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Faculty of Mechanical Engineering**

**Pattantyús-Ábrahám Géza Mechanical Sciences
Graduate School**

**The metallurgical background of the production technology of
aluminium killed low carbon steels for forming purposes**

PHD THESES

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*Theses critiques and minutes recorded on the defence can be viewed later
in the Dean's Office of Faculty of Mechanical Engineering
of Budapest University of Technology and Economics*

1. Introduction

My PhD thesis is connected to the field of material science, its title is: The metallurgical background of the production technology of aluminium killed mild steels for plastic working purposes. The aluminium killed mild steel sheets are frequently used for cold worked parts or housings. The thesis deals with the production technology of DC04 and DC05 steels manufactured according to EN ISO 10130:2007. The chemical composition of these steels is characterised by the followings: 0,02-0,05% C, 0,18-0,3% Mn, 0,008-0,01% Si, 0,018-0,025% Cu, 0,015-0,028% Cr, 0,03-0,06% Al and 0,004-0,006% N. The specification of these steels allow larger alloying and impurity levels; however, in order to satisfy the criteria of yield strength and formability, it is advisable to keep the chemical composition in the range given above. The mechanical properties of DC04-05 steels is characterised by tensile tests. The qualification procedure involves the testing of the elongation at fracture, the logarithmic strain at the end of uniform deformation and the minimal value of plastic anisotropy (r-value) is prescribed as well. The production technology involves seven main steps: preheating of the continuously cast slabs, hot rolling, coiling, burnishing, cold rolling, annealing and skin pass rolling.

The steps of the proper production technology are given in Fig. 1.

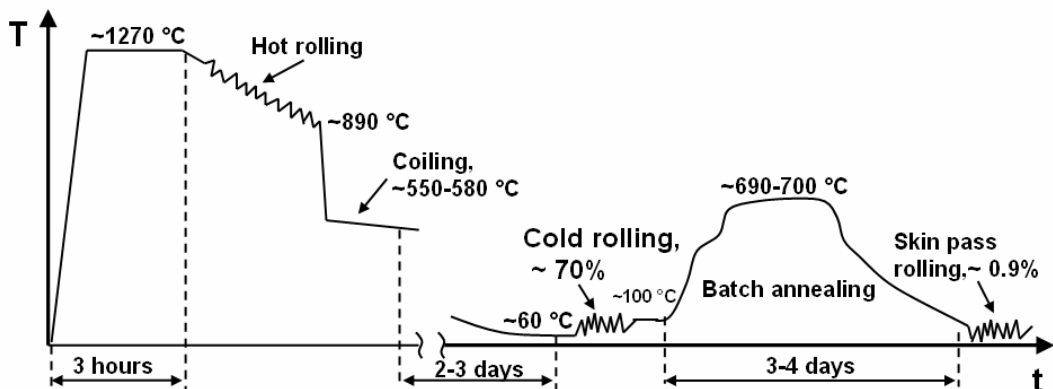


Fig. 1: The main steps of the production technology of aluminium killed low carbon steels (Mucsi, 2014 b)

The slabs are heated up in gas furnaces up to approx. 1270 °C. This heating up needs 190-210 minutes, after that hot rolling follows. The hot rolling is performed on the roughing and finishing mills, always in the austenite region. The hot rolled strip is cooled down using water jets to the coiling temperature (proper value: 550-580 °C) after the last step of hot rolling. The coiled strip cools very slowly, in 2-3 days to the further processing temperature (~ 60 °C). After the burnishing procedure, the hot rolled strip is formed further by cold rolling. In spite of the application of intensive cooling-lubricating fluids, the strip warms to 100-120 °C during cold rolling. The cold rolled strip is coiled again, and 3 or 4 coils are packed on each other to perform an annealing using bell-type furnaces. The annealing requires 3-4 days.

The softened steel strip is not advantageous in this state to plastic forming operations due to the discontinuous yielding effect. To abolish the discontinuous yielding, skin pass rolling is performed at high strain rate to approx. 0.9 % thickness reduction. The excellent formability requires the strict fulfilment of several technological parameter. The key element of the production technology of excellent formable steel sheet is the precipitation of nitrogen

containing phases and their interaction with the recrystallisation process. These processes should occur during the annealing, therefore the most important task is the dissolve the nitride precipitates present in the continuously cast slab, and keep the nitrogen in solid solution until the beginning of the annealing. In order to ensure that, small interpass times during the hot rolling, approx 900 °C finishing temperature and smaller than 600 °C coiling temperature is necessary.

The observance of these technological parameters is not enough to get excellent deep drawable steel sheet. The phase shift between the nitride precipitation and recrystallisation strongly affect the formability of the end-product. Since the nitride precipitation has a great importance in the production technology, one of the aims of my thesis is to develop a methodology for measuring the nitride precipitation and to establish the precipitation kinetics. Further question was the effect of hot rolled grain size on the nitride precipitation and the relationship between the optimal formability and the phase shift between the nitride precipitation and recrystallisation.

The other topic of my thesis formed during the tensile tests of heat treated Al-killed steels. In the case of heat treated tensile test specimens, a strange behaviour has been observed. In some cases, the upper yield strength was much larger than the tensile strength, but in other cases, its value was even larger than the lower yield strength. According to the literature, the large deviation in the upper yield strength is caused by the eccentric loading of the tensile test piece in the elastic region. Since clear and correct experimental work has not been published yet, the other aim of my thesis is to develop, test and application a new gripping system, which can provide centric (or in a predefined extent) eccentric loading.

2. Literature review

The basic of the production technology of DC04-05 thin sheets is the precipitation kinetics of nitrides (usually aluminium nitrides). There are many experimental and simulation result on the precipitation of nitrides in soft and deformed austenite, less for undeformed ferrite and only a few for deformed ferrite. Since the nitrides present in DC04-05 steels are mainly aluminium nitrides (but usually other nitrides can also form) the most of the simulations are concerning with the precipitation of aluminium nitride. However, the experimental methods provide the measurement of the amount of all of the nitrides or the free nitrogen content of the steel. Other methods measure the change of some physical property like electrical conductivity. Therefore, the measurements pertain to the precipitation of all of the nitrogen containing phases. The free nitrogen content of steels can be measured using selective dissolution techniques, internal friction or thermoelectric power based methods. The nitrides forming at large temperature (>550-600 °C) are usually hexagonal aluminium-nitrides, whilst those forming in cold rolled microstructure at low temperature are usually cubic aluminium-nitrides or mixed aluminium-chromium nitrides. The nitrides formed in cold rolled microstructure are gradually transform into pure hexagonal aluminium-nitride.

The nucleation of nitrides is occurring usually at the grain boundaries and in the vicinity of dislocations. The question is: what is the effect of the hot rolled grain size on the precipitation of nitrides in hot and cold rolled material. Clear experimental work on this topic is not published yet, only several simulation results are available. According to the simulation results of Radis and Kozeschnik (2010), the hot rolled grain size has a large effect on the precipitation kinetics, however, experimental results do not confirm their simulations. I did not find any experimental result on how the hot rolled grain size affects the precipitation in cold rolled state; therefore, my investigations are also concerned with that.

The other topic of my thesis is the measurement of the upper yield strength of low carbon, cold worked and heat treated steels. The uncertainties of the gripping of a tensile test piece and its effect on the measured limit of elasticity appeared in Davis monograph in 2004. According to the estimation published in this work, in order to establish the limit of elasticity within 1 % precision, the eccentricity between the resultant loading force and the axis of symmetry of the test piece should be less than $0.00125 \cdot d$ (d is the diameter of the test piece). This theory-based approximation pertains to the limit of elasticity, but the upper yield strength could exhibit similar sensitive behaviour. Hutchinson (1957) and Sun (2005) measured the upper yield strength of inhomogeneously heat treated low carbon steel wires. They demonstrated, if the stress concentration at the grips is eliminated (by application of cold drawn wires which were annealed only in the middle), then extremely large (larger than the tensile strength) upper yield strength can be reproducibly measured. Gray and McCombe used strain gauges mounted on specimens to investigate the bending and axial stress ratio during elastic loading. According to their experimental results, the bending stress could reach the 60-80% of the axial stress. In spite of the published experimental and theoretical results, the exact value of the upper yield strength and its dependence on the gripping uncertainty are not clearly described.

4. Experimental materials and methods

My experimental materials have been prepared from the first coil, from 2 metres from the head end and from the centreline of the strip of hot and cold rolled low carbon steel coils. The composition and some important technological parameters of the experimental materials are given in table 1.

| Sign | Quality | Finishing temp. (°C) | Coiling temp. (°C) |
|------|-----------|----------------------|--------------------|
| A | S235JR +N | 886 | 562 |
| B | DC05 | 883 | 564 |
| C | St24 | 886 | 566 |
| D | DC04 | 882 | 614 |

| Chemical composition, weight pct. | | | | | | | | | | | | |
|-----------------------------------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Sign | C | Si | Mn | P | S | Al | Cu | Cr | Ni | Mo | N | B |
| A | 0.110 | 0.015 | 0.61 | 0.010 | 0.015 | 0.060 | 0.094 | 0.049 | 0.040 | 0.002 | 0.004 | 0.000 |
| B | 0.044 | 0.009 | 0.26 | 0.008 | 0.009 | 0.031 | 0.028 | 0.018 | 0.015 | 0.002 | 0.006 | 0.000 |
| C | 0.024 | 0.008 | 0.20 | 0.005 | 0.012 | 0.041 | 0.009 | 0.021 | 0.032 | 0.002 | 0.005 | 0.003 |
| D | 0.05 | 0.018 | 0.23 | 0.011 | 0.006 | 0.029 | 0.037 | 0.033 | 0.032 | 0.003 | 0.004 | 0.000 |

Table 1: The experimental materials and their important technological parameters

Steel A and B were received in hot rolled (4 mm thick) condition, whilst steel C and D were cold rolled to 1 mm thickness in the steel plant. Steel A showed layered microstructure along the thickness of the material. The distribution of grain size was uneven within the thickness of the sheet (Fig. 2). The grain size was determined according to the standard EN ISO 643:2003 : the grain size in the 0.8 mm thick near-surface layer was approx. 23 μm (grain size number = 8) whilst at the center of the sheet it was approx. 9 μm (grain size number =

11). The difference in the chemical composition of the layers was in the range of the uncertainty of the measurement.

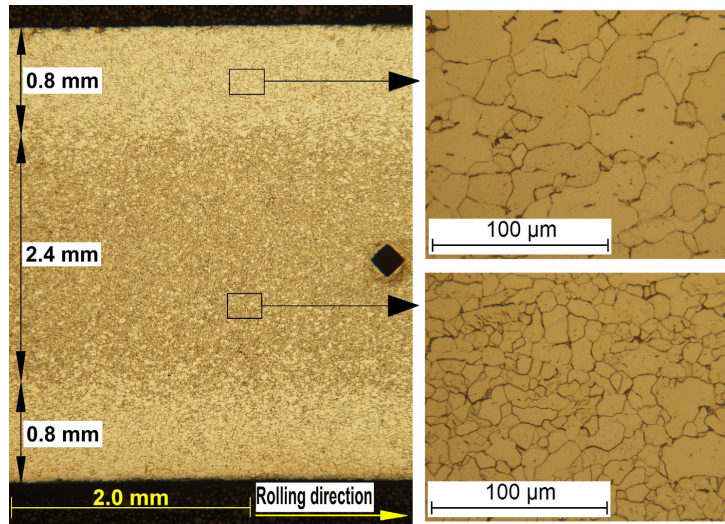


Fig. 2: The layered microstructure of steel B (Mucsi, 2014 a)

I established the nitride precipitation kinetics using the decrease of the free nitrogen of the steels, using special heat treatment, cold working procedures and the measurement of thermoelectric power. I used the methodology introduced by Massardier et. al (2003) for determining the precipitation kinetics of nitrides in hot rolled state, but for cold rolled state the I have modified their experimental method.

During a thermoelectric power test, a wire or narrow band shaped specimen is placed between two copper blocks. The voltage arising due to the Seebeck-effect is proportional to the temperature difference and to some microstructural property.

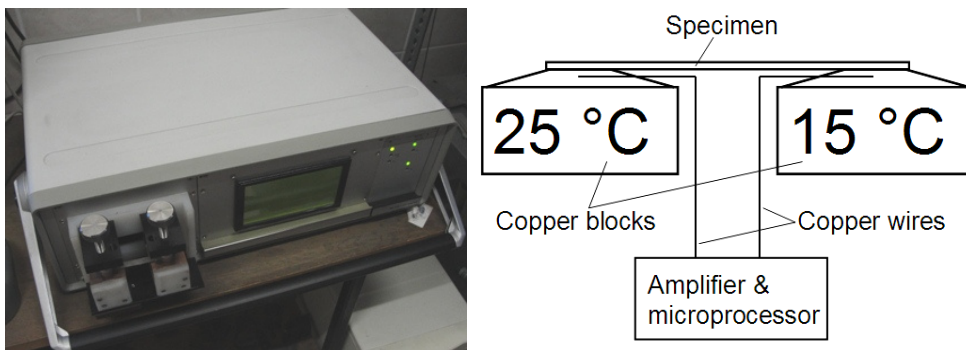


Fig.3: Thermoelectric power measuring device and its layout

The amount of free nitrogen is measured by a special four-step methodology. In the first step, performed at 550-700 °C, the precipitation of nitrides is induced. In the second step a equilibrating heat treatment at 270 °C has been performed. After that cold rolling to 75% thickness reduction and finally aging at 120 °C for 45 minutes were applied. The value of the thermoelectric power before and after the aging carries the information on the amount of free nitrogen in steel.

In cold rolled state, the precipitation inducing heat treatment is performed in range 430-510 °C, which was followed by a rapid recrystallisation treatment at 700 °C for 1 minute. After that equilibrating treatment at 270 °C, cold rolling to 75 % thickness reduction and aging at 120 °C for 45 min. were performed. This method was applied also for partially recrystallised samples.

Avrami- and Arrhenius equations have been used to describe mathematically the nitride precipitation. The interaction between the nitride precipitation and recrystallisation has been also investigated. The formability of the microstructure arising during the interaction process is tested by Erichsen cupping tests (According to EN ISO 20482:2003 and by measuring the r-value according to EN ISO 10113:2006. The mechanical properties of tensile test specimens heat treated by different methods has been also determined. This is performed in cooperation with ISD Dunaferr steel plant.

The other topic of my thesis is the effect of nonaxial loading on the measured upper yield strength of tensile test specimens. I have developed a novel gripping system, which can provide uniaxial loading. This fact was proved by strain gauge experiments and tensile tests. The assembly of the novel gripping system is given in Fig. 4.

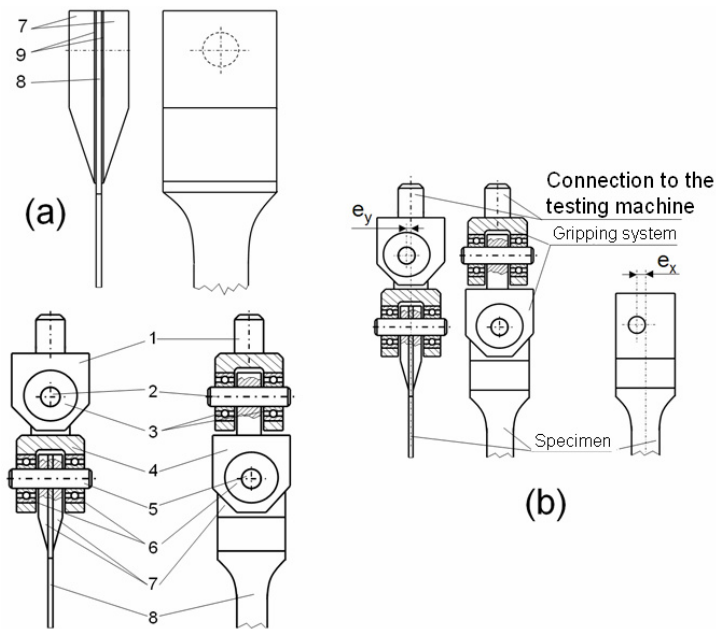


Fig. 4: The new gripping system for tensile tests

The working principle is the following: Fortifications (7) were stuck using high strength glue (9) to the grip section of the tensile test specimen (9), which serve as load transferring elements. A spider (1-6 parts) performs the load transfer from the machine to the test piece. The spider is connected to the fortification's hole. The line of the resultant loading force is determined by the location of the holes in the fortification. The spider made possible to compensate the alignment errors between the machine and test piece.

The testing of the new gripping system is performed on steel C and D. The tensile test specimens were in heat treated condition. The heat treatment is performed in the laboratory, using the following steps: heating up at 30 °C/h to 650 °C, holding at this temperature for 5 hours and finally cooling in furnace. The geometry, dimensions and allowances of the test pieces are given in Fig. 5.

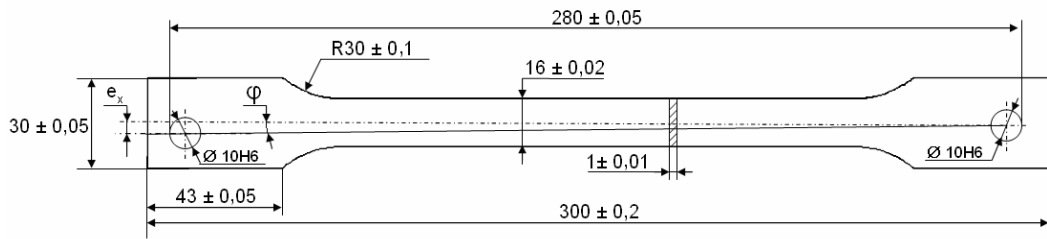


Fig. 5: Special tensile test specimens used for investigate the upper yield strength

5. The main results of the thesis

The effect of hot rolled grain size on the precipitation of nitrides

According to my experimental work, the hot rolled grain size has a large effect on the nitride precipitation. Figure 6 shows the decrease of free nitrogen content of the steel on different isotherms between 550 and 700 °C. Diagrams show the results for steel B, for grain sizes 9 and 23 μm .

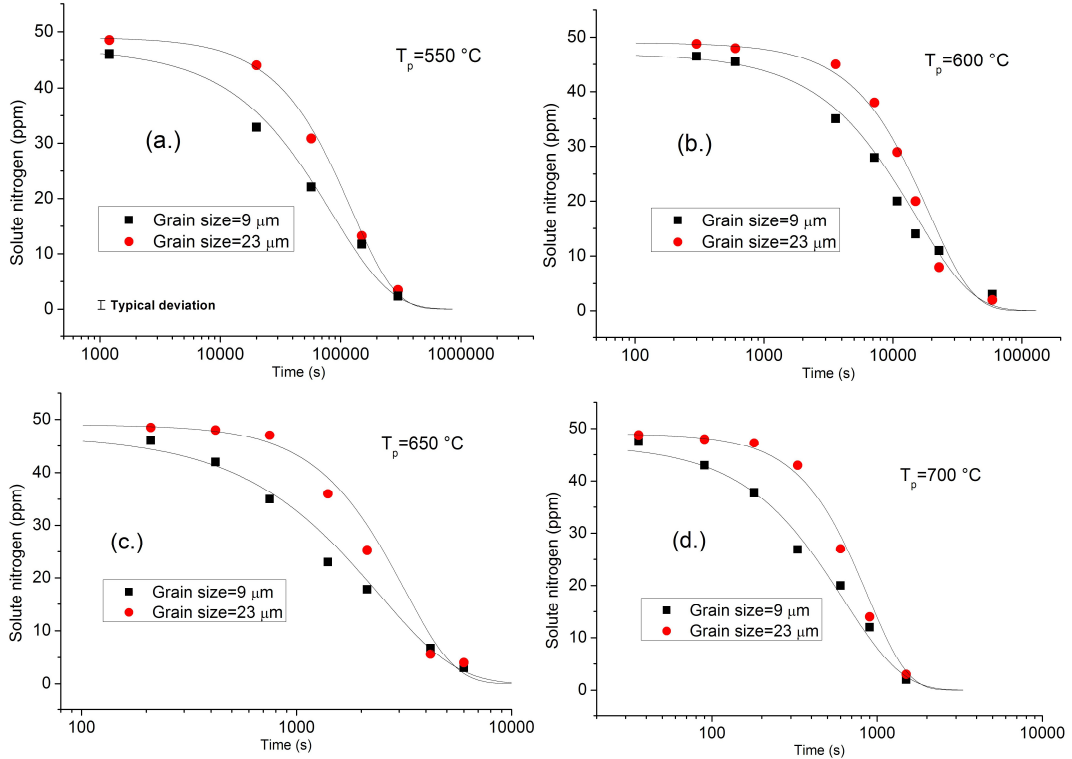


Fig. 6: The change of free nitrogen in steel B. The effect of grain size is remarkable (Mucsi, 2014 a)

It can be established for every temperature, that the decrease of free nitrogen in the 9 μm grain size material occurs much intensively than in 23 μm grain size material. This is due to the larger number of nucleation sites in the 9 μm grain size material. (Because the specific grain boundary area and therefore the possible sites for nucleation is approx. 2.5 times larger

in the 9 μm grain size material than in the 23 μm grain size material.) Moreover, the smaller grain size cause shorter diffusion distances from the grains to the grain boundaries.

Furthermore, I have established that the curves corresponding to the different grain sizes are approaching each other with increasing treatment time. This means, that the preferential nucleation and growth sites are the grain boundaries until the precipitated fraction reaches ~ 70%, after that the precipitation continues inside the grains along dislocations and in the vicinity of other lattice defects.

The effect of hot rolled grain size on the precipitation in cold rolled state is tested on specimens prepared before cold rolling from the different layers in steel B. The prepared specimens were cold rolled to 75 % thickness reduction and precipitating treatments at 430-510 $^{\circ}\text{C}$ were performed. Figure 7 shows the decrease of free nitrogen content of sold rolled steel B; for initial, hot rolled grain sizes of 9 μm and 23 μm .

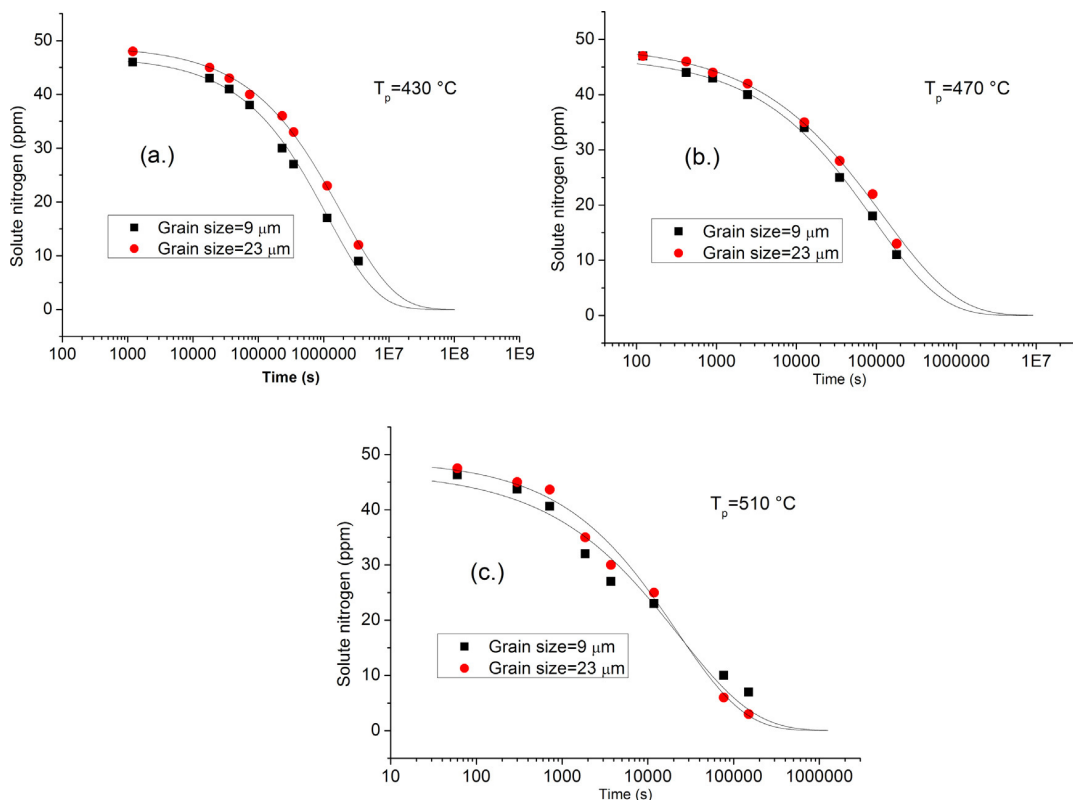


Fig. 7: The effect of hot rolled grain size on the decrease of free nitrogen in cold rolled state specimens (steel B) (Mucsi, 2014 a)

As it can be seen in Fig. 7, the rate of decrease of free nitrogen in the cold rolled specimens is almost independent of grain size. Comparing this with the precipitation kinetics in hot rolled state, it can be established that the hot rolled grain size has much smaller effect on the precipitation of nitrides in cold rolled state. This is because the preferential nucleation sites are the lattice defects inside the grains (mainly dislocations) and therefore the grain boundaries loss their significancy. After cold working, the density of lattice defects (and therefore the number of nucleation sites) is much larger than in hot rolled state.

The kinetics of nitride precipitation is described using the $Y = 1 - \exp(-(k \cdot t)^n)$ Avrami-type and the $k = A \cdot \exp(-Q/(R \cdot T))$ Arrhenius-type equation. In the equations, Y is the precipitated fraction of nitrides (the ratio of precipitated and initial free nitrogen), R is the universal gas constant, t is the time (in seconds), T is the temperature in Kelvin.

Using the fitted equations the amount of nitride precipitation during the slow cooling after the coiling process was simulated. The question was how many nitrogen precipitates before and after the coiling procedure. In Fig. 8, the amount of precipitated nitrides forming during the slow cooling after coiling at different temperatures is given.

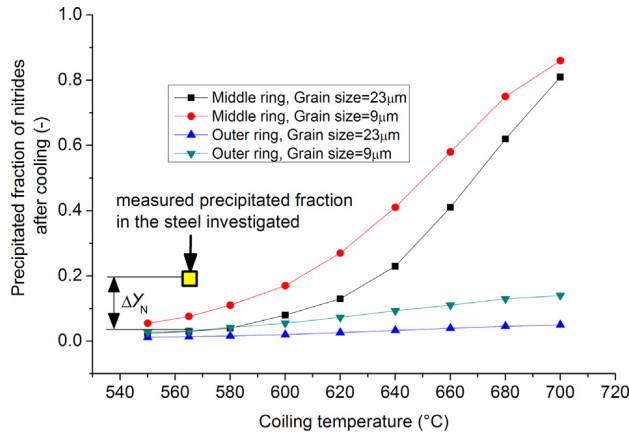


Fig. 8: The amount of nitride precipitation during the slow cooling after coiling at different temperatures (Mucsi, 2014 a)

As it is revealed in Fig. 8, the coiling temperature applied for steel B (564 °C) cause only approx. 3-5 % nitride precipitation, depending on the grain size of the material. In steel B, the total nitrogen content of the steel was ~ 60 ppm, whilst the average free nitrogen content in cooled coils was approx. 48 ppm. This means that the 20 % of the nitrides are precipitated in this state. Since ~ 3-5 % is precipitating during the slow cooling after coiling if 564 °C coiling temperature is applied, approx. $\Delta Y_N=15-17$ % of the nitrogen content of the steel forms precipitates during the technological steps before the coiling.

Some result of the investigation of the interaction between precipitation and recrystallisation

In order to investigate the nitride precipitation-recrystallisation interaction, specimens from the centre of steel B were prepared. These specimens were cold rolled to 75 % thickness reduction. The cold rolled specimens were isothermally heat treated at different temperatures between 520 and 600 °C for different times. The recrystallised fraction of the specimens was measured in the section parallel to the rolling direction; moreover, the precipitated nitride fraction was also evaluated. The results are given in Fig 9 and 10.

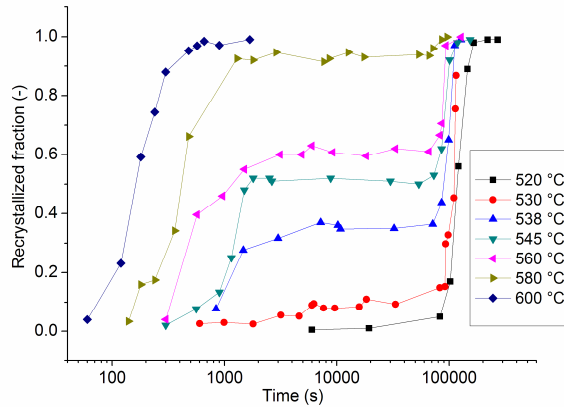


Fig. 9: The change of recrystallised fraction in cold rolled steel B during isothermal heat treatments (Mucsi és Felde, 2014)

In Fig. 9, it is remarkable that a strong retardation appears in the recrystallisation process (except at 520 and 600 °C). The retardation appears at different recrystallised fractions depending on the temperature: at 530, 538, 545, 580 és 580 °C the plateau starts at 10, 35, 50, 62 és 93% recrystallised fraction. In order to clarify the connection between the appearance of the retardation effect and nitride precipitation, the precipitated fraction of nitrides has been also measured. Using the recrystallised and precipitated fractions, the recrystallisation-precipitation time temperature (RPTT) diagram was constructed (Fig. 10).

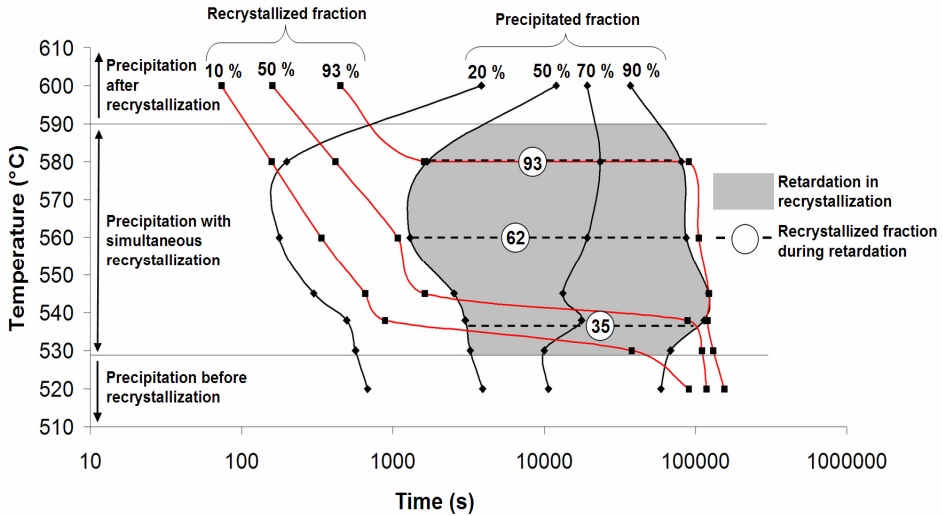


Fig. 10: Isothermal recrystallisation-nitride precipitation-time-temperature chart (Mucsi és Felde, 2014)

According to my experimental results, the strong retardation in the recrystallisation starts when the precipitated nitride fraction reaches approx 45-50%, independently on temperature. The retardation effect finishes, when the precipitated nitride fraction reaches approx. 85-95%. The formability of the microstructure arising during recrystallisation is tested on continuously heated specimens. Erichsen and tensile test pieces were heated up at 20, 30, 55, 85 and 120 °C/h heating rate to 690 °C, and they were held at this temperature for 6 hours. Their formability test results are shown in Fig. 11.

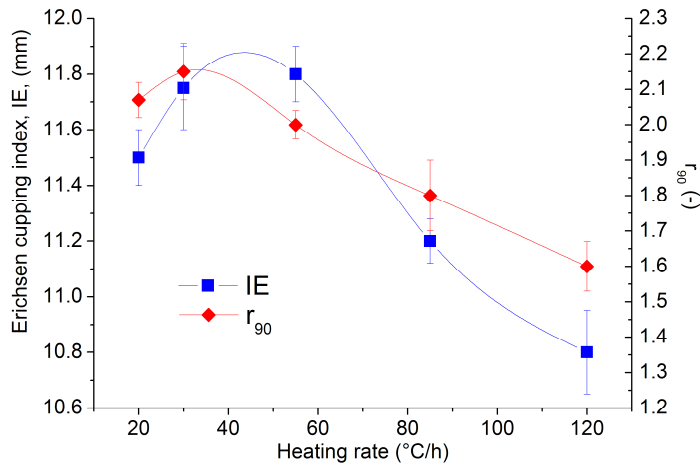


Fig. 11: A Effect of heating rate on formability of steel B (Mucsi, 2014 b)

On the basis of industrial experiences, and my experimental results given in Fig 11, the optimal heating rate is ranging between 30 and 45 °C/h. The good formable microstructure is connected to the interaction of nitrides and recrystallisation. Since the heating rate in the coils during the bell-type batch annealing procedure is not constant, my aim was to connect the optimal formability not to the heating rate but to the correct phase shift between the recrystallisation and nitride precipitation. In order to give such approximation, I heated up at 20, 30, 55, 85 és 120 °C/h heating rate until the precipitated fraction reached approx 5% (to approx. 525...530 °C), after that I measured free nitrogen content and evaluated the precipitated nitride fraction (Fig. 12.).

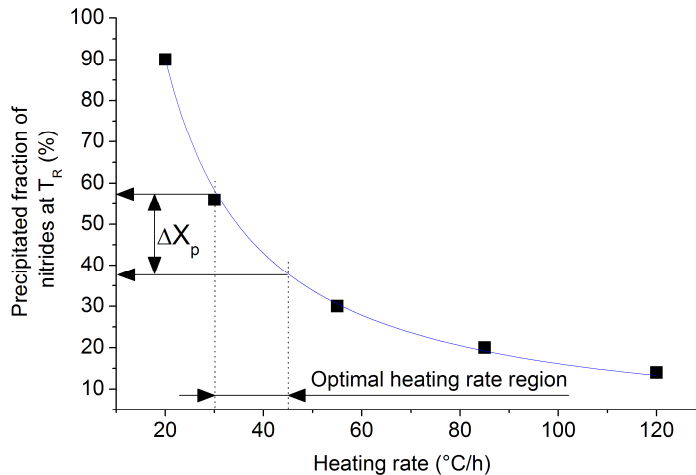


Fig. 12: The relation between the optimal heating rate and nitride precipitated fraction at the beginning of the recrystallisation (Mucsi, 2014 b)

The experimental results clearly show that if optimal heating rate is applied, then the precipitated nitride fraction is approx. 37-57 %. The criterion for the development of good formable microstructure is that the nitride precipitation should occur in 37-57% extent before the recrystallised fraction reaches 5%.

The results of the investigations of the upper yield strength

The prepared cold rolled tensile test specimens (cold rolling was performed in the steel mill) have been heated up at 30 °C/h to 650 °C, which was followed by 5 hours holding at this temperature, finally, the specimens cooled down in the furnace.

Specimens made of steel “C” were loaded at different eccentricities ($e_x=0,056, 0,15, 0,3$ illetve $0,8$ mm See Fig. 5). The tensile tests performed on an electromechanical testing machine, at 25 °C, at 2 mm crosshead speed, which lead to $1.72 \cdot 10^{-4}$ 1/s elastic uploading.

The results of the tensile tests are presented in Fig. 13.

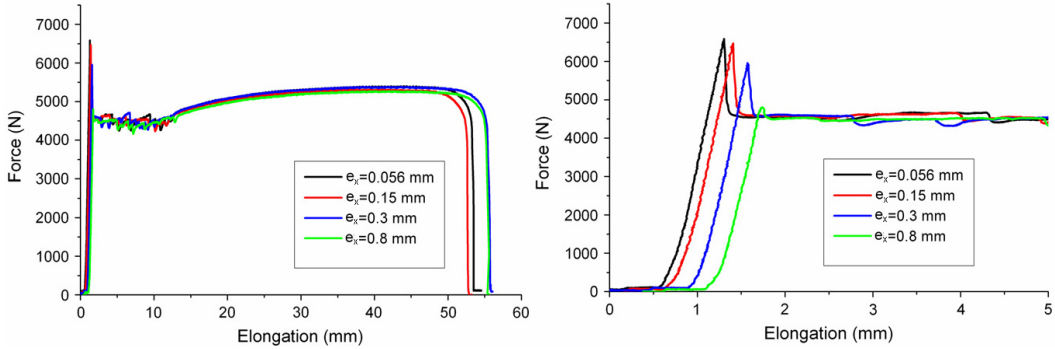


Fig. 13: The dependence of the upper yield strength on the initial loading eccentricity

As it can be seen in previous figures, the measured upper yield strength is much larger at 0.056 mm eccentricity, but its value is even larger than the lower yield strength at 0.8 mm eccentricity. The upper and lower yield strength and the tensile strength are plotted together against the loading eccentricity (Fig. 14).

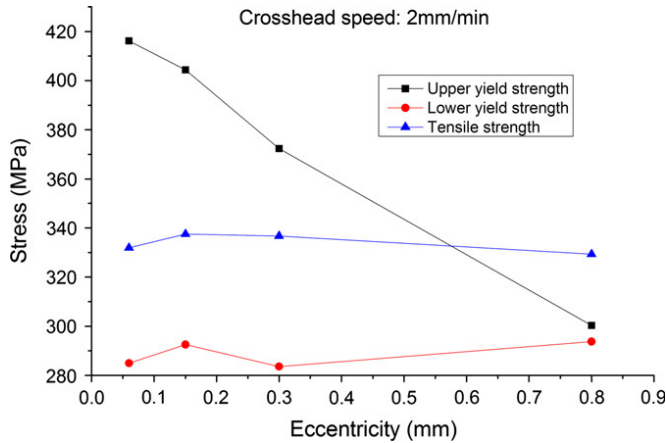


Fig. 14: A The dependence of upper- lower and tensile strength due to loading eccentricity (Mucsi, 2013 a)

The upper yield strength depends strongly on the loading eccentricity, but the lower and tensile strengths do not change with eccentricity. The reason for it is that the lower and tensile strengths are measured after large plastic deformation, during which the test piece align itself to the axis of loading.

Similar results were obtained for steel D. The value of the upper yield strength against loading eccentricity is described by the following equation:

$$R_{eH,mért} = R_{eH,0} - d \cdot e_x \quad (1)$$

where $R_{eH,0}$ is the upper yield strength measured at zero eccentricity (so-called extrapolated upper yield strength) (MPa), which could be a new quantity; d is the slope factor (MPa/mm), e_x is the eccentricity (mm). Parameters for steel C and D are given in table 2.

| Parameter | Material | |
|---|---------------|---------|
| | Steel C | Steel D |
| Extrapolated upper yield strength $R_{eH,0}$ (MPa) | 424,8 (~ 425) | 368 |
| Slope factor, d (MPa/mm) | 157,3 | 62,9 |
| Correlation coefficient, R^2 (-) | 0,9951 | 0,9841 |

Table 2: Parameters of Eq. 1 for steel C and D (Mucsi, 2013 a)

The upper yield strength of steel C decreases with 16 MPa due to the 0.1 mm eccentricity increase. However, this value for steel D is approx. 6 MPa.

In order to express in a general manner the eccentricity of loading, I introduced the angularity error φ (See Fig. 5) between the resultant loading force and the axis of symmetry of the test piece. The measured upper yield strength against the angularity error φ for steel C is:

$$R_{eH,m\acute{e}rt,C} = R_{eH,0} - f \cdot \varphi = 424,8 - 741,11 \cdot \varphi \text{ (MPa)} \quad (2)$$

whilst for steel D:

$$R_{eH,m\acute{e}rt,D} = 368 - 296,41 \cdot \varphi \text{ (MPa)} \quad (3)$$

In equations, the φ should be substituted in degrees.

5. Industrial application of the results

The results of my researches were applied in ISD Dunaferri to optimise the production technology of DC04-05 thin sheets. Before the optimisation, DC05 quality sheets could be produced very rarely, because it was difficult to ensure lower than 180 MPa yield strength and greater than 1.9 r-value. As a result of my research works many other empirical model has been developed, which can take into account the:

- effect of cold rolling reduction,
- the chemical composition,
- the grain coarsening occurring during the annealing heat treatment
- and the effect of the skin pass rolling

on the final mechanical properties. Using the experiment-based mathematical models, the following technological modifications have been introduced:

- the chemical composition should be in the range 0.02-0.045% C, 0.16-0.25% Mn, 0.03-0.06% Al 0.004-0.007 % N
- the finishing temperature should be in the range 885-900 °C
- the coiling temperature should be in the range 550-580 °C-os
- the cold rolling reduction should be in the range 65-75% (depending on the composition). Moreover,
- a new annealing treatment method was introduced (No. 827), which lead to smaller than 180 MPa proof strength and higher than 1.9 r-value after skin pass rolling.

As the result of the optimisation, the producibility of DC05 became possible and the deviation in the mechanical properties of DC04 decreased.

6. The new scientific results, theses

The new scientific results are connected to the nitride precipitation in DC05 steel and to the special tensile tests performed on St24 steel. The nitride precipitation and its relation with the recrystallisation is the key element of the production technology of aluminium killed low carbon steel strips.

I investigated the nitride precipitation on specimens prepared from the first ring of a DC05 steel coil. The coil is characterised by 883 °C finishing and 564 °C coiling temperature. The chemical composition of the steel (expressed in wt. pct.) is: 0.044% C, 0.26% Mn, 0.009% Si, 0.009% S, 0.008% P, 0.031% Al, 0.02% Cr, 0.015 Ni, 0.006% N és (Ti, Mo, Nb, V<0.001%). The 4 mm thick strip is characterised by three layers along the thickness. In the two 0.8 mm thick near surface layer the grain size number was 8 (grain size is 23 µm), whilst in the central 2.4 mm thick layer the grain size number was 11 (the grain size is 9 µm). The nitride precipitation process was investigated in specimens prepared from the large and fine grain size layers. In order to investigate the nitride precipitation in cold deformed state, the prepared specimens cold rolled to 75% thickness reduction. I used a thermoelectric power test based methodology to investigate the nitride precipitation. I described the nitride precipitation using Avrami- and Arrhenius-type equations.

I used a St24 steel to investigate the dependence of measured upper yield strength on loading eccentricity. The composition of the steel in wt. pct.: 0.024% C, 0.008% Si, 0.195% Mn, 0.041% Al, 0.021% Cr, 0.005% N és 0.003% B. The test pieces prepared from a 75 % cold rolled coil having 886 °C finishing temperature and 566 °C coiling temperature. The tensile test pieces were heat treated in laboratory furnace: they were heated up at 30 °C/h to 650 °C which was followed by 5 hour holding, finally they cooled down in the furnace.

1. thesis:

I showed using thermoelectric power experiments, that a DC05 quality steel strip containing 60 ppm by weight total nitrogen contains only 48 ppm free nitrogen in a hot rolled, coiled and cooled to room temperature condition. The 80% of the total nitrogen content is not included in precipitates and its 20% is free. I showed using experiment-based simulations, that during the cooling after coiling of a hot rolled coil having 850 mm inner, 1990 mm outer diameter and 1200 mm height only 3-5% of the free nitrogen forms nitrides. Consequently, the 15-17% of the free nitrogen forms nitrides during the technological steps before the coiling. (Mucsi, 2014 a)

2. thesis:

In Table T1, I summarized the parameters of the Avrami- and Arrhenius equations referring to the nitride precipitation in DC05 hot rolled steel in temperature interval 550-700 °C. I proved using kinetic investigations that both of the parameters (k and n) in the Avrami kinetic function depend on the hot rolled ferrite grain size. The average value of Avrami-exponent in temperature range 550-700 °C for 9 µm grain size steel is $\bar{n}_g = 1,07$, whilst for 23 µm grain

size steel it is $\bar{n}_{23} = 1,52$. The value of the fitted $k(T)$ function is larger by 34-38% at 9 μm grain size than at 23 μm grain size. (Mucsi, 2014 a)

Table T1.

| Average grain diameter (μm) | T ($^{\circ}\text{C}$) | n (-) | k (1/s) | Correlation of Y(t) function R^2 (-) | Q (kJ/mol) | A (1/s) | Correlation of k(T) function R^2 (-) |
|--|--------------------------|-----------------------|----------------------|--|------------|--------------------|--|
| 9 | 550 | 0.89 | $1.18 \cdot 10^{-5}$ | 0.994 | 221 | $1.196 \cdot 10^9$ | 0.998 |
| | 600 | 0.98 | $6.63 \cdot 10^{-5}$ | 0.978 | | | |
| | 650 | 1.18 | $4.21 \cdot 10^{-4}$ | 0.992 | | | |
| | 700 | 1.22 | $1.60 \cdot 10^{-3}$ | 0.990 | | | |
| | | $\bar{n}_9 = 1.07$ | | | | | |
| 23 | 550 | 1.19 | $8.13 \cdot 10^{-6}$ | 0.992 | 222 | $9.967 \cdot 10^8$ | 0.998 |
| | 600 | 1.26 | $5.28 \cdot 10^{-5}$ | 0.986 | | | |
| | 650 | 1.82 | $3.17 \cdot 10^{-4}$ | 0.976 | | | |
| | 700 | 1.79 | $1.14 \cdot 10^{-3}$ | 0.986 | | | |
| | | $\bar{n}_{23} = 1.52$ | | | | | |

3. thesis:

In Table T2, I gave the parameters of the Avrami- and Arrhenius equations referring to the nitride precipitation in DC05 cold rolled steel in temperature interval 430-510 $^{\circ}\text{C}$. The average Avrami exponents referring to the nitride precipitation in cold rolled, but initially 9 and 23 μm hot rolled grain size material in temperature interval 430-510 $^{\circ}\text{C}$ is equal to the second decimal, their value: $\bar{n}_9 = \bar{n}_{23} = 0,52$; however, the ratio of the rate constants (k_9/k_{23}) at 430, 470 and 510 $^{\circ}\text{C}$ is 1,63, 1,30, and 0,95, respectively. (Mucsi, 2014 a)

Table T2.

| Average grain diameter (μm) | T_p ($^{\circ}\text{C}$) | n (-) | k (1/s) | k_9/k_{23} | Correlation of Y(t) function R^2 (-) | Q (kJ/mol) | A (1/s) | Correlation of k(T) function R^2 (-) |
|--|------------------------------|-----------------------|----------------------|--------------|--|------------|-----------------------|--|
| 9 | 430 | 0.56 | $8.71 \cdot 10^{-7}$ | 1.63 | 0.994 | 225 | $5.255 \cdot 10^{10}$ | 0.983 |
| | 470 | 0.51 | $1.07 \cdot 10^{-5}$ | 1.30 | 0.997 | | | |
| | 510 | 0.49 | $4.38 \cdot 10^{-5}$ | 0.95 | 0.988 | | | |
| | | $\bar{n}_9 = 0.52$ | | | | | | |
| 23 | 430 | 0.53 | $5.33 \cdot 10^{-7}$ | | 0.998 | 256 | $6.259 \cdot 10^{12}$ | 0.990 |
| | 470 | 0.47 | $8.22 \cdot 10^{-6}$ | | 0.996 | | | |
| | 510 | 0.55 | $4.61 \cdot 10^{-5}$ | | 0.998 | | | |
| | | $\bar{n}_{23} = 0.52$ | | | | | | |

(Hutchinson, 1957) Hutchinson, M., M., 1957. High upper yield point in mild steel. *J. Iron Steel Inst.* 186, 431–432.

(Kwon et. al, 1990) Kwon, O., Kim, G., Chang, R. W., 1990. Effect of Hot Rolling Conditions on the Mechanical Properties of Cold Rolled and Annealed Ultra-Low Carbon Steels, *Metallurgy of Vacuum-Degassed Steel Products, The Minerals, Metals & Materials Society*, 215-228.

(Massardier et. al, 2003) Massardier, V., Guétaz V., Merlin, J., Soler, M., 2003. Kinetic and microstructural study of aluminium nitride precipitation in a low carbon aluminium-killed steel, *Materials Science and Engineering A* 355, 299-310.

(Massardier et. al, 2004) Massardier, V., Lavaire, N., Merlin, J. 2004. Quantitative evaluation of the interstitial content (C and/or N) in solid solution in extra-mild steels by thermoelectric power measurements, *Scripta Materialia* 50, 131–135.

(Mucsi, 2009) Mucsi A., 2009. Termikusan aktivált folyamatok modellezése új módszerrel, *Bányászati és Kohászati Lapok, Kohászat* 5, 1-4.

(Mucsi, 2012) Mucsi A., 2012. Lágycélok felső folyáshatárának vizsgálata, In: Bitay Enikő (szerk.) *FMTÜ XVII. Nemzetközi Tudományos Konferencia*. Kolozsvár: Erdélyi Múzeum-Egyesület, 251-254.

(Mucsi et al., 2012 a) Mucsi, A., Földi, J., Kardos, I., Felde, I., Palkovics, M., 2012. Hidegen hengerelt szalagok lágycélok műveletének gyártástechnológiai felülvizsgálata, optimalizálása, *ISD Dunaferri Műszaki Gazdasági Közlemények* 165, 120-125.

(Mucsi et. al, 2012 b) Mucsi, A., Felde, I., Réger M., Földi J., Szabados O., 2012. Simulation of Annealing Process for Cold-Rolled Strip Steel, In: D Scott Mackenzie (szerk.) *6th International Conference on Quenching and Control of Distortion: Including the 4th International Distortion Engineering Conference*. ASM International, 839-847. (ISBN:978-1-61503-980-7)

(Mucsi et. al, 2012 c) Mucsi, A., Földi J., Kardos, I., 2012. Hidegen hengerelt alumíniummal csillapított lágycél szalagok lágycélok műveletének gyártástechnológiai optimalizálása, In: Tóth Tamás (ed.) *XXV. Hőkezelő és Anyagtudomány a Gépgyártásban Országos Konferencia és Szakkiállítás*. 182-187. (ISBN:978-963-9915-48-0)

(Mucsi and Felde, 2013 a) Mucsi, A., Felde, I., 2013. Simulation and measurement of aluminium– nitride precipitation in hot rolled Al killed low carbon steel coil, *International Heat Treatment and Surface Engineering* 7, 171-174.

(Mucsi and Felde, 2013 b) Mucsi, A., Felde, I., 2013. Simulation and quantitative evaluation of aluminium-nitride precipitation in hot rolled Alkilled steel coils, In: *International Conference and Exhibition in Heat Treatment and Surface Engineering: Concurrent Event 27th Surface Modification Technologies*. Chennai, India, 1-6.

(Mucsi, 2013 a) Mucsi, A., 2013. Effect of gripping system on the measured upper yield strength estimated by tensile tests, *Measurement* 46, 1663-1670.

- (Mucsi, 2013 b) Mucsi, A., 2013. AlN Kiválás Mérése és Szimulációja Melegen Hengerelt Lágyacél Tekercsben. In: Bitay Enikő (szerk.) Fiatal Műszakiak Tudományos Ülésszaka XVIII.: Nemzetközi Tudományos Konferencia. Kolozsvár: Erdélyi Múzeum-Egyesület, 257-260.
- (Mucsi, 2013 c) Mucsi, A., 2013. Analysis of Stress Distribution in Tensile Test Specimens Using Modified Versions of a Novel Gripping System, *Universal Journal of Mechanical Engineering* 1, 109-113.
- (Mucsi, 2013 d) Mucsi, A., 2013. Lágyacélok Felső Folyási Pontjának Fémtani és Méréstechnikai Elemzése. In: Bitay Enikő (szerk.) Fiatal Műszakiak Tudományos Ülésszaka XVIII.: Nemzetközi Tudományos Konferencia. Kolozsvár: Erdélyi Múzeum-Egyesület, 261-264.
- (Mucsi, 2013 e) Mucsi, A., 2013. Alumíniummal csillapított acélszalagok nitridkiválási folyamatai a meleghengerlést követő technológiai műveletek során, *Bányászati és Kohászati Lapok, Kohászat* 146, 1-6.
- (Mucsi, 2014 a) Mucsi, A., 2014. Effect of hot rolled grain size on the precipitation kinetics of nitrides in low carbon Al-killed steel, *Journal of Materials Processing Technology* 214, 1536-1545.
- (Mucsi and Felde, 2014), Mucsi, A., Felde, I., 2014. Analysis of interaction between recrystallization and nitride precipitation in cold rolled Al-killed low carbon steel, *International Journal of Microstructure and Materials Properties*, (vol. 9, no. 6: tervezett megjelenés, elfogadott cikk)
- (Mucsi, 2014 b) Mucsi, A., 2014. Thermoelectric power study of nitride precipitation and recrystallization in continuously heated low carbon Al-killed steel, *Acta Politechnica Hungarica* 11, 87-102.
- (Mucsi and Dévényi, 2015) Mucsi, A., Dévényi, L., 2015. Recrystallization of boron containing and boron-free low carbon steels investigated by thermoelectric power and hardness measurements, *Materials Science Forum*, elfogadott konferenciák
- (Radis and Kozeschnik, 2010) Radis, R., Kozeschnik, E., 2010. Kinetics of AlN precipitation in microalloyed steel. *Modelling and Simulation in Materials Science and Engineering* 18, 1-16.
- (Ray et. al, 1994) Ray, R. K. , Jonas, J. J., Hook, R. E., 1994. Cold rolling and annealing textures in low carbon and extra low carbon steels. *International Materials Reviews* 39, 129-172.
- (Sun et. al, 2006) Sun, H.-B., Kaneda, Y., Ohmori, M., Yoshida F., 2006. Effect of Stress Concentration on Upper Yield Point in Mild Steel. *Materials Transactions* 47, 96-100.