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Microalloying of Steel

Mikrolegiranje jekla

F. **Vodopivec**, *Inštitut za kovinske materiale in tehnologije, Lepi pot 11, 61001 Ljubljana*

Mechanisms of the effect of microalloying on strength and toughness of steels. Influence on grain size, precipitation hardening, processes of hot deformation, and economy of microalloying with Al, Nb, V, and Ti.

Mehanizmi vpliva mikrolegiranja na trdnostne lastnosti in žilavost jekla. Vpliv na velikost zrn, izločilno utrditev, procesi vroče deformacije in gospodarnost mikrolegiranja z Al, Nb, V in Ti.

1 Introduction

The microalloying of steel is a technology which has been intensively developed for about 25 years, and it exploits the theoretical knowledge on mechanisms of precipitation hardening, grain size control, and deformation of steel. The term "microalloying" is used because steels are alloyed with up to 0.05% of various elements, and an important influence on the following characteristics and properties is achieved:

- austenite and ferrite grain size are diminished, and because of it yield stress, strength, and toughness are increased while the ductile/brittle fracture transition temperature is diminished;
- precipitation hardening is achieved, this increases the yield stress and strength of steel, diminishes the toughness and increases the ductile/brittle fracture transition temperature;
- the hardenability is improved and austenite/ferrite transition temperature is lowered;
- the susceptibility of steel to strain ageing is eliminated;
- the content of dissolved oxygen and sulphur in steel are diminished and the purity of steel is improved;
- the shape and composition of non-metallic inclusions are changed and the isotropy of properties and the machinability of steel are improved;
- the texture in non oriented electrical sheets is improved and the energy losses diminished.

Microalloying elements are: aluminium, base element for steel deoxidation and for the decrease of oxygen is solution, niobium, titanium, vanadium, zirconium, boron, calcium, tellurium, antimony, tin, nitrogen, and in some cases also sulphur and lead. In this paper only microalloying elements in the narrower sense will be discussed, i.e. those which influence the microstructure, strength and toughness of steel: aluminium, niobium, titanium, vanadium, and nitrogen which are in various combinations the basic constituents of high-strength structural steels and modern machine-building steels. In order to understand better the influence of microalloying elements on the mechanical properties and the hot working process it is necessary to know the processes and reactions in steel involving these elements, and their compounds with nitrogen and carbon which form precipitates called in the following as dispersoide phases. The influenced processes are austenite grain growth, precipitation hardening in ferrite, and recrystallization of austenite during hot rolling.

2 Size and stability of austenite grains

The first condition for the formation of small ferrite grains during the cooling of steel are small austenite grains and are obtained either by recrystallization of austenite after hot rolling at a relatively low temperature if a suitable delay of austenite grain growth is achieved during the hot working, or during the cooling after normalization. Austenite grains grow through migration of boundaries, which can be hindered or stopped if the boundary is pinned to precipitates of dispersoide phases. When migration progresses, at first a concavity is formed at the precipitate, then the grain boundary envelopes it and finally bypasses it. This process requires an additional energy. The driving force for the growth is the tendency of material to reach a minimal total energy (E_s) through the change of the shape and the size of grains, and is obtained by the minimal specific surface energy of grains. The total energy consists of the volume (E_v) and the surface component (E_p). E_v is proportional to the grain volume, thus to D^3, if D is linear dimension of grain, while the surface component is proportional to D^2. Schematically it can be written $E_s = KD^2 + K_1 D^3$. The specific energy is thus:

$$\frac{E_s}{D^2} = \frac{1}{D+1}$$

E.g.: for $D = 1$, $E_s/D = 2$; for $D = 2$, $E_s/D = 1.5$; for $D = 3$, $E_s/D = 1.33$, etc. Thus total energy is the lower the coarses is the grain size.

The prevention of the migration of a grain boundary is achieved when the distance among the precipitates is below a critical value. Instead of the distance between the precipitates, which is difficult to be measured, the more easily measurable precipitation size (d) and volume part of dispersoide phase (f) are used in the analytical treatment of grain growth. The relationship between the grain size—D, the volume part of precipitates—f, and their size—d is according to Zener[1] given by the equation:

$$\frac{D}{2} = \frac{4d}{3f}$$

The above equation was further developed for the growth of austenite grains in structural steel by Gladmann and Pickering[2]. They have assumed that in grain growth the energy

$$E = \frac{2Sy}{D}\left(\frac{2}{Z} - \frac{3}{2}\right)$$

is released. In the equation S—represents the boundary migration, y—the surface energy of austenite, and Z—the ratio between the size of a growing grain and the average grain size in the matrix.

It is evident that the grain growth is possible only if $Z > 4/3$, otherwise the growth energy change is positive and a spontaneous process is not possible. An exception represents the cases of very great growth driving force, e.g. a grain shapes which greatly deviates from the equilibrium. The equation was further transformed into the expression connecting the critical size of precipitates, d_k, with other easily measurable parameters:

$$d_k = \frac{6Df}{2\pi}\left(\frac{3}{2} - \frac{2}{Z}\right)^{-1}$$

The grain growth occurs if the size of precipitates is $d > d_k$. The equation shows that grains grow with the growth of the critical size and the decrease of the content of precipitates, as well as with the increasing non-uniformity of grain size. A spontaneous growth is initiated the easier the greater is the initial non-uniformity of austenite grain size. For better understanding it can be mentioned that after one-hour of heating of a Cr-Ni carburizing steel at 920°C, i.e. before anormal grain growth, the ratio of maximal and minimal grain size is $Z = 3.18$.

By the same quantity of the dispersoide phase the precipitates are the more efficient the smaller is their size, i.e. the greater is their volume density and thus the smaller is their mutual distance. Precipitates are not completely stable at the grain growth temperature and grow at prolonged annealing time and especially at higher temperatures loosing the pinning efficiency. In structural steel the precipitates of sizes below 10 nm represent a low hindrance for grain growth because of their instability caused by the high ratio of surface to the total energy.

Efficient precipitates are formed by dispersoide phases which are dissolved in austenite at the heating of steel before the hot rolling or forging. As steels are becoming cool, the solubility of dispersoide phase is diminished, and precipitates are formed with size depending on the temperature and the length of isothermal annealing.

During the transformation and the recrystallization the growth rate of all grains is not uniform, single grains grow faster, reach a lower total energy, become more stable, and at sufficient temperature grow at the expense of their neighbours. This is the explanation why a microstructure of grains of different size is found in normalized steel with a too low quantity of the precipitates for complete pinning of the migration of austenite grain boundaries. The grains can grow also by coalescence if their space orientation is similar and are parted by low-angle boundaries. This occurs in textured materials.

The boundary migrating at the extent of a neighbour grain is concave. A simplified explanation is that the atoms on the concave side are on average more time bound in the crystal lattice. The migration of crystal boundary is produced by the difference in the number of atoms which are deplaced over the grain boundary because of thermal oscillation. The number of jumps from the convex to the concave side of the boundary is equal to the number of jumps in the reverse direction, but on the concave side more of oscillating atoms are retained. This produces a flow of atoms from the convex to the concave side, i.e. the shift of crystal boundary in the opposite direction.

The theoretical explanation for the migration process of a crystal boundary towards the centre of curvature is found in ref.[3], where it is suggested that the driving force for the boundary migration is the decrease of surface energy. The rate of migration is described by a parabola of the form

$$D = D_0 + K^{1/n}$$

with D_0—an initial grain size, D—the grain size after an annealing time t, and n—the growth exponent. Theoretically n is 2 while empirically the values between 2 and 4 were measured.

The connection between the grain size (D) and the yield stress (R_E) is given by the Hall-Petch equation

$$R_E = R_{E_0} + KD^{-1/2}$$

with R_{E_0} as a constant depending on the composition and the microstructure of steel[4]. The constant K is a measure for the hindering effect of crystal boundaries on the mobility of dislocations.

In **Fig. 1** taken from the ref.[5] the relation between the grain size, expressed by $D^{1/2}$ and the ASTM number, and the yield stress of steel with 0.17% C and 0.8% Mn is shown. The decrease of the grain size from ASTM number 5 to ASTM number 10, obtained through the microalloying produces an increases in yield stress of steel for about 50%. This increase takes place at an increased toughness and a decreased ductile/brittle fracture transition temperature (T_p) at notch toughness test. The proposed relation is

$$\frac{1}{T_p} = T_0 + KD^{-1/2}$$

with T_0 and K constants depending on the composition and the microstructure of the steel[4].

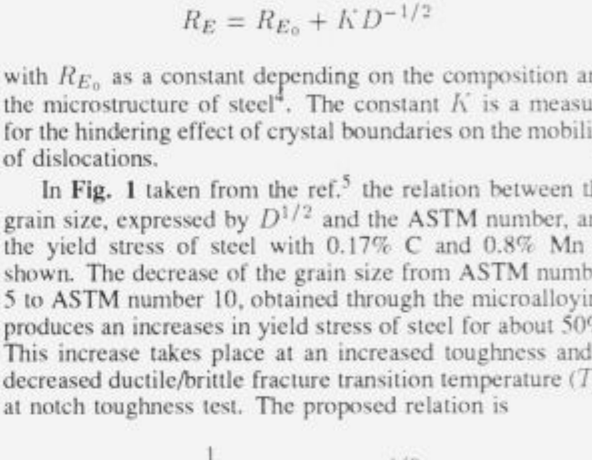

Figure 1. Relation between the grain size expressed as $D^{-1/2}$, the ASTM number, and the yield stress of steel with 0.17% C and 0.8% Mn (Ref.[5]).

Slika 1. Odvisnost med velikostjo zrn izraženo kot $D^{-1/2}$ in ASTM razredom ter mejo plastičnosti jekla z 0.17% C in 0.8% Mn. Po viru[5].

The movement of dislocations in the lattice is hindered by the Peierls-Nabarro force (τ_{pn}), and each crystal boundary produces an additional obstacle for the movement. The total force (T_s) essential for the movement of dislocations in polycrystalline material is:

$$T_s = \tau_{pn} + K D^{-1/2}$$

A piling-up of dislocations at the grain boundary is required in order to accumulate a sufficient driving force for the penetration of dislocation into the neighbour grain with a different space orientation[6].

3 Dispersoide phases

Dispersoide phases are carbides and nitrides, very frequently also carbonitrides since carbides and nitrides of microalloying elements are mutually completely soluble. The composition of dispersoides depends on the amounts of microalloying elements, nitrogen, and carbon in steel. If the content of microalloying elements, nitrogen or carbon is too high, dispersoide phases can form already in the melt or during the solidification of steel. The size of precipitates in this case is 100 nm or more, accordingly small is their volume density, and low the hindering effect at standard size of austenite grains. In microalloyed steel in which the content of microalloying elements for the most part does not exceed 0.05%, the sufficient volume density of precipitates is not achieved if they are formed in the melt or during the solidification. In this case they are enriched on the solidification interfaces or in eutectic clusters, which decreases the ductility of the steel. Such example represent AlN and Nb(CN) formed during the solidification of steel manufactured in electric arc furnace[7], with a high content of nitrogen, aluminium, and niobium.

The mechanism of growth of precipitates involves the solution of small particles with a greater specific surface energy and the diffusion of microalloying components on coarse, more stable particles.

The growth of precipitates, often named as Ostwald ripening, is described by the Wagner[8] equation

$$d_t^3 - d_0^3 = \frac{16\sigma DCV}{9RT} t$$

with

d_t	precipitate diameter after the annealing time t
d_0	precipitate diameter in time 0
σ	surface tension between the matrix and precipitate
D	diffusivity of constitutive atoms
C	concentration of constitutive atoms
V	molar volume of precipitate
R	gas constant
T	absolute temperature

The equation shows that the rate of precipitate growth will be at constant other conditions the faster, the faster is the diffusivity, the greater is the concentration of constitutive atoms in solution, and the higher is temperature. Thus the ideal dispersoide is that with the lowest solubility of constituents, and with the lowest diffusivity of microalloying element, since the diffusivity of nitrogen and carbon in interstitial solution is very fast.

Let us assume that the steel contains 0.03% AlN which ensures the austenite grains size after normalization of 6–7 ASTM number[9]. **Fig. 2** presents the calculated AlN precipitate size for such a steel after one hour holding at various temperatures, the content of aluminium nitride, the volume density of precipitates, and the relative austenite grain size. The solubility product used for the calculation is in good agreement with the AlN solubility determined for Cr-Ni carburizing steel[9]. If the heating temperature of steel is increased from 900 to 950°C, the same hindering effect can be obtained with an about 40% higher content of nitride, while above 1000°C the pinning effect of aluminium nitride is very rapidly diminished.

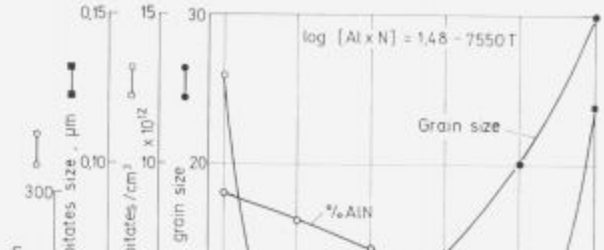

Figure 2. Relation between the annealing temperature and the precipitate size, the number of precipitates per unity of volume, the content of AlN in solution, and the austenite grain size. The theoretical AlN content is 0.03%. The calculation is based on the AlN solubility product given in ref.[2].

Slika 2. Odvisnost med temperaturo žarjenja in velikostjo izločkov, številom izločkov na enoto prostornine, količino AlN v raztopini in velikostjo zrn austenita. Teoretična vsebnost AlN 0.03%. Izračun je izvršen na osnovi topnostnega produkta za AlN v viru[2].

In microalloyed steel usually there are 2 or 3 grain growth inhibitors; AlN, Nb(CN), TiC and VN. The presence of precipitates formed by the addition of 0.03% niobium to the steel with 0.10–0.20% C ensures grain sizes of ASTM number 10–11 after normalization.

The most frequent dispersoide is aluminium nitride (AlN) which is found in all steels deoxidized, and thus microalloyed with aluminium. The solubility of AlN and of other dispersoide phases in austenite in structural steels is given by the solubility product. Ref.[10] gives the following solubility product for aluminium nitride

$$\log(\mathrm{Al} \times \mathrm{N}) = -6770/T + 1.48$$

In the above equation N and Al represent the weight content of both elements in solution in the steel, and T is the temperature in K. According to ref. [10], [11], and [12] the solubility products for other dispersoide phases are

$$\begin{aligned}
\log(\mathrm{Ti} \times C) &= -10475/T + 5.33 && {}^{11}\\
\log(\mathrm{Ti} \times N) &= -\ 8000/T + 0.32 && {}^{12}\\
\log(\mathrm{V} \times C) &= -\ 9500/T + 6.72 && {}^{11}\\
\log(\mathrm{V} \times N) &= -\ 8330/T + 3.46 && {}^{10}\\
\log(\mathrm{Nb} \times C + N) &= -\ 6770/T + 2.26 && {}^{10}
\end{aligned}$$

In some references also other equation for the solubility of dispersoides is found but they do not differ significantly from the above given.

The solubility of all the dispersoides, but of vanadium carbide, in austenite with up to 0.2% C and 0.01% N is small and at the normalizing temperature less than 10% of the quantity at the temperature of about 1200°C. On the contrary, the solubility of vanadium carbide in austenite is very high, and this dispersoide is completely dissolved already at about 900°C in steel with 0.2% C. Other dispersoides are very stable because of the low solubility at the normalizing temperatures and the inhibition of grain growth is diminished only at higher temperatures.

During the cooling from the solubility temperature and at isothermal holding during such cooling the formation of precipitates is very slow (**Fig. 3**) due to slow formation of nuclea though the solid solution is highly oversaturated[13]. The explanation for the slow formation of nuclea is the great dilution since the content seldom exceeds 0.03% which e.g. represents 3 atoms of titanium per 10000 atoms of iron. The number of atoms of microalloying elements is thus very low and consequently the rate of formation of sufficient statistic aggregations of atoms from which precipitation nuclea are formed is very slow. The kinetics of the precipitation during the holding after direct cooling from the solubility temperature is a slow parabola highly different from that describing the formation of precipitates in austenite quenched from the solubility temperature and then reheated (**Fig. 3**). The kinetics of AlN formation is in this case a step parabola indicating that the rate of growth of precipitates is determined by the diffusion rate of aluminium on the nuclea formed during the reheating of steel, due to the high oversaturation because of the cooling to ambient temperature or to the double transition of the austenite/ferrite phase boundary on which the solubility of AlN is changed strongly.

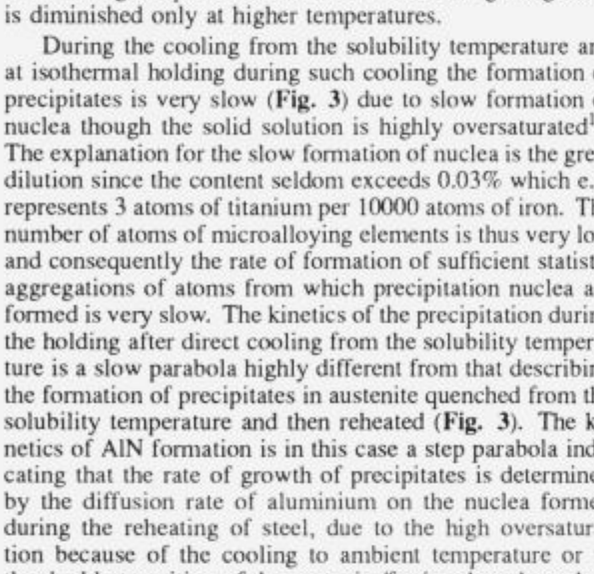

Figure 3. Kinetics of AlN precipitation after various thermal history of steel with 0.11% C, 0.49% Mn, 0.029% Al, and 0.0063% N.
Slika 3. Kinetika precitipacije AlN po različni termični zgodovini jekla z 0.11% C, 0.49% Mn, 0.029% Al in 0.0063% N.

It must be mentioned that niobium if its concentration exceeds about 0.035% and at high nitrogen contents—the limit is at about 0.012%, is bound during the solidification process into a carbonitride very rich in nitrogen and practically unsoluble during heating the steel before the rolling[7]. Niobium bound in this phase is lost as active microalloying element, thus the microalloying with niobium in steel molten in electric arc furnace is economical only up to about 0.03%. In CrMn case hardening steel by already 0.02% Nb the same stability and size of austenite grains is achieved as with the same amount of aluminium or with 0.1% vanadium (**Fig. 4**). The specific weight of niobium carbide is higher than that of aluminium nitride, the weight solubility of both in austenite is similar, thus the same weight content of niobium in austenite gives less precipitates. Consequently, if seems probable that niobium hinders the migration of boundaries also by some other mechanism, e.g. by a segregations on grain boundaries which produces a greater number of precipitates on these boundaries as it could be expected from the average niobium content in steel. Ref.[14] presents micrographies showing that the boundaries or subboundaries of austenite grains are marked with strings of precipitates which confirm the possibility of an intercrystalline segregation of niobium. The size of austenite grains is thus related to the thermal deformation history of steel. Ref.[15] describes a bimodal size distribution of precipitate after the rolling of niobium steel from 1050°C which can also be explained supposing an intercrystalline segregation of niobium.

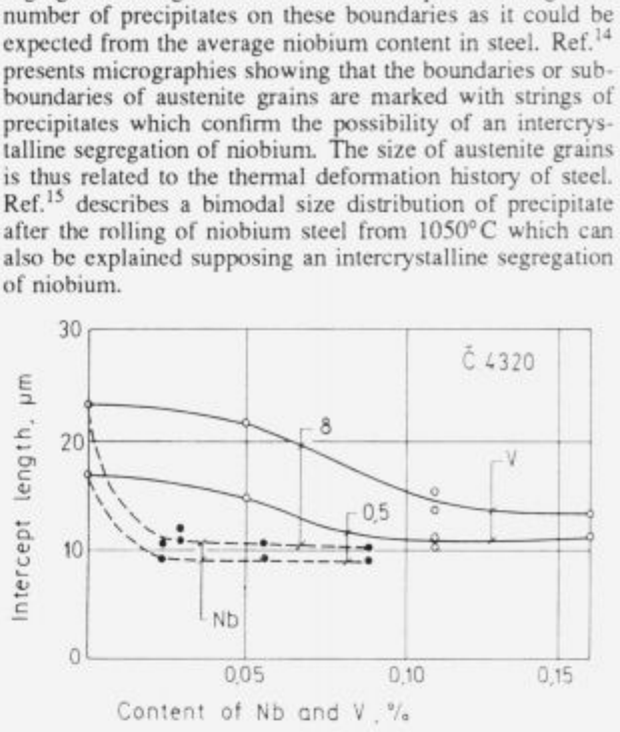

Figure 4. Relation between the amounts of niobium and vanadium in steel and the size of austenite grain after half-hour and 8-hour austenitizing at 920°C. Basic steel composition: 0.18% C, 0.95% Mn, 0.28% Si, 1.0% Cr and, below 0.002% Al (Ref.[16]).
Slika 4. Odvisnost med količino niobija in vanadija v jeklu in velikostjo zrn austenita po polurni in 8 urni austenitizaciji pri 920°C. Osnovna sestava jekel: 0.18% C, 0.05% Mn, 0.28% Si, 1.0% Cr, pod 0.002% Al_t. Po viru[16].

4 Microalloying and precipitation hardening

The precipitation hardening is one form of dispersion hardening, i.e. hardening caused by a new phase which is found in small quantities in the metallic matrix. The general expression describing the relations between the quantity of precipitates (f), their size (d), the shear modulus (G), the Burgers vector of dislocations (b), and increase of strength (ΔR_T) was proposed by Hornbogen[17] in the following form

$$\Delta R_T = K \frac{G b f^{1/3}}{d}$$

K is a constant with a value $K = 1$ for a polycrystalline material and uniformly distributed spheroidal particles of the new phase. The hardening is proportional to the third root of the quantity of precipitated phase and inversely proportional to the particle size of that phase. It is thus more strongly dependant on the size than on the quantity of precipitates. The precipitation hardening is stable only till the shear moduls is not diminished because of the temperature change or the precipitates do not hinder the moving of dislocations. In microalloyed steel the precipitates formed at the normalizing temperature, which are a very efficient hindrance for grain growth, do not cause precipitation hardening. This would be obtained only by a much greater number of precipitates, at least for one order of magnitude greater than it is usually found in microalloyed steel. In such a case the ductility and the toughness of steel would be diminished.

The highest precipitation hardening of microalloyed steel is obtained if precipitates are formed below about 620°C when the shear modulus of ferrite is high enough, and the internal stresses due to the formation of coherent precipitates are not relaxed. Coherent precipitation occurs by carbonitrides, carbides, and nitrides of niobium, vanadium, and titanium which have a cubic crystal lattice, but not by the hexagonal aluminium nitride which produces thus virtually no precipitation hardening of ferrite. The lattice parameter of cubic precipitate is different than that of ferrite. Both lattices can accommodate by elastic deformation and the internal stresses on the contact surfaces are proportional to the hardening, generally called as coherent hardening. The stress field around the precipitates hinders the movement of dislocations in a greater volume of matrix than the precipitate alone. At increasing size of precipitates the coherence is lost and the boundary between the precipitates and the matrix becomes an actual phase boundary without elastic accommodating stresses. The hardening is achieved only by hindering of dislocations moving at plastic deformation. This hardening is called a dispersion hardening and it can be calculated according to the Hornbogen equation. In this type of hardening all carbide and nitride phases, including aluminium nitride and cementite, behave in equal way, and the effect depends on the amount and the size of precipitates.

The moving dislocation can cut small precipitates without stress field[18]. The critical size of precipitate depends mainly on their shear modulus, e.g. for copper precipitates in ferrite the critical size is about 10 nm and, for TiN precipitates only 3 nm. Precipitation hardening of microalloyed steel is relatively strong. For the evaluation of the hardening effect of niobium carbonitride the following semiempirical expression was developed by Yeo and coworkers[19]

$$\Delta Re = \frac{1575}{d}(\%\mathrm{Nb}^{1/3} - 0.12)$$

with Nb as niobium content in weight %, d—the size of niobium carbonitride precipitates, and ΔRe—the increase of yield stress.

The exponent at the niobium content proves that the expression was derived through simplification of the Hornbogen equation. A disadvantage of the expression is the lack of parameters considering the temperature of formation of precipitates and the shear modulus, thus it can be used only for heat treatment by quenching and ageing at a selected temperature.

Fig. 5 presents the influence of precipitates size at constant niobium content, and the content of niobium at constant size of 50 nm precipitates on the hardening effect. Already a small amount of niobium is efficient if present in steel in small precipitates. The increase of the content of niobium does not improve the hardening effect to an economically justified extent. Fig. 5 further proves that precipitates of an average size of 25 nm, which can be found in microalloyed steel after normalizing, cause hardly a hardening effect.

Practically only a part of precipitation hardening effect can be industrially exploited however it is not negligible

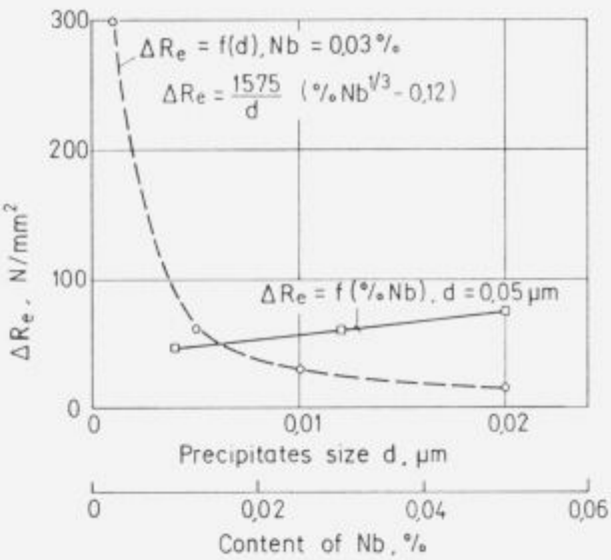

Figure 5. Relation between the size of precipitates in steel with 0.03% Nb or NbC concentration in 5 nm precipitates, and the increase of yield stress.

Slika 5. Odvisnost med velikostjo izločkov v jeklu z 0.03% Nb oz. količino NbC v izločkih z velikostjo 5 nm in povečanjem meje plastičnosti.

from the viewpoint of the material strength. E.g. a small change in basic composition of the steel with a yield stress above 350 N/mm^2, and microalloying with niobium and vanadium can give a yield stress above 470 N/mm^2, where precipitation hardening due to formation of vanadium carbide during the cooling of steel after normalizing contributes for about 50 N/mm^2 [20]. As already mentioned, the precipitates formed in the approximate temperature range 570 to 620°C are efficient. At lower temperatures the formation of precipitates is too slow due to the slow diffusion of vanadium, and it could be exploited only by a longer annealing or in a very slow cooling which is economic only in coils. The effects of the diminution of grain size and of the precipitation hardening on the yield stress are additive, their influence on the other two very important properties, the notch toughness and the ductile/brittle fracture transition temperature, is opposite. Diminished grain size increases the toughness and decreases the transition temperature while the precipitation hardening has an opposite effect. **Fig. 6** presents, according to data in ref.[4], some relations which confirm the above conclusions for a standard as normalized Nb-V microalloyed steel. By thermal treatment, e.g. by normalizing and through the rate of cooling, a rather different relation between the yield stress and the toughness transition temperature can be achieved, even an unacceptable transition temperature can be obtained which nullifies all the advantages of microalloying.

5 Microalloying and hot deformation

Most steel products are manufactured by hot rolling when the steel cross section is reduced from pass to pass at dropping temperature till a final thickness of plate, strip or bar is obtained. A similar sequence of events is found by forging only the sequence of partial deformations is less uniform. During the rolling process the steel is cooled partially by radiation and the convection into the surroundings, and partially by contact with the cooling water, rolls, hammers or

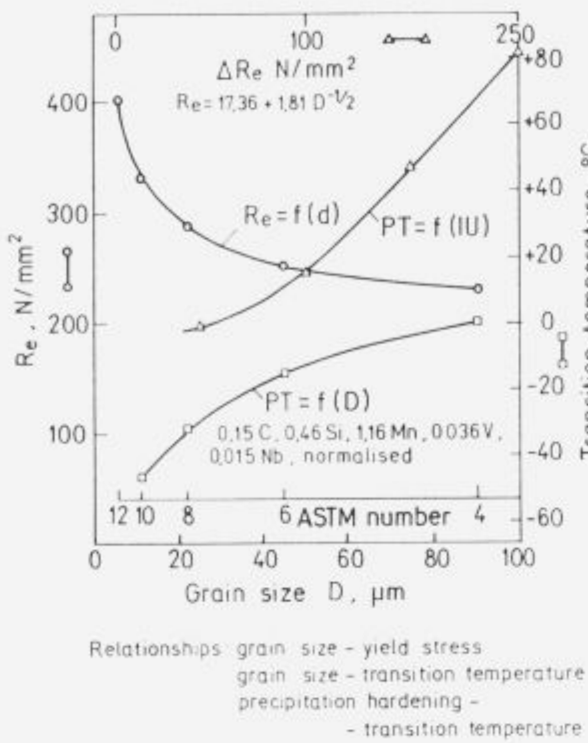

Figure 6. Relation between the grain size in as normalized steel, the precipitation hardening, and the yield stress increase due to the precipitation hardening (ΔRe), and the notch toughness transition temperature (PT).

Slika 6. Odvisnost med velikostjo kristalnih zrn v normaliziranem jeklu, oz. izločilno utrditvijo in mejo plastičnosti povečano zaradi izločilne utrditve (ΔRe) ter prehodno temperaturo žilavosti (PT).

other cooler parts of equipment. Because of the successive deformations the steel is in deformed state for some time and it contains a great number of point and line defects. The rate of diffusion processes in the deformed matrix is very fast. Jonas and coworkers[21,22] found that the nucleation rate of precipitates was for an order of magnitude faster during the deformation, and that the rate of precipitates growth in deformed austenite was for two orders and during the deformation even for three orders of magnitude greater than in not deformed or in recrystallized austenite. The static recrystallization which eliminates from austenite the deformation energy delayed for a few seconds corresponds thus to a 100 or even 1000 sec. long annealing. Any component which delays the recrystallization thus highly accelerates the process of precipitaton but only as long as austenite remains unrecrystallized. As soon as the recrystallization is finished the rate of precipitation is diminished again. E.g. in laboratory rolling of 12 mm plates from 60 mm billets the steel remained between the rolls for 0.47 seconds, and total time of rolling was 70 seconds. Let us assume a great rate and an uniform precipitation in the period when steel is deformed between the rolls. The rate of precipitates growths is described by approximate cubic parabola which can be simplified for a rough evaluation into the expression $d^{1/3} \approx Kt$, t being the time. The calculation shows that the ratio of precipitates size in unrecrystallized austenite (d_{an}) and in recrystallized austenite (d_{ar}) is $d_{an}/d_{ar} = 4.5$. If steel is rolled by uncompleted interpass recrystallization and if it contains a small quantity of microalloying elements the unhomogenity of microstructure represented by the number of anormally grown grains is the greater the lower is the rolling temperature[9,23] because of the unhomogenity of precipitation during the rolling. During the rolling of low and medium alloyed steel with an austenite microstructure static recrystallizaton is the basic process for the elimination of deformation energy. Dynamic softening processes and static recovery are virtually negligible. In absence of interpass recrystallization static recovery rapidly eliminates the deformation hardening, and it does not change the size of austenite grains. Niobium is the microalloying element which has the strongest delaying effect on the rate of static recrystallization of austenite. Two explanations are proposed for the mechanism of the effect of niobium. The first claims that the effect is linked to niobium in solid solution in austenite[24]. The process of static recrystalization is initiated on the grain boundaries, it seems thus that the inhibition of formation of recrystallization nuclea on boundaries is connected to the presence of niobium at these boundaries. **Fig. 7** shows that the temperature of completed interpass static recrystallization of austenite is already by 0.02% niobium increased for about 100°C in the CrMn carburizing steel. The weight content of 0.02% of niobium means that the solution in austenite contains appr. 1.1 niobium atom per 10^4 iron atoms. A logic conclusion is that such a dilution could hardly influence the process linked to shifts of iron atoms and it seems justified to conclude that the austenite grains boundaries are richer in niobium due to a segregation. This explanation is supported also by the fact that small amounts of niobium improve the hardenability of steel through the delaying the nucleation of ferrite below the transformation temperature. Thus niobium can hinder the formation of recrystallization nuclea and ferrite by a similar mechanism.

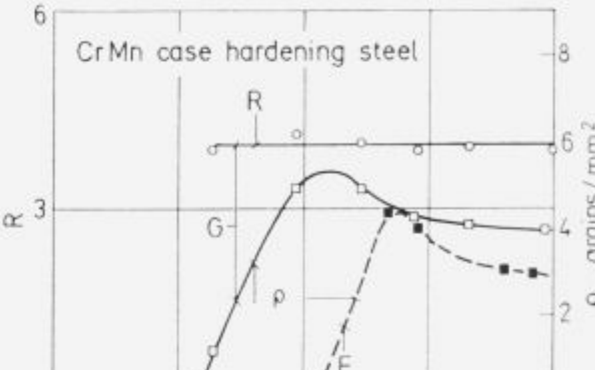

Figure 7. Influence of the initial rolling temperature on the ratio length/width (R) and on the number of unrecrystallized austenite grains (P). Steel G: 0.14% C, 1% Mn, 0.85% Cr, 0.02% Nb, and 0.0078% N; steel F: 0.16% C, 1.1% Mn, 0.98% Cr, 0.025% Al, and 0.0095% N.

Slika 7. Vpliv začetne temperature valjanja na razmerje dolžina/širina (R) in na število nerekristaliziranih zrn austenita (P). Jeklo G: 0.14% C, 1% Mn, 0.85% Cr, 0.02% Nb in 0.0078% N; jeklo F: 0.16% C, 1.1% Mn, 0.98% Cr, 0.025% Al in 0.0095% N.

The second hypothesis links the influence of niobium on the recrystallization on precipitates formed during the deformation. Two questions are not explained by this hypothesis: why the precipitates of other microalloying elements, e.g. TiC, and VN and AlN, which are also formed during the deformation, hinder the static recrystallization of austenite to a much lesser extent (**Fig. 8**), and why the recrystallization process takes place when the content of niobium in solid solution is diminished below a limit of about 0.005% due to the formation of precipitates. Both explanations of the effect of niobium are found in recent papers on microalloying, and it is left to the reader to chose the more probable significance weighting the significance of empirical findings.

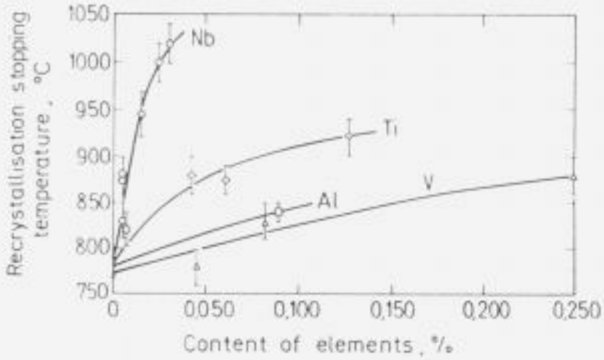

Figure 8. Influence of the content of various microalloying elements on the hindering temperature of static recrystallization of austenite.
Slika 8. Vpliv vsebnosti raznih mikrolegirnih elementov na temperaturo zaustavitve statične rekristalizacije austenita.

In **Fig. 9** the effect of rolling temperature on the content of AlN and NbC in various steels, and on the ferrite grain size given as intercept length by rolling 15 mm plates from 60 mm billets in 7 passes is shown. All the steels were heated to 1200°C before the rolling. In steel without niobium where the interpass recrystallization of austenite is fast and complete, only few precipitates are formed during the rolling and the influence of temperature on the amount of precipitates is hardly perceivable because at decreasing rolling temperature the content of AlN formed during the rolling is very slowly increased. The precipitation behaviour in niobium steel is significantly different because austenite remains between passes for longer time unrecrystallized, or the quantity of austenite which does not recrystallize at all between passes is increased, and thus the precipitation is faster. Below a limit temperature austenite remains completely unrecrystallized between passes and the precipitation is accelerated to such extent that practically all AlN and NbC are precipitated in the relatively short rolling time of 1 minute.

On the base of the processes of recrystallization and of precipitation two technologies of rolling of microalloyed steel were developed. In thermomechanical rolling the slabs are rolled to a thickness which is 30–50% greater than the final thickness of plates, the rolling is stopped till steel temperature drops below about 950°C, and then the plates are rolled to the final thickness in several passes, the number depends on the strength of the rolling stand, and cooled in air. Deformed austenite is during the cooling very rapidly transformed into finegrained ferrite and pearlite[25], while AlN and NbC precipitates hinder the growth of ferrite grains after the transformation. A finegrained microstructure with high strength and toughness is obtained, and it supports the precipitation hardening with VC during the air cooling of plates with an acceptable deteriorating effect on notch toughness.

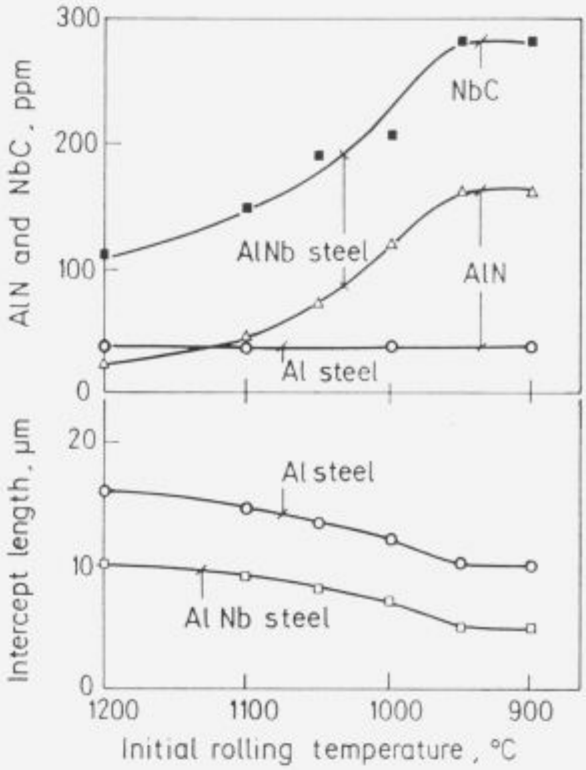

Figure 9. Relation between the initial temperature of two steel with a similar basic composition, one microalloyed with niobium, the amounts of AlN and NbC precipitated during the rolling and the grain size after air cooling.
Slika 9. Odvisnost med začetno temperaturo dveh jekel s podobno osnovno sestavo, eno pa mikrolegirano z niobijem na količino AlN in NbC, ki sta nastala med valjanjem in na velikost zrn po ohladitvi na zraku.

This technology is applied for steel microalloyed with niobium and vanadium which can achieve yield stresses up to 500 N/mm^2 at carbon contents below 0.15%. Similar properties are obtained with the combination of rolling in less controlled temperature range and normalization annealing. **Fig. 10** represents the various hardening mechanisms in normalized steel microalloyed with aluminium, niobium, and vanadium.

The advantages of microalloying can be exploited also through the rolling process with controlled recrystallization. This method demands an exact harmonization of steel composition with the degree of deformation and the pass sequence, since the temperature and the per pass deformation must enable the complete interpass recrystallization, and simultaneously also the formation of precipitates which hinder the growth of recrystallized austenite grains. **Fig. 11** presents mechanical properties of three steel of similar composition which were rolled under conditions of controlled recrystallization. In both microalloyed steels much better properties are achieved than in the comparative steel down to about 800°C when the transformation of austenite during the rolling, the deformation hardening, and the formation of texture during rolling start to occur. By the same rolling conditions the microstructure of vanadium steel is more homogeneous because of less of microstructural unhomogeneity due to the or incompleted interpass recrystallization. At still lower rolling temperatures the deformation hardening,

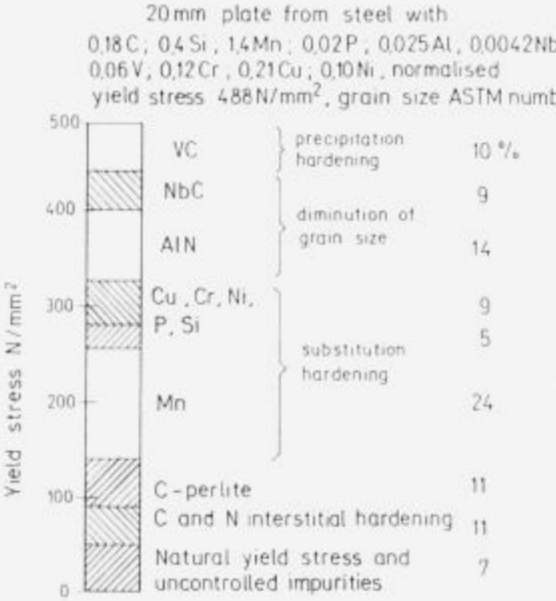

Figure 10. Constitution of yield stress in a 20 mm sheet of normalized microalloyed steel with 0.18% C, 0.4% Si, 1.4% Mn, 0.025% Al, 0.042% Nb, 0.06% V, 0.12% Cr, 0.21% Cu, and 0.10% Ni.

Slika 10. Zgradba meje plastičnosti v 20 mm pločevini iz normaliziranega mikrolegiranega jekla z 0.18% C, 0.4% Si, 1.4% Mn, 0.025% Al, 0.042% Nb, 0.06% V, 0.12% Cr, 0.21% Cu in 0.10% Ni.

microstructural nonhomogeneities, and strain anisotropy increase, therefore a too low finishing temperature has a harmful effect. An even higher strength can be achieved by a proper coiling temperature since slow cooling enables a greater precipitation hardening.

6 Economy of microalloying

Microalloying is the more efficient the more dispersoide is dissolved at heating before hot working. The quantity of dissolved dispersoide is the greater the closer are the concentrations of the constituting elements to the stoichiometric ratio; e.g. the amount of dissolved AlN in austenite will be the greatest if the weight contents of aluminium and nitrogen in steel are 2 : 1. A too great deviation of one or the other element causes that less dispersoide is dissolved in austenite, and less precipitates are formed during the rolling and the cooling. This explains why at high aluminium contents, over 0.04%, austenite grains are coarser and less stable than at a lower content of aluminium and at the same content of nitrogen about 0.01%.

For the stability of austenite grains the nature of precipitates is not important, only their number and stability matter, or more correctly, the number of precipitates per unity of volume of austenite. Theoretically the presence of about 0.03% AlN or of a corresponding quantity of other dispersoides of precipitates of equal size is needed to attain a sufficient stability of austenite grains. The contents of microalloying elements and of dispersoide phases giving equal volume densities of precipitates are given in **Table 1** for the most frequent dispersoides. Aluminium assures a sufficient density of precipitates already at the lowest content, while the highest content is required in the case of vanadium carbide since this carbide is much more soluble

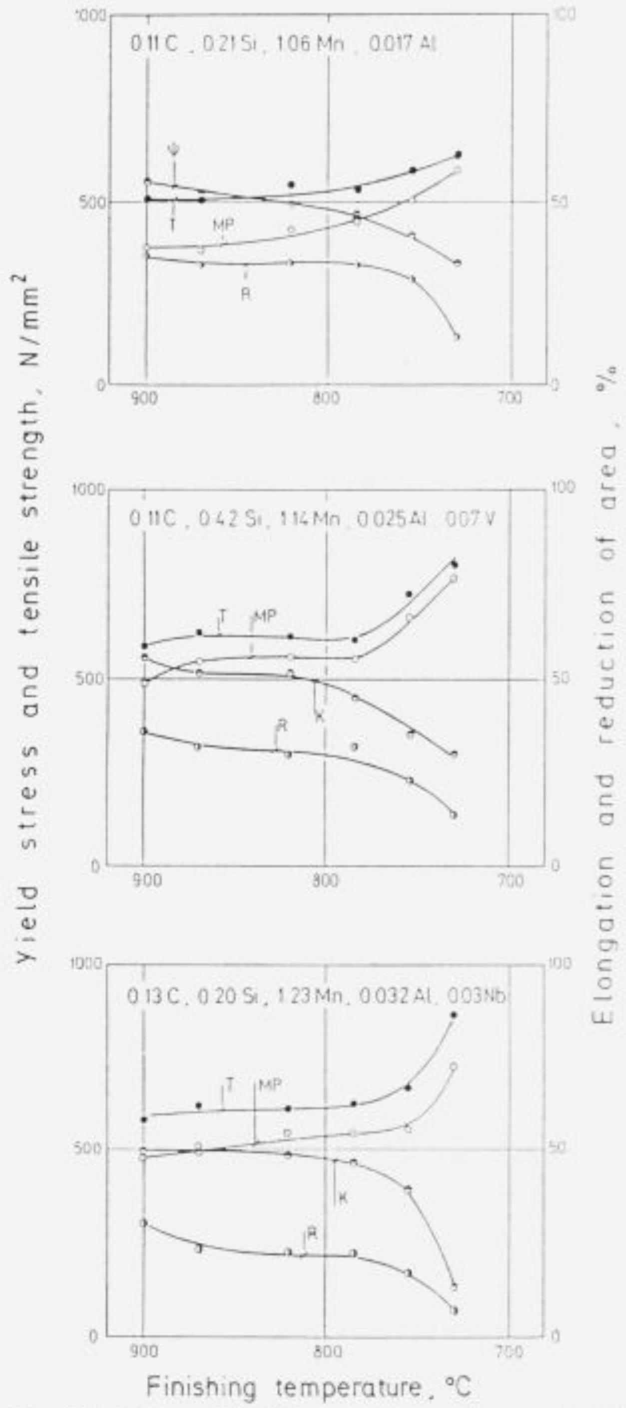

Figure 11. Influence of final rolling temperature on the properties of three steel (Ref.[26]).

Slika 11. Vpliv temperature na koncu valjanja na lastnosti treh jekel. Po viru[26].

in austenite than other phases. **Fig. 4** shows the influence of vanadium and niobium in a case hardening CrMn steel of the same composition, and without aluminium, on the size of austenite grains after annealing at the temperature of 920°C [16]. The equal efficiency in hindering the austenite grain growth is achieved by an about 5 time smaller content of niobium. The reason is the previously mentioned higher solubility of vanadium carbonitride in austenite at the normalizing temperature. The better efficiency of niobium in the control of the austenite grain size indicates that it is a more economic microalloying element. Its deficiency is a lower precipitation hardening during the cooling after the normalizing, thus the properties of steels are improved only because of grain refining. In order to estimate the economy of microalloying it is necessary to know also the interacting effects of dispersoide phases, i.e. the capability of an element to disintegrate the dispersoide phase of other elements, the reactivity of microalloying elements with other elements in steel which do not form efficient dispersoide phases, the diffusivity of microalloying elements, and their minimal efficient contents. Data on the free formation energies of dispersoide and on the diffusivities of microalloying elements in austenite are gathered in **Table 2.** The higher is energy of formation the greater is the stability of the dispersoide phase.

Table 1.

Element		Dispersoide
A, %	B, %	
Al 0.01	Al 0.015 at 0.008 N	AlN
Nb 0.024	Nb 0.036 at 0.18 C	NbC
Ti 0.015	Ti 0.022 at 0.18 N	TiC
V 0.018	V 0.039 at 0.02 N	VN
	V 0.15 at 0.18 C	VC
	V 0.05 at 0.5 C	VC

A—Content of microalloying element which ensures an equal volume of precipitates, and
B—Minimal content of microalloying element which hinders the growth of austenite grains at 920°C.

Table 2. Free energies of formation of dispersoide and the diffusivities of constitutive metals

Free energy of formation				Diffusivity, cm^2/s
kcal/mole		kcal/mole		at 920°C
AlN	46.7			Al 7.0×10^{-9}
TiN	53.5	TiC	40	Ti 7.3×10^{-12}
VN	17.5	VC	18	
NbN	32	NbC		Nb 8.85×10^{-12}

The most stable compound is titanium nitride. At simultaneous presence of several microalloying elements, nitrogen will in equilibrium conditions first of all bind to titanium, probably already in the melt, during the solidification, or soon after the solidification of steel. Titanium consumed, nitrogen can bind to aluminium, then to niobium, and finally to vanadium. This occurs only at annealing which ensures the equilibrium. By shorter annealing, also at normalizing, also the rate of precipitation must be considered. The latter is the higher the higher is diffusivity of cations in austenite (nitrogen and carbon are interstitials and their diffusivity is for several orders of magnitude greater, therefore their diffusion can be neglected when compared with that of aluminium, titanium, etc.). Therefore the highest formation rate would be expected for AlN, than by VN, NbN, and finally TiN. The rate of precipitate formation depends also on the content of microalloying elements in the neighbourhood of precipitation nuclea. The greater is the content expressed in atom.% the higher is its amount in precipitate though its diffusivity is lower than the diffusivity of element with a smaller content in steel.

Among the carbides the most stable is titanium carbide, followed by niobium, and finally vanadium carbide which is completely dissolved in austenite already at the normalizing temperature. Also the solubility of vanadium nitride is relatively high. Thus vanadium is efficient as microalloying element for the control of austenite grain size only at concentrations above 0.1%, while at lower contents it produces a precipitation hardening if such hardening is possible due to the thermal regime.

Microalloying elements react also with other elements and form compounds which do not harden the steel neither influence the mobility of austenite grain boundaries, thus they have no influence on the grain size. E.g. aluminium is first bound to oxygen and only then to nitrogen. Similar is the behaviour of titanium which reacts additionally also to sulphur. Niobium and vanadium react in normally deoxidized steel only to nitrogen and carbon. Therefore the microalloying with aluminium and titanium is efficient only if care is taken that they are not consumed in reactions to oxygen or oxygen and sulphur.

Considering all the influential parameters, the microalloying with aluminium is the least expensive. In steel manufactured by melting in electric arc furnace one finds habitually 0.008 to 0.012% nitrogen and thus with 0.02% aluminium which is not bound to oxygen a sufficient stability of austenite grains is achieved if the annealing temperature does not exceed 920°C. For additional safety a higher content of aluminium 0.025 to 0.030% is recommended. Greater amount does not increase the effect of microalloying since the solubility of AlN in austenite is diminished and a higher temperature of heating of the steel before rolling is required. This is not economical and it is often also harmful for the steel properties after the rolling. A higher aluminium content is also not required for deoxidation since already 0.01% Al reduces the solubility of oxygen in steel melt to about 5 ppm[27]. Aluminium does not bind to carbon and sulphur therefore its efficiency does not depend on the amount of those two elements in steel. Data on the AlN solubility in austenite containing medium and high concentrations of carbon are not disponible, therefore it is not known whether the solubility product in those steels is equal to that in steel with up to 0.2% C. Also if the solubility product would be the same, a different effect of the same quantity of precipitates as in the lower carbon steel is to be expected. The reason is that the mobility of austenite grain boundaries depends also on the surface energy of austenite which further depends on the quantity of alloying elements and impurities in solution.

Titanium diminishes the effect of AlN since it could desintegrate this phase at longer annealing, e.g. during the case hardening annealing. Titanium decreases also the effect of niobium and vanadium. Therefore the combination of titanium and other microalloying elements does not give an effect proportional to the level of alloying. Also the combination of aluminium and vanadium is not especially efficient at a normal nitrogen content, it is successful only by a nitrogen content of above 0.015% and a vanadium contents over 0.1%. This is used in modern steel for thermomechanical (controlled) die forging of parts for car motors. Forgings made of those steel do not require the heat treatment after forging because the controlled cooling ensures a suitable microstructure of steel and the required combination of strength and toughness. This steel contains also 0.01 to 0.02% Ti with the aim that TiN precipitates formed at the cooling after the solidification (**Fig. 12**), hinder an excessive austenite grain growth during the heating before the die forging. In order to achieve an efficient complex microalloying of such steel with aluminium, nitrogen, vanadium, and titanium it must be continuously cast into billets with a cross sections up to 150 × 150 mm with magnetic stirring.

Therefore it is evident that the most suitable combination of microalloying elements in standard steel with normal nitrogen is aluminium, niobium, and vanadium. The first is bound to nitride, the second into carbonitride with about 90% of carbide, therefore they do not interfere mutually. Both are efficient during the rolling, while vanadium contributes for the precipitation hardening during the cooling from the rolling or normalizing temperature. Niobium also does not react with oxygen and sulphur therefore it is all available for the improvement of steel properties.

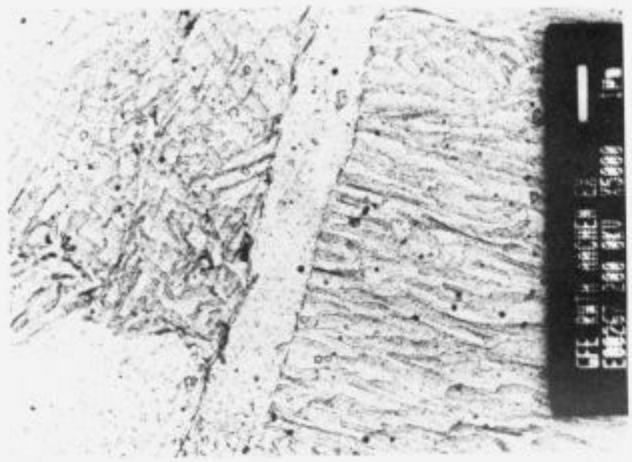

Figure 12. TiN precipitates in steel with 0.32% C, 0.02% Ti, 0.015% N, 0.12% V, 0.025% Al, 0.60% Si, and 1.4% Mn. Carbon extraction replica was prepared from a die forged shaft. TiN precipitates were formed during the cooling below the solidification temperature of steel.

Slika 12. Izločki TiN v jeklu z 0.32% C, 0.02% Ti, 0.015% N, 0.12% V, 0.025% Al, 0.60% Si in 1.4% Mn. Ogljena ekstrakcijska replika je bila pripravljena na utopno skovani ojnici. Izločki TiN so nastali pri ohlajanju kmalu pod temperaturo strjenja jekla.

Titanium also reacts with oxygen and sulphur, therefore an economic microalloying required a good preceding deoxidation and desulphurisation of the steel, i.e. oxygen and sulphur must be bound to aluminium and calcium before titanium is alloyed. The solubility of titanium nitride in molten steel is small, and TiN is formed in the melt already by 0.02% Ti and 0.015% N. Titanium nitride formed in the melt on during the solidification is useless or even harmful. Recent references[28] recommend the titanium contents in steel for controlled forging to be close to 0.01% which ensures that more nitrogen is free for binding into VN precipitates below the solidification temperature which hinder the grain growth at heating before the forging.

In general for structural steels the aluminium/niobium/vanadium combination is the most efficient and the majority of microalloyed steel is based on. The steels for controlled forging and some steels for strips represent an exception. Additional effects are due to the fact that niobium strongly hinders the interpass static recrystallization of austenite already at the level of microalloying. Titanium is used in some hot rolled strips, steels for controlled forging, and case hardening steels with higher grain stability and a narrow-band hardenability microalloyed also with boron. The role of titanium in these steels is not the control of austenite grain size or precipitation hardening but the prevention of the binding of boron to nitrogen which is a precondition for the strong boron effect on steel hardenability.

7 Summary

The paper gives a short review on the influence of aluminium, niobium, titanium, vanadium and nitrogen as microalloying elements on the properties of steel. The size and stability of austenite grains, dispersoide phases formed from microalloying elements, precipitation hardening, influence of microalloying elements on the hot deformation, and the economy use of various elements for microalloying of steel are discussed.

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