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CONCRETE AND TUBE STEELS MICROALLOYED BY VANADIUM AND NITROGEN

R. Halbrstatova

Iron & Steel Research Institute
Dobra, Czechoslovakia

Tasilo Prnka

Iron & Steel Research Institute
Dobra, Czechoslovakia

Vladimír Smlid

Iron & Steel Research Institute
Dobra, Czechoslovakia

Vlastimil Navrat

Iron & Steel Research Institute
Dobra, Czechoslovakia

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The quality of microalloyed concrete reinforcing steels for building purposes is chiefly determined by precipitation hardening of vanadium carbide and vanadium carbonitride on the inter-phase boundary. Their precipitation effect depends first of all upon their dispersity. Optimal results of rolling these steels for concrete reinforcement are achieved by high rolling speed with relatively high finishing mill train temperatures.

1. Introduction

Improvement of the strength properties of the reinforcing steels for concrete is a permanent subject matter in the field of metallurgy and building industry. The moving force of that interest is the need for ever more effective utilization of metal that would be otherwise got lost for ever from the circulation of raw materials in our national economy. In the ČSSR some 600 000 tons of reinforcing steels are produced per year; this aspect is the main impetus for the steel producers to develop new steel grades that would be able to meet the demands laid on the concrete reinforcement with simultaneous reduced consumption of steel.

In the CSSR the concrete steels are produced in the majority of cases in form of ribbed sections of 6 to 40 mm in dia. in the quality grades up to 410 MPa by the yield limit, see Table 1. The produced proportion of ribbed steel with yield limit above 430 MPa is negligible. To achieve the desirable material savings there is indispensable to pass over to the concrete steels with higher strength properties /with yield limit above 450 MPa/ that would be simultaneously competitive for the common grades in view of the technico-economical parameters associated with manufacture and

application of such steels.

The desirable strength properties can be achieved either by modification the chemical composition of steel /inclusive of microalloying/, by rolling and cold torsion or by controlled cooling of the steel bars from the final-rolling temperature. Nevertheless, the ever more stringent demands for the weldability of steel do not allow in any case enhancement of the carbon content, but rather the opposite of it. One of the acceptable ways how to reach yield limit above 450 MPa is microalloying of steel - utilization of the precipitation hardening and strengthening due to refining of the ferrite grains. In this respect particular emphasis should be laid on utilization of the effect of vanadium in combination with nitrogen.

2. Effect of vanadium and nitrogen on yield limit

Vanadium precipitates in steel in form of carbides, nitrides and/or mixed carbonitrides. The chemical composition, dispersity, the size and hardening effect of the precipitates vary with the analysis of steel /the content of vanadium, carbon and nitrogen/, the thermomechanical processes and the cooling rate from the final-rolling temperature. In the case of steel with vanadium, carbon and nitrogen the thermodynamical analysis showed the precipitation of vanadium nitrides in austenite to take place at first, while precipitation of carbides in austenite has started after depletion of free nitrogen. At free cooling of steel in air the vanadium nitride precipitates already in the austenite. This is associated with a certain proportion of vanadium-nitride precipitates strain induced at the final-rolling temperatures within 850 and 1 000 °C /enhancement of the rate of precipitation in the intercrystallized structure/. When the final-rolling temperature varies closely above 850 °C, then all nitrogen is present in form of precipitates of vanadium nitride /the amount of nitrogen in solid solution can be neglected/ /1/. Then, only vanadium carbide precipitates at the transformation boundary.

With decrease of the final-rolling temperature below 850 °C the strain-induced precipitation of vanadium carbide takes place already in the austenite /2/. This precipitation in austenite does not contribute much to the precipitation hardening, however, it retards substantially the growing rate of the austenite grain, which produces favourable effect on refining the ferritic grains and thus, on steel hardening.

Considerable precipitation-hardening role play such precipitates only that precipitate at the transformation boundary of ferrite and austenite, and/or in the ferrite. In view of the common content of vanadium /0,01 to 0,12%/, carbon /up to 0,25% and nitrogen /0,009 to 0,016% in steel and in view of the dissolubility of these elements in austenite and ferrite and their mutual interaction, there is possible to consider precipitation of vanadium carbide or vanadium carbonitride at the transformation boundary and the precipitation of vanadium carbide only in the ferrite. Accordingly, the mixed vanadium carbonitride precipitates providing that higher final-rolling temperatures /above 1 000 °C/ were reached, when the strain-induced precipitation of vanadium nitride was suppressed. The proportion of vanadium nitride is also rising with increasing cooling rate /suppressed precipitation of vanadium nitride in austenite/. Under normal cooling conditions in free air the amount of vanadium nitride, precipitating at the transformation boundary in the mixed vanadium carbonitride, is given by different dissolubility of vanadium nitride in austenite and ferrite.

Precipitation in ferrite starts at suppressed precipitation in austenite and at the interphase boundary especially by elevating the final-rolling temperature above 950 °C and by a high cooling rate from the final-rolling temperature. However, the minimum cooling rate needed for suppressing the interphase precipitation is not as yet exactly known, like its dependence on the percentages

of the accompanied elements. In case of manufacture of concrete-steel bars by the orthodox production technology no precipitation of vanadium nitride take place in ferrite due to too low cooling rate.

At manufacture of the microalloyed concrete steels the precipitation hardening is particularly influenced by the precipitates of vanadium carbide and of vanadium carbonitride precipitating at the interphase boundary. Their precipitation-hardening effect is governed above all by the dispersity, i.e. by their size and average mutual distance. By decreasing transformation temperature /by increasing the cooling rate, by a higher content of the alloying elements such as silicon, manganese/, the average distance is falling down and the dispersity is rising and thus, even the precipitation-hardening effect is stronger and the proportion of vanadium nitride, precipitating from austenite, is decreasing.

When summarizing the above-mentioned knowledge for the practical need of rolling concrete-steel bars microalloyed by vanadium and nitrogen, it is obvious that the optimum mode consists of a high rolling speed with relatively high final-rolling temperatures /to suppress the strain-induced precipitation/ associated with intensive cooling down the bars /to suppress precipitation in austenite, to decrease the transformation temperature and to increase the dispersity/.

For the sake of completeness, however, it is necessary to emphasize the significant role of reheating temperature prior to rolling. The optimum utilization of V + N can be ensured by correctly selected temperature at which maximum dissolution of precipitates and maximum growth of austenite grain could take place.

3. Manufacture of concrete steels on V-N basis

The efficiency of vanadium for precipitation hardening and hardening due to refining of the ferrite grains is more intensive sofar the steel is enriched with nitrogen to 0,010 - 0,020% - precipitation of vanadium nitride and vanadium

carbonitride, a greater dispersity of precipitates, a smaller susceptibility of the precipitates of vanadium nitride and vanadium carbonitride to coarsening in comparison with vanadium carbide.

Nevertheless, attainment of the required nitrogen content in steel has been and remains to be a considerable metallurgical problem, when applying the orthodox methods of nitriding, i.e. nitrogen-containing ferromanganese or nitrogen lancing into steel bath /relatively poor and above all variable efficiency/. This problem is almost completely solved by usage of the admixture called NITROVAN manufactured by the Union Carbide Co. /USA/.

NITROVAN contains vanadium, nitrogen and carbon in combined form and in view of the possible admixtures such as Si, Mn, Al, S and P, the producer warrants its high purity. In the case of further undesirable elements such as As, Ti, Ta, Zr atc their content is limited to 0,01% max.

For manufacture of the concrete steels NITROVAN with designation VN-13 has been used under Czechoslovak conditions, whereby its basic chemical composition was as follows:
79,46% V; 6,85%C; 11,81% N.

The carbon content in VN-13 NITROVAN is high enough, however, in view of the fact that alloying is made to 0,15% V at least, it is possible, with the help of the above-cited data, to calculate the contribution of 0,0096% N and 0,02% C in the steel. Thus, in the common cases of structural steels the contribution of carbon is considered to be immaterial. The uniform graining and good dissolution power of NITROVAN in liquid steel provide its rapid dissolution /within several seconds/ and reasonable homogeneity of the steel bath. Therefore, NITROVAN is added into ladle, when the ladle is filled approx. one-third the height.

To ensure maximum yield of vanadium NITROVAN should not be added sooner, until profound deoxidation is made. However, even here the yield of vanadium does not reach 100%. The teeming is

accompanied by vigorous stirring of bath and part of vanadium is then oxidized by the oxidic slag and passes into slag. Accordingly, utilization of vanadium /as given by the producer/ attains about 90% and that of nitrogen some 80%.

4. Field testing

When selecting the basic chemical composition for melting the experimental heats one has gone out from both the required quarantees for weldability and the necessity for reaching the yield limit of 490 MPa at least with a reasonable reserve.

The experimental heats were melted in the steelworks of Třinec Ironworks in 80 t - OH furnaces and at the Švermovy Ironworks at Podbrezová in 50 t - OH furnaces. In total 10 experimental heats were melted out of which 7 heats at Třinec Ironworks and 3 heats at Švermovy Ironworks. The chemical compositions are given in Table 2.

The proper alloying by NITROVAN VN-13 was done into ladle after thorough deoxidation by ferromanganese, ferrosilicon and aluminium. The addition into the individual heats is obvious from Table 3.

Further processing of the experimental heats was made in either steelworks according to the relevant technological prescriptions for the 10 424 quality at present commonly melted.

The ingots rolled down into billets were further rolled to get bars of 12, 20 and 32 mm in dia. The reheating temperatures, the final-rolling temperatures and the rolling speed in the last roll stands are well arranged in Table 4.

From the rolled ribbed rods samples were taken for each heat and for each diameter. The measured mechanical properties are listed in Table 5.

5. Results and discussion

As can be seen of Table 2 the contents of carbon, manganese, silicon, vanadium and nitrogen fluctuated within a wide range. Thus, for the sake of complex evaluation of the achieved re-

sults and especially for evaluation of the effect of vanadium in association with nitrogen of the yield limit of the concrete steel bars it was necessary to eliminate the effect of other hardening phenomena.

First of all the effect of manganese and silicon was eliminated, i.e. the effect of elements that do not take part at the precipitation hardening /the effect on the total volume and on dispersity of the precipitates of vanadium carbonitrides/; reduction of the Ac_3 -transformation temperature is negligible in the just-considered scatter range of manganese and silicon; these elements do not take part at hardening due to refining of the ferrite grains. In this respect the following formula of Gladman /3/ was applied:

$$R_e^* = R^* + 88 + 37Mn + 83Si + 2920N_{free} + 15,1 D_{\alpha}^{-1/2} \quad (1)$$

where

R_{α}^* is the yield limit of ferrite, MPa

R^* precipitation hardening, MPa

D_{α} size of ferrite grains, mm

Mn, Si, N - content of elements, wt-%

Thus, the contribution of Mn and Si to the yield limit is expressed as

$$R^0 = 88 + 37Mn + 83Si \quad (2)$$

The other terms of Eq (1) are influenced by the presence of vanadium and nitride. Accordingly, the effect of vanadium and nitrogen on the yield limit of ferrite can be summarized as follows

$$R_V = R^* + 15,1 D^{-1/2} + 2920 N_{free} = R^* + R_V^* \quad (3)$$

The above-cited Eq (1) refers to the case of a purely ferritic structure. However, our case of 0,20 - 0,25% C is due to a certain proportion of pearlite, also with hardening effect. For the case of ferrite-pearlitic structure the following equation should be taken into account:

$$R_e = V^{1/3} \cdot R_{\alpha}^* + (1 - V)^{1/3} R_e^P \quad (4)$$

where

R_e^P is the yield limit of pearlite, MPa

V proportion of the ferritic phase, %
 $1/3$ exponent referring to the non-linearity
 in change of R_e with varying proportion
 of pearlite.

The proportion of ferrite by volume can be written
 as follows:

$$V_{\alpha} = 1 - 1,307 C \quad (5)$$

At calculation we have considered the amount of
 "free" carbon, i.e. carbon not combined in the
 vanadium precipitates /the C-content in solid so-
 lution of ferrite was considered to be negligible/.

To express the yield limit by Eq (4) the yield
 limit of pearlite should be calculated as

$$R_e^P = 178 + 3,8s_0^{-1/2} + 63 Si \quad (6)$$

where

s_0 is the interlamellar distance, mm.

Thus, by Eqs (1-6) one obtains the effect of
 the individual factors on the yield limit of steels
 microalloyed by V + N. When expressed summa-
 rily, one obtains

$$R_e = /1 - 1,307 C/^{1/3} \cdot /R^* + R^o + R_V/ + \\ + /1 - (1 - 1,307 C)^{1/3}/ \cdot R_e^P \quad (7)$$

The contribution of manganese and silicon to
 the yield limit of ferrite is given by Eq (2) and to
 the total yield limit by the following formula

$$R_V^o = /1 - 1,307 C/^{1/3} /88 + 37Mn + 83Si/ + \\ + /1 - (1 - 1,307 C)^{1/3}/ \cdot 63Si \quad (8)$$

To enumerate the just-mentioned formula
 there is necessary first of all, to determine the
 content of "free" carbon, which is possible pro-
 viding that

- at the end of precipitation of vanadium nitrides
 the nitrogen content in solid solution of ferrite
 would be negligibly small,
- all the vanadium would be present in form of
 precipitates.

The proportion of vanadium determined in the
 individual precipitates and the proportions of
 carbon in the precipitates and in pearlite are lis-
 ted in Table 6.

The effect of present pearlite on the yield limit
 in Eq (7) is given by the term $/1 - V/^{1/3} R_e^P$ and
 can be enumerated hardly due to difficulties asso-
 ciated with determination of the interlamellar
 distance. Thus, in the first approach the contri-
 bution of pearlite to the yield limit is considered
 such as determined by Pickering and Gladman /4/
 i.e. some 2,5 MPa per 1% lamellar pearlite.

By subtracting the contribution of manganese,
 silicon and pearlite to the yield limit /7/ one ob-
 tains complex effect of V + N + C caused by pre-
 cipitation hardening and hardening by the ferrite
 grain. The figures of the individual contributions
 to hardening at the experimental heats are given in
 Table 7.

The reheating temperatures were selected
 within 1200 and 1250 °C. Accordingly, all the
 vanadium precipitates were dissolved prior to
 rolling. The final-rolling temperatures at the
 Švermovy Ironworks varied within 800 and 900°C
 and at the Třinec Ironworks within 980 and 1020°C.
 In no case the temperature was less than 850 °C.
 Thus, by the above-mentioned theoretical precon-
 ditions no strain-induced precipitation of carbides
 encountered. In this respect only vanadium nitride
 precipitates in the austenite; its strain-induced
 precipitation starts at the temperature interval
 of 850 - 1 000 °C, i.e. in the zone in which the
 final-rolling draughts were performed in all the
 investigated cases.

The main contribution of the precipitates of
 vanadium nitride to elevation of yield limit is due
 to refining of austenite /retarding its growth/ and
 thus, even the ferrite grains.

In the concrete-steel bars of 20 mm in dia.
 made of steel to ČSN 10 425 grade the average
 grain size is as a rule 10 by the scale to ČSN
 420463. At selected heats on the basis of NITRO-
 VAN, melted by similar technology and with simi-
 lar C-content, the obtained grain size is as a rule
 11. No differences in grain size were found out
 among the individual experimental heats. By

alloying the concrete-steel bars with NITROVAN the size of ferrite grains has fallen from 0,012 mm down to 0,009 mm. From the above-mentioned formulae, expressing the effect of ferrite grain on the yield limit, the contribution was found to be 30 MPa.

From the data given in Table 7 follows the overall contribution of V + N to the yield limit of the concrete-steel bars. While the hardening effect due to refining of the ferrite grain is constant over the entire interval of the chemical composition, say 30 MPa, the role of the precipitation hardening is strongly dependent on the contents of vanadium and nitrogen in steel and on their mutual ratio within the range 0,04 to 0,13% V and 0,009 to 0,016% N. The hardening effect varied within 150 and 215 MPa. The contribution of the precipitation hardening to the yield limit in relation with V-content is illustrated in Fig. 1. The linear regression was applied to determine the effect of vanadium precipitating at the transformation boundary on the yield limit of the concrete-steel bars of 20 mm in dia. For each 0,01% V within the interval of 0,02 - 0,06% V in the precipitate of vanadium carbide the yield limit is rising by 20 MPa.

Detailed analysis into the effect of vanadium, carbon and nitrogen on the yield limit has been performed for bars of 20 mm in dia. Similar effect on the yield limit can be assumed from the results attained with diameters of 12 and 32 mm. Somewhat lower yield limit of bars of 32 mm in dia. is due both to a smaller degree of deformation and to a lower cooling speed, i.e. due above all to a larger ferrite grains and a smaller proportion of precipitates originating at the transformation boundary. For the case of bars of 12 mm in dia. the circumstances are to the contrary, i.e. a greater deformation and a higher cooling speed that is a smaller grain and a higher proportion of precipitates originating at the transformation boundary.

6. Usage of microalloying by vanadium and nitrogen in carbon steel for seamless tubes

The favourable and encouraging results obtained with usage of NITROVAN at melting steel for concrete reinforcements under Czechoslovak conditions were verified even with further assortment of the rolling stock, i.e. the heavy plates of weldable structural steels, the helically welded tubes of KX 70 steel and even the seamless tubes of low-alloyed steel to be applied at elevated temperatures /5/.

At the Švermovy Ironworks some 3 experimental heats were melted with application of microalloying by VN-13 NITROVAN at manufacture of extruded, hot-reduced and cold-drawn tubes of quality to VN 12 O25-standard. The fundamental target parameters of the mechanical properties of seamless tubes of a wall thickness up to 12 mm specified in the VN 12O25 standard are as follows:

| | |
|--------------------------|------------------|
| Yield limit Re | - 320 MPa minim. |
| strength Rm | - 440 to 600 MPa |
| ductility A ₅ | - 23% minim. |

The steel was melted in the electric arc furnaces of a capacity of 40 tons and then rolled on a continuous-rolling mill into billets of 200 mm in dia. and 200 mm long that were subjected to extrusion to form tubes of 32 mm in dia. and of a wall thickness of 3 mm. The final-rolling temperatures after the tube-reducing mill varied, according to the applied technological regime, within 800 and 840 °C, i.e. closely to or immediately above the Ar₃-transformation temperature. The hot-reduced tubes of Ø 32 x 3 mm were subjected to two-draught cold drawing without intermediate annealing to produce tubes of Ø 28 x 2,5 mm and tubes of Ø 22 x 2,0 mm. The last drawing operation was followed by normalizing within 900 and 920 °C.

The obtained results of the mechanical properties and of structural analyses after the re-

levant operations that is after hot rolling, cold drawing and after normalizing are given in Table 8. From the results follows that the yield limit, the strength and the ductility achieved with tubes of $\varnothing 32 \times 3$ mm surpass considerably the conditions specified in the 12O25 standard and/or in other cases present sufficient reserve in the properties even in as-normalized state. Accordingly, eventual enhancement of the specified values can be considered with the hot-rolled tubes or possible modification of the chemical composition toward a decrease in carbon and/or manganese content can be taken into account. The two possibilities would lead to further improvement of weldability of that steel and/or to more uniform distribution of the mechanical properties across the sectional area and to a drop in the transversal anisotropy due to a lower susceptibility to origination of bonded structure.

The size of structural grain in as hot-rolled state and/or in as cold-formed state varies within 11 and 13 by the ASTM. By introduction of normalizing the grain is growing to 11. In any case these characteristics are by two or three degrees higher than those commonly achieved with seamless tubes of VN 12O25 quality without usage of NITROVAN. The proportion of the structural components such as pearlite and ferrite is here in mutual relation / 20 and 80%, respectively/. By cold forming the value of the bonded structure is simultaneously diminished by one degree.

The results of evaluation of substructure by the electron microscope showed that the precipitate attains the size of several nanometers / 10^{-9} mm/. Nevertheless, the substructure is in principle identical to that of steel to 12O25 grade without NITROVAN.

It can be said, on the basis of the preliminary results and analyses, that, apart from improvement of the mechanical properties and/or possible modification of the chemical composition to improve the weldability of steel, the

greatest effect would consist obviously in improvement of the creep resistance of steel melted with NITROVAN due namely to further precipitation effect of the submicroscopic nitride particles.

7. Conclusion

From the just-described analysis follows that encouraging results were achieved at enhancement of the yield limit of the concrete and tube steels by application of NITROVAN that is alloying by vanadium and nitrogen. Alloying the concrete and tube steels by VN-13 NITROVAN also enables to attain the required yield limit without any change in the melting technology.

To attain the yield limit of 490 MPa at rolling of concrete-steel bars of 12, 20 and 32 mm in dia. The optimum content of vanadium proved to be 0,06 - 0,10% and that of nitrogen within 0,008 and 0,010%. Thus, the nitrogen content in NV-13 NITROVAN is too high and it cuts considerably down the precipitation hardening effect of vanadium. By application of NV-7 NITROVAN with a smaller nitrogen content the minimum required yield limit is assumed to be attained by a smaller amount of that admixture.

Application of NITROVAN at manufacture of seamless tubes of VN 12O25 quality is supported by the fact that the results of the field and laboratory tests confirm reasonable technical and economical targets by application of microalloying by means of NITROVAN at the Czechoslovak boiler steels and/or enables development of new lean-alloyed steels that would be able to replace and to surpass economically some boiler-steel grades melted till now according to the ČSN-standard.

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Table 1: The quality grades of the concrete steels melted in the ČSSR

| Quality by the ČSN | Yield limit $R_{p0,2}$ | Tensile strength R_m | Ductility A_5 |
|--------------------|------------------------|------------------------|-----------------|
| | MPa | MPa | % |
| 10216 | 204 | 539 | 24 |
| 10335 | 325 | 470-706 | 18 |
| 10338 | 325 | 390 | 12 |
| 10425 | 410 | 570-770 | 14 |
| 10607 | 590 | 850 | 8 |

Table 2: The chemical compositions of heats for manufacture of the ribbed rods

| No. of heat | C | Mn | Si | P | S | V | N |
|-------------|------|------|------|-------|-------|------|--------|
| | % | | | | | | |
| 1 | 0,25 | 1,41 | 0,42 | 0,018 | 0,027 | 0,07 | 0,0127 |
| 2 | 0,25 | 1,42 | 0,48 | 0,017 | 0,030 | 0,07 | 0,0121 |
| 3 | 0,23 | 1,32 | 0,35 | 0,028 | 0,032 | 0,12 | 0,0164 |
| 4 | 0,23 | 1,38 | 0,44 | 0,028 | 0,032 | 0,09 | 0,0136 |
| 5 | 0,20 | 0,93 | 0,30 | 0,011 | 0,020 | 0,11 | 0,0156 |
| 6 | 0,20 | 1,19 | 0,50 | 0,024 | 0,030 | 0,10 | 0,0163 |
| 7 | 0,23 | 1,38 | 0,46 | 0,020 | 0,023 | 0,09 | 0,0157 |
| 8 | 0,25 | 1,33 | 0,66 | 0,020 | 0,027 | 0,04 | 0,0095 |
| 9 | 0,25 | 1,12 | 0,53 | 0,015 | 0,024 | 0,04 | 0,0093 |
| 10 | 0,20 | 1,21 | 0,73 | 0,026 | 0,022 | 0,07 | 0,0098 |

Table 3: The amount of NITROVAN added to the concrete steels

| No. of heat | Weight of heat t | NITROVAN kg/heat | kg/heat |
|-------------|------------------|------------------|---------|
| 1 | 75 | 85 | 1,1 |
| 2 | 80 | 85 | 1,1 |
| 3 | 80 | 112 | 1,4 |
| 4 | 70 | 72 | 1,0 |
| 5 | 80 | 125 | 1,6 |
| 6 | 80 | 110 | 1,4 |
| 7 | 75 | 100 | 1,3 |
| 8 | 48 | 44 | 0,9 |
| 9 | 50 | 44 | 0,9 |
| 10 | 50 | 60 | 1,2 |

Table 4: The technological data on rolling the billets into ribbed rods of 12, 20 and 32 mm in dia.

| Rolled dia. mm | Works | Reheating temperature °C | Holding time hours | Rolling speed m/s | Final-rolling temperature °C |
|----------------|-------------------------------|--------------------------|--------------------|-------------------|------------------------------|
| 12 | Třinec Ironworks | 1230 | 3,0 | 15,0 | 980-1020 |
| | Švermovy Ironworks Podbrezová | 1220 | - | 5,2-6,0 | 850-900 |
| 20 | Třinec Ironworks | 1270 | 2,5 | 11,5 | 980-1020 |
| | Švermovy | 1230 | - | 4,4-5,0 | 850-900 |
| 32 | Třinec Ironworks | 1300 | 2,0 | 6,0 | 980-1020 |
| | Švermovy | 1230 | - | 3,8-4,2 | 850-900 |

Table 5: The mechanical properties of the rolled ribbed rods

| No. of heat | Dia of rod mm | Yield limit Re /MPa/ | Tensile strength Rm MPa | Ductility A ₅ % |
|-------------|---------------|----------------------|-------------------------|----------------------------|
| 1 | 12 | 612 | 747 | 25,0 |
| | 20 | 546 | 710 | 25,0 |
| | 32 | 538 | 718 | 23,1 |
| 2 | 12 | 575 | 710 | 26,7 |
| | 20 | 553 | 716 | 23,0 |
| | 32 | 522 | 701 | 22,9 |
| 3 | 12 | 616 | 762 | 23,3 |
| | 20 | 612 | 782 | 20,8 |
| | 32 | 587 | 759 | 19,4 |
| 4 | 12 | 589 | 723 | 24,2 |
| | 20 | 572 | 728 | 24,0 |
| | 32 | 548 | 726 | 22,5 |
| 5 | 12 | 594 | 723 | 25,0 |
| | 20 | 544 | 696 | 21,0 |
| | 32 | 529 | 688 | 23,1 |
| 6 | 12 | 618 | 742 | 23,1 |
| | 20 | 564 | 734 | 21,0 |
| | 32 | 547 | 707 | 20,6 |
| 7 | 12 | 618 | 754 | 25,0 |
| | 20 | 597 | 757 | 23,0 |
| | 32 | 564 | 743 | 19,4 |
| 8 | 12 | 572 | 775 | 25,3 |
| | 20 | 520 | 717 | 24,5 |
| | 32 | 527 | 742 | 18,1 |
| 9 | 12 | 561 | 770 | 26,6 |
| | 20 | 510 | 707 | 27,0 |
| | 32 | 507 | 712 | 18,8 |
| 10 | 12 | 565 | 775 | 24,1 |
| | 20 | 595 | 755 | 22,0 |
| | 32 | 595 | 735 | 19,5 |

Table 6: The proportion of vanadium and carbon in the individual types of the precipitates, the proportion of carbon in pearlite and the volume proportion of pearlite and ferrite in the examined heats

| No. of heat | V _{VN} | V _{VC} | C _{VC} | C _P | V _P | v ⁺ |
|-------------|-----------------|-----------------|-----------------|----------------|----------------|----------------|
| 1 | 0,046 | 0,024 | 0,006 | 0,244 | 32 | 68 |
| 2 | 0,044 | 0,026 | 0,006 | 0,244 | 32 | 68 |
| 3 | 0,060 | 0,060 | 0,018 | 0,212 | 28 | 72 |
| 4 | 0,050 | 0,040 | 0,009 | 0,221 | 29 | 71 |
| 5 | 0,057 | 0,053 | 0,012 | 0,188 | 25 | 75 |
| 6 | 0,059 | 0,041 | 0,009 | 0,191 | 25 | 75 |
| 7 | 0,057 | 0,033 | 0,008 | 0,222 | 29 | 71 |
| 8 | 0,035 | 0,005 | 0,001 | 0,249 | 33 | 67 |
| 9 | 0,034 | 0,006 | 0,001 | 0,249 | 33 | 67 |
| 10 | 0,036 | 0,034 | 0,008 | 0,192 | 25 | 75 |

V_{VN} proportion of vanadium in the precipitates of vanadium nitride
V_{VC} proportion of vanadium in the precipitates of vanadium carbide
C_{VC} proportion of carbon in the precipitates of vanadium carbide
C_P proportion of carbon in pearlite
V_P volume proportion of pearlite
v⁺ volume proportion of ferrite

Table 7: The figures of the individual contributions of hardening at the examined heats

| No. of heat | R ^o MPa | R ^{o+} MPa | Re ^P MPa | R ⁺ MPa | ΔV MPa |
|-------------|-----------------------|------------------------|------------------------|-----------------------|-----------|
| 1 | 175 | 157 | 80 | 154 | 184 |
| 2 | 180 | 162 | 80 | 157 | 187 |
| 3 | 166 | 151 | 70 | 235 | 265 |
| 4 | 176 | 159 | 71,5 | 185 | 215 |
| 5 | 147 | 138 | 62,5 | 181 | 211 |
| 6 | 174 | 161 | 62,5 | 176 | 206 |
| 7 | 177 | 160 | 72,5 | 211 | 241 |
| 8 | 192 | 173 | 82,5 | 104 | 134 |
| 9 | 173 | 156 | 82,5 | 112 | 142 |
| 10 | 193 | 179 | 61,5 | 198 | 228 |

R^o contribution of Mn and Si to the yield limit of ferrite
R^{o+} contribution of Mn and Si to the total yield limit
R^P yield limit of pearlite
R⁺ contribution of the precipitation hardening
ΔV total effect of NITROVAN on the yield limit

Table 8: The mechanical and structural properties of the seamless tubes of 12025 quality manufactured by addition of NITROVAN

| Size of tube mm | State of material | Yield limit Re /MPa/ | Tensile strength Rm /MPa/ | Ductility % | Proportion of phases % | Grain size | Bonded structure by ON 420 469 |
|--------------------|------------------------|-------------------------|------------------------------|----------------|-----------------------------|------------|-----------------------------------|
| ∅ 32x3,0 | in as hot-rolled state | 422 | 551 | 31,5 | ferrite 80% pearlite 20% | 12/11/20%/ | 2 |
| ∅ 28x2,5 | in as cold-drawn state | 750 | 813 | 11,0 | ferrite 80% pearlite 20% | 13/12/40% | 1 |
| | in as-normalized state | 367 | 489 | 33,0 | ferrite 80% pearlite 20% | 11 | - |
| ∅ 22x2,0 | in as cold-drawn state | 879 | 897 | 9,0 | ferrite 80% pearlite 20% | 13/14 | 1 |
| | in as-normalized state | 359 | 462 | 33,0 | ferrite 80% pearlite 20% | 11 | - |

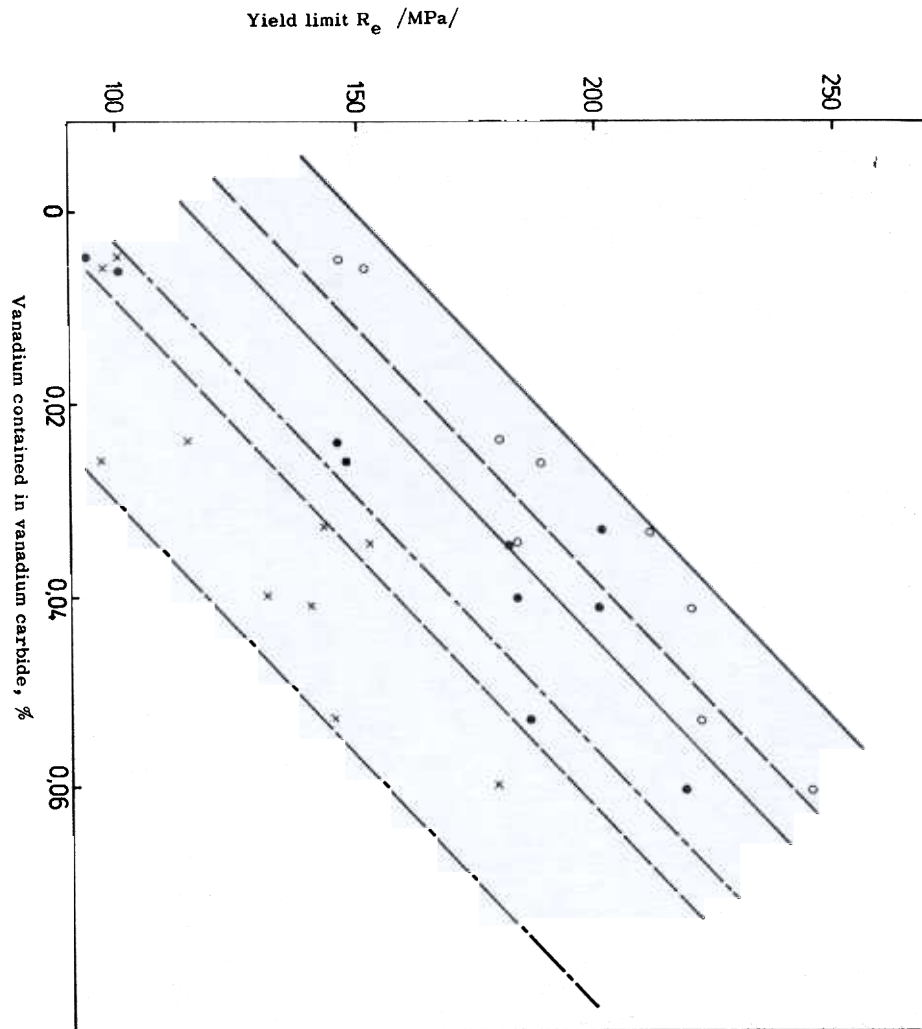


Fig. 1 The effect of vanadium precipitating in vanadium carbide on the yield limit of ribbed steel of 12, 20 and 32 mm in dia