, under special conditions, be advantageous when applied in the case of cold-rolled sheet.

Phosphorus (26)

Phosphorus is regarded as an undesirable tramp element in structural steel. In the case of cold-rolled sheet, however, use can be made of the considerable increase in strength that is caused by the dissolved phosphorus in the ferrite. In order to limit phosphorus-induced embrittlement the alloy content is generally adjusted to below 0.1 %. Phosphorus tends to cause considerable segregations during solidification which can appear as shadow lines in the cold-rolled sheet.

Tellurium (27)

Tellurium can be used as an alloying element for the manganese sulfides. Because it is related to sulfur it is incorporated in the sulfides as a solid solution forming agent. It also surrounds MnS as MnTe which may have a "lubricating" effect during deformation. Its content has to be adjusted to that of the sulfur and is confined to the range below 50 ppm.

USE OF THE MICROALLOYING ELEMENTS

Microalloying elements are nowadays used for such a broad range of applications that it is here only possible to list the steel grades and products. The most important ones are undoubtedly the high-strength, weldable structural steels which are used in a normalized, thermomechanically treated or quenched and tempered condition. Thermomechanical treatment or rolling at controlled temperatures is primarily applied in the case of plate and hot-rolled strip. Microalloying elements are also used to increase the strength of sectional steel and merchant bars, and in particular of reinforcement bar steel. Higher-strength sheet made from steels microalloyed with niobium, titanium, vanadium or phosphorus is used for automobile construction. Use can be also made of the grain refining or precipitation hardening effect of microalloying elements in the manufacture of high-strength forgings or castings. The welding filler metal properties are important when performing welding operations on steel. Here also, microalloying elements such as niobium, titanium and boron are applied to advantage because of their effect on the transformation behaviour.

When using microalloying elements in the steelmaking shop, special aspects have to be taken into consideration because of the elements' thermodynamic and physical properties. The great affinity of some of them to oxygen should, above all, be mentioned here because it can lead to unwanted losses, in particular in the case of prolonged casting times. The introduction of continuous casting requires that the application of the microalloying elements be made compatible with this new technology. Here also, undesirable oxidation can cause difficulties during casting. Among the microalloying elements there is a toxic element, tellurium, which has a relatively high vapour pressure at liquid steel temperatures. The resultant problems have to be taken into account when using tellurium.

The problems mentioned here can be of importance in particular cases. They have not, however, impaired the successful and ever increasing application of microalloying elements. The broad range of applications for which microalloying elements are used can be illustrated by means of one example. The number of works-internal steel grades containing niobium, titanium or vanadium produced in a large steel mill that concentrates on flat-rolled steel, yet also produces a broad range of sections, bars and rails, is approx. 500.

FUTURE DEVELOPMENT AND TASKS

In spite of the successful development of microalloyed steels, both metallurgically and economically, some tasks can be formulated for the future whose solution would help further develop the application of microalloying elements.

- In the past, microalloying elements were mostly used singly or, as in the case of high-strength steels used for line pipes, in combination of two. New element combinations have to be found and optimized. At the same time the property spectrum of the specific elements has to be taken into account. Fig. 16 shows an example of the complex use of various microalloying elements in one steel. In order to obtain a minimum yield strength of 700 N/mm^2 in thermomechanically treated hot-rolled strip, the elements boron, niobium and titanium were combined with a thermomechanical treatment and the classic alloying elements manganese and molybdenum in such a way that it was possible to advantageously use all the familiar strengthening mechnisms. The various possibilities for combining the different microalloying elements and also for combining them with other alloying elements are far from exhausted.
- Special consideration should also be given to the use of higher cooling rates in connection with hot forming processes. Cooling water could thus be included as an effective "alloying element" among the range of other alloying possibilities.
- The discovery of new microalloying elements is not very probable in view of the conditions prevailing in the periodic table of elements. Nevertheless, the effects of other elements on the steel properties should be examined from this point of view. At the same time, however, the questions concerning alloy costs and availability should not be left unconsidered.
- The use of microalloying elements could certainly be improved if more complete basic data were available on the elements' mode of action. There is still a great deal of quantitative data to be determined within the multidimensional space made up by the complex reaction mechanisms, the possibilities of mechanical and thermal treatment, and the variation of the steel's basic composition. This data could create the prerequisites for a "quantitative microstructural control" in steel development.
- New areas of application for microalloyed steels could be opened up if, in addition to the classic material properties such as strength and toughness, more data were available on important secondary properties. Such properties include, for example, fatigue resistance, resistance to abrasion and corrosion, and in particular resistance to stress corrosion cracking. One should aim at a practical combination of basic and application-related research in this work.
- The progress that is made in these fields should make it possible for microalloyed steels to be also used for those grades and pro-

ducts where microalloying elements have not yet been applied. They should have advantageous property combinations and be relatively low in cost. For important applications in steel constructions that are subject to particular regulations an approval would also have to be obtained.

- Last but not least, the application of microalloying elements in the steelmaking shop would be made easier, the yield improved and the scatter of properties restricted if it were possible to solve the problems that still exist during alloying and casting.

It is certainly a realistic assessment to say that the future of microalloyed steels and thus that of the production of microalloying elements will develop positively if the described tasks are accepted as a challenge and are accomplished through the joint cooperation of the ferro-alloy producers, the steel producers and the steel consumers.

CONCLUSIONS

Microalloying elements in steel are characterized by their relatively low concentrations. They generally bind the steel's tramp elements into stable inclusions or into finely dispersed precipitates. As such elements one could name the metals aluminium, niobium, titanium, vanadium and zirconium. The non-metals boron, phosphorus and tellurium can also be used as microalloying elements to bring about transformation retardation, ferrite strengthening and sulfide shape control.

The presence of dissolved elements and in particular the precipitation of particles within a broad temperature range extending from the solidification temperature to austenite and ferrite influence significantly the steel properties by means of different microstructural mechanisms. On the one hand, this is used to improve the material properties. On the other hand, certain effects which are caused by the microalloying elements also have to be taken into account during steel production in the steelmaking shop, in the hot rolling mill and during heat treatment.

Microalloyed steels, which were first used for the large family of high-strength, weldable structural steels, include at present a great number of other steel grades and products and could be used even more extensively if certain objectives connected with steel production, material properties and applications were reached.

REFERENCES

(1) Gladmann, T., and F. B. Pickering: JISI 205 (1967), p. 653 - 64

(2) Meyer, L., H. -E. Bühler, and F. Heisterkamp: Thyssen-forschung 3 (1971), p. 8 - 43

(3) Microalloying 75: Proceedings of an International Symposium on High-strength, Low-Alloy Steels. Union Carbide Corp., New York 1977

(4) Baker, T. N.: Microalloyed steels, Science Progress, Oxf. 65 (1978), p. 493 - 542

(5) Oberhauser, F. M.: Radex-Rdsch. (1980), p. 134 - 45

(6) Meyer, L., F. Heisterkamp, and W. Müschenborn: Columbium, Titanium and Vanadium in Normalized, Thermo-Mechanically Treated and Cold-Rolled Steels. In: (3), p. 153 -67

(7) Meyer, L.: Stahl und Eisen 101 (1981), p. 483 - 91

(8) Mintz, B., and J. M. Arrowsmith: Influence of microalloying additions on hot ductility of steels. In: Hot working and forming processes. TMS, London 1979, p. 99 - 103

(9) Birat, J. P., et al.: Steelmaking practice for niobium containing steels. Paper presented in the conference Niobium 81, San Francisco 1981

(10) Ouchi, C., and K. Matsumoto: Trans. ISIJ 22 (1982), p. 181 - 89

(11) Robiller, G., and L. Meyer: Work hardening and softening behaviour of Ti- and Nb-alloyed steels during hot deformation. In: Recrystallization and Grain Growth of Multi-Phase and Particle Containing Materials. 1st Risø International Symposium on Metallurgy and Materials Science, 1980, p. 311 - 16

(12) Maehara, Y., T. Kunitake, and N. Fujino: Tetsu to Hagané 67 (1981), p. 362 - 71

(13) Matsukura, K., and K. Sato: Trans. ISIJ 21 (1981), p. 783 - 92

(14) Ouchi, C., T. Sampei, and I. Kozasu: Trans. ISIJ 22 (1982), p. 214 - 22

(15) Kanazawa, S., et al.: Trans. ISIJ 16 (1976), p. 486 - 95

(16) Berns, H.: Stahl und Eisen 98 (1978), p. 662 - 64

(17) DeArdo, A. J., J. M. Gray, and L. Meyer: Fundamental Metallurgy of Niobium in Steel. Paper presented in the conference Niobium 81, San Francisco 1981

(18) Meyer, L., F. Heisterkamp, and D. Lauterborn: Titanium as a strengthening and sulfide controlling element in low-carbon steels. In: Processing and Properties of Low-Carbon Steels. AIME, Warrendale 1973, p. 297 - 320

(19) Schneider, E. -J., and B. Pollard: Titanium bearing high strength cold rolled steels. In: Mechanical working and steel processing XVIII. Proceedings of a conference in Toronto, 1980. AIME, Warrendale 1980, p. 398 - 428

(20) Vanadium in High-Strength Steel. Preprints of Technical Papers of a conference in Chicago, III., November 1979. Vanadium

International Technical Committee, 1979.

(21) Amin, R.K., M. Korchynsky, and F.B. Pickering: Met. Technol. (1981), p. 362 - 71

(22) Almond, E.A., and R.S. Irani: Met. Technol. (1981), p. 339 - 51

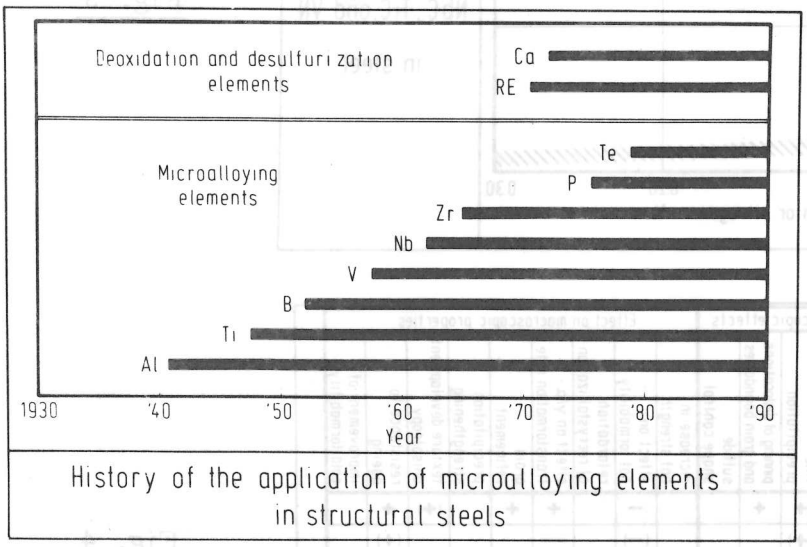
(23) Brandis, H., and S. Engineer: Fachber. Hüttenpraxis Metallverarbeitung 19 (1981), p. 666 - 69

(24) Espenhahn, M., H.-E. Bühler, and H. Litterscheidt: Thyssenforschung 1 (1969), p. 136 - 43

(25) Boron in Steel. Proceedings of a conference, Milwaukee, Wis., 1979. TMS/AIME Warrendale, Pa., 1980

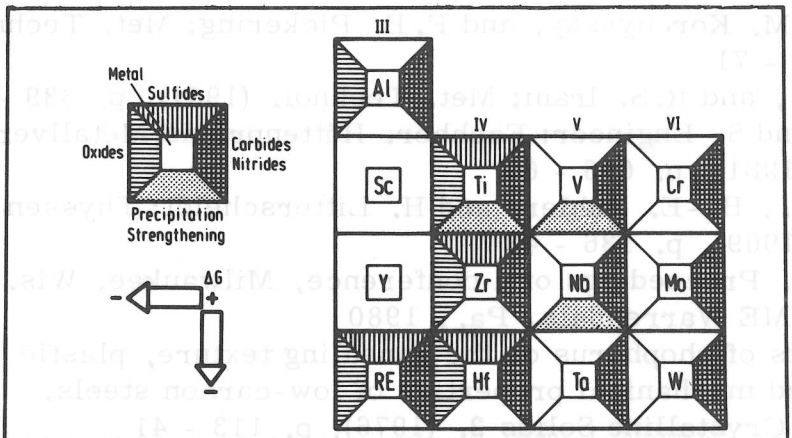
(26) Hu, H.: Effects of phophorus on the annealing texture, plastic anisotropy, and mechanical properties of low-carbon steels. In: Texture of Crystalline Solids 2. (1976), p. 113 - 41

(27) Massip, A., and L. Meyer: Thyssen Technische Ber. 10 (1978), p. 26 - 34



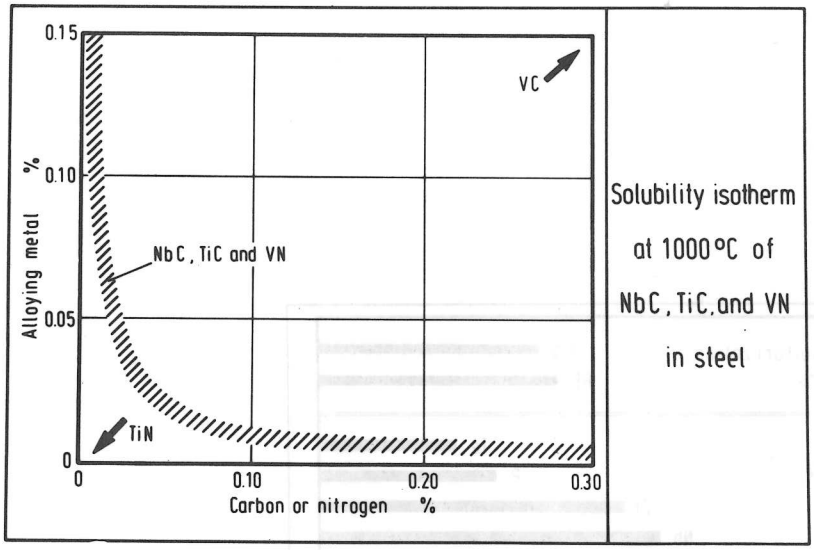
History of the application of microalloying elements in structural steels

Fig. 1



The potential of certain metals to form oxides, sulfides, carbides and nitrides and their precipitation strengthening potential (arrangement as in the periodic table)

Fig. 2



Solubility isotherm at 1000 °C of NbC, TiC, and VN in steel

Fig. 3

Element	Affinity to				Microscopic effects				Effect on macroscopic properties								
	O	S	N	C	coarse precipitation	fine precipitation	pinning of dislocations and grain boundaries	sulfide shape control	increase in hot strength	effect on hot formability	retardation of recrystallization	effect on γ/α-transformation rate	grain refinement	precipitation strengthening	texture development, anisotropy	resistance to ageing	improvement of cold formability
Al	++		+			+	+			−		+	+		(+)	+	
B	+		+			(+)				(−)		−−				(+)	
Nb	+		+	+		+	+		+	−	++	*)	++	++	+	+	
P															(+)		
Te		(+)						+									+
Ti	++	++	++	+	+	+	+	+	+	+	++	*)	+	++	+	+	+
V	+		+	+		+	+				(+)	−	+	+		+	
Zr	++	++	++	+	+			+								+	+

+ positive effect − negative effect open: no significant effect *) depending on the thermal history

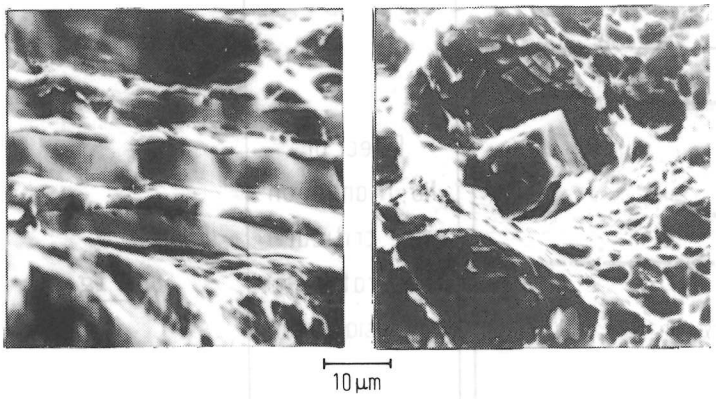
Effects of microalloying elements on microstructure and properties of steel

Fig. 4

Type and size of precipitates	Kind of precipitation	Example
Decreasing precipitation temperature ↓		
o coarse, angular "inclusions" $\sim 10^4$ nm	precipitation before or during solidification	TiN, ZrN
o coarse precipitates $\sim 10^2$ nm	precipitation at γ-grain boundaries and substructures	NbC, TiC
o fine precipitates $\sim 10^1$ nm	strain-induced precipitation	NbC, TiC
o rows of fine precipitates $\sim 10^1$ nm	γ/α-interphase precipitation	NbC, V(C,N)
o extremely fine, semicoherent precipitates, clusters $< 10^1$ nm	precipitation in α-phase	NbC, TiC, V(C,N)

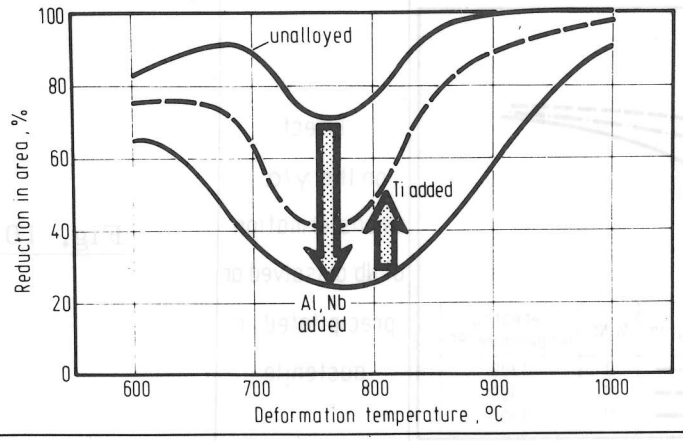
Various types of carbonitride precipitates occurring in microalloyed steels

Fig. 5



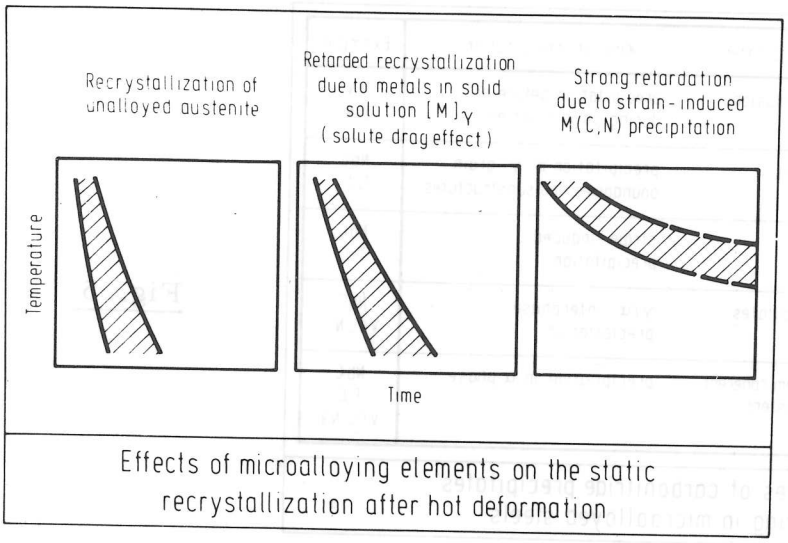
Elongated MnS inclusions (left) and shape-controlled, inclusions containing Ti (right) in a fracture surface of flat rolled steel

Fig. 6



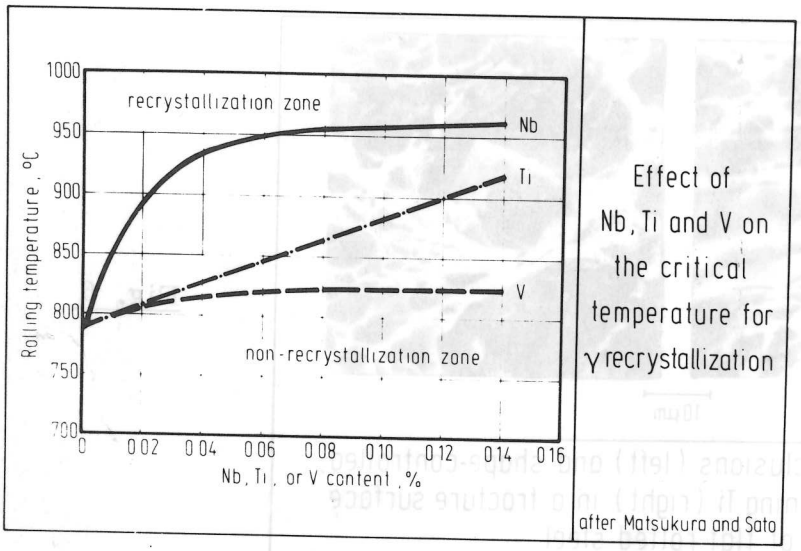
Hot ductility at low strain rate of C-Mn-steels as affected by microalloying additions

Fig. 7



Effects of microalloying elements on the static recrystallization after hot deformation

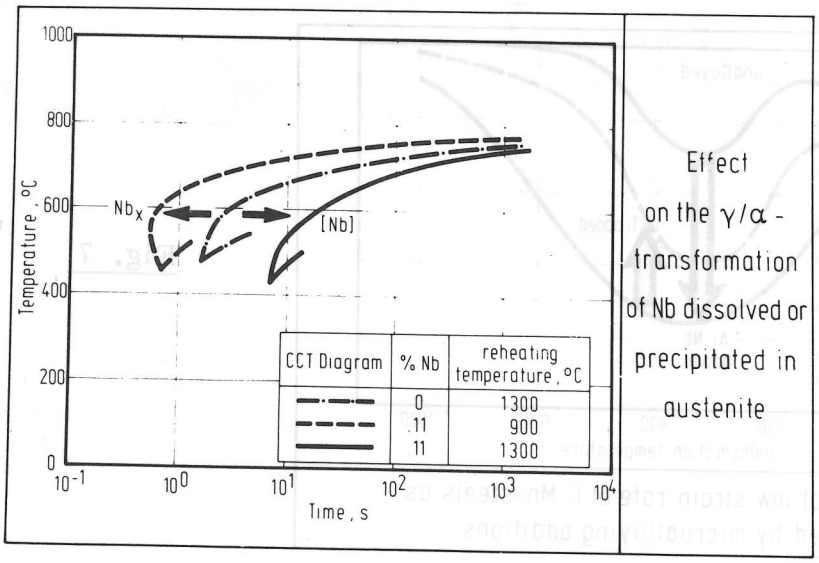
Fig. 8



Effect of Nb, Ti and V on the critical temperature for γ recrystallization

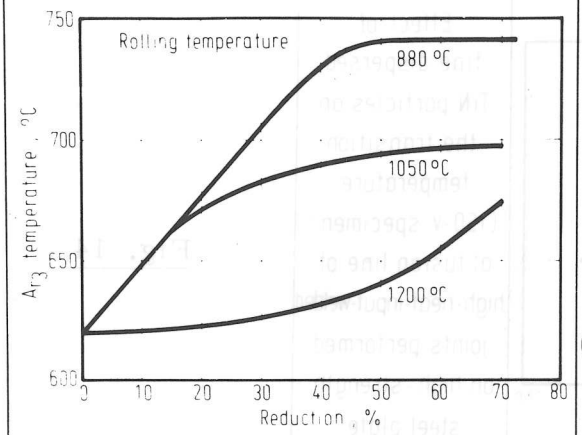
after Matsukura and Sato

Fig. 9



Effect on the γ/α - transformation of Nb dissolved or precipitated in austenite

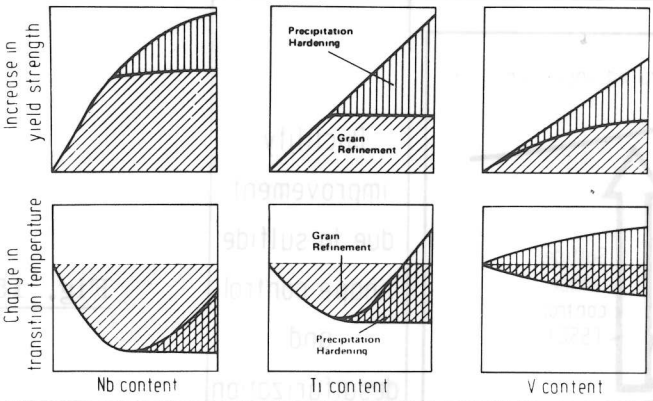
Fig. 10



Effect of rolling temperature and reduction on the Ar_3 temperature of Nb steel (reheating: 1250°C)

after Ouchi et al.

Fig. 11



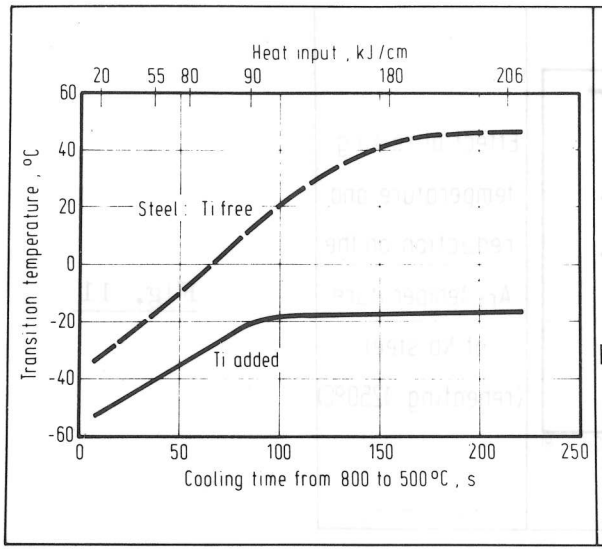
Schematic correlation between alloy content, increase in yield strength, and change in transition temperature as a result of grain refinement and precipitation strengthening in hot rolled, low-carbon steel

Fig. 12

Steel product	Predominant texture	Effect on mechanical properties
Thermomechanically treated plate or hot strip	{112} ⟨110⟩	Yield strength anisotropy: $YS_{trans} > YS_{long}$ (texture strengthening in transverse direction)
Cold-rolled and recrystallized sheet	{111} ⟨112⟩ {554} ⟨225⟩	Favourable plastic anisotropy: $r_m > 1.0$

Textures occurring in microalloyed steels

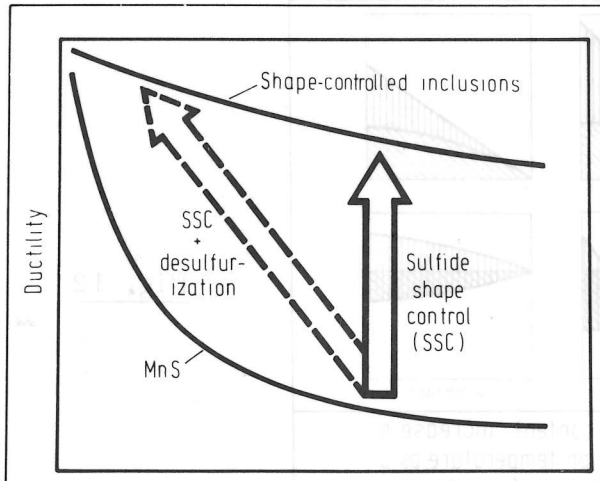
Fig. 13



Effect of fine, dispersed TiN particles on the transition temperature (ISO-V specimen) at fusion line of high-heat-input-welded joints performed on high-strength steel plate

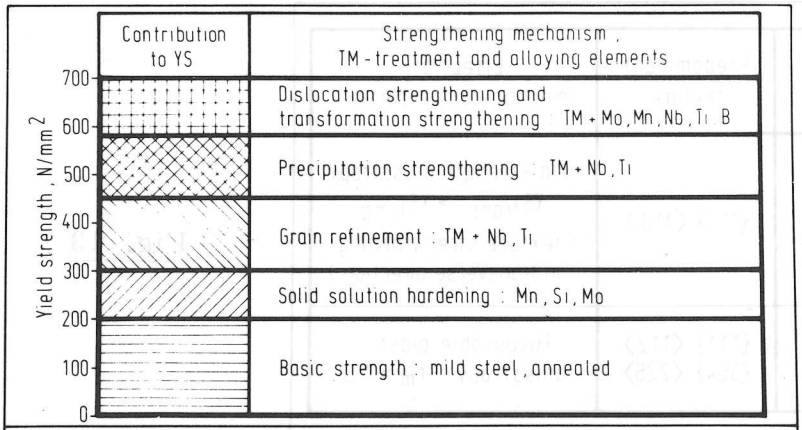
after Kanazawa et al

Fig. 14



Ductility improvement due to sulfide shape control and desulfurization

Fig. 15



Contributions of the strengthening mechanisms of various alloying elements and a thermomechanical treatment to achieve 700 N/mm² yield strength in hot strip

Fig. 16