Mechanical Properties of Steel AISI 4135 after Three Different Experimental Heat Treatment Procedures for Production of High Pressure Cylinders

Mechanické vlastnosti oceli AISI 4135 po třech různých experimentálních procedurách tepelného zpracování pro výrobu vysokotlakých lahví

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AISI 4135 steel is a steel grade generally used for production of various demanding products, including the high pressure steel cylinders. For achievement of demanded higher level of mechanical properties micro-alloying with V and N was applied. Three types of different variants of heat treatment with controlled accelerated cooling were used leading to different segregation banding, combinations of microstructures and their refining having impact on final mechanical properties. The most favourable variant of heat treatment resulted in strength at the level of 1272 MPa, with 9.8 % of elongation, balanced level of notch toughness (34/35 J·cm^{-2}*), fine microstructure (grade 11) and restricted segregation banding with predominantly martensitic microstructure and lower portion of acicular ferrite and low bainite.*

Key words: *AISI 4135; controlled cooling process; intercritical zone; mechanical properties; microstructure*

Z oceli AISI 4135 jsou vyráběny různé náročné produkty, mezi něž se řadí i ocelové láhve pro stlačené plyny. Stále vyšší požadovaná úroveň mechanických vlastností, včetně vodíkové odezvy, je dosahována přísadami mikrolegujících prvků (Nb, Ti, V, Zr, N atd.) spolu s kombinacemi tepelného zpracování s cílem získat multifázovou strukturu. Publikovaná práce se zabývá třemi typy zpracování daného typu oceli s přísadou V a N, kde varianta A byla založena na austenitizaci v režimu 700 °C/kalení do 20 °C a popouštění na 470 °C, což vedlo k výrazně segregované struktuře se všemi negativními důsledky. Pevnost dosahovala hodnoty 824 MPa, tažnost 17,6 % a velikost primárního austenitického zrna odpovídala stupni 10. Druhá varianta B zahrnovala opět austenitizaci s ochlazením na vzduchu do interkritické oblasti s navazujícím kalením těsně nad teplotu M_s*, následným ochlazením na vzduchu do 40 °C pod* M_s*, finálním kalením do 20 °C a popouštěním na 470 °C/vzduch. Tato varianta vykazovala pevností úroveň téměř na horní požadované hranici (1257 MPa) při 14,5% tažnosti a vysokou, vyváženou úroveň výsledků rázových zkoušek (34/35 J.cm*$^{-2}$*) s nejjemnější strukturou (stupeň 11). Segregační pásování bylo částečně potlačeno a mikrostruktura vykazovala v převážné míře martenzitickou matrici s nižším podílem acikulárního feritu a spodního bainitu. U varianty C byla provedena austenitizace s následným ochlazením na vzduchu do interkritické oblasti, navazujícím kalením do 200 °C nad teplotu* M_s*, s dalším ochlazením na vzduchu do 90 °C nad* M_s *a finálním kalením do 20 °C, což vedlo sice ke sporadickému výskytu segregačního pásování, zato však k nejhrubší struktuře (stupeň 8) a byla detekována vysoká pevnostní úroveň (1397 MPa) s tažností 9,8 %.*

Klíčová slova: *AISI 4135; řízené ochlazování; interkritická zóna; mechanické vlastnosti; mikrostruktura*

The AISI 4135 steel type represents a good balance of different properties, such as strength, toughness, fatigue and corrosion resistance under extreme working conditions, and therefore it is used for a variety of industrial and structural applications, such as forgings, rolled plates, cranes, wind turbines, mining equipment and also for production of high pressure steel cylinders (HPSC) and vessels, including compressed natural gas (CNG) transportation and storages, etc. [1-4]. Variations of micro-alloying by Nb, V, Ti, B and N are often used in the AISI 4135 [5, 6]. Steel purity, deformation temperatures, strain rate, chosen heat treatment (HT) and cooling processes (CP) influence the final microstructure and mechanical properties. Nűrnberger [2, 7] confirmed the important influence of the cooling rate and strain level on final microstructure, however without consideration of the accelerated cooling process (ACP). In [8] authors showed the low cycle lifetime response of the 42CrMo4 steel after normalization and after tempering related to the change of the modulus of elasticity. Alvino [9] studied corrosion cracks of the HPSC from AISI 4135 steel after 10 years of service and came to the conclusion that given damage was progressive, but without sudden, catastrophic impact. Chen [10] detected in the steel AISI 4135 quenching cracks caused by uneven surface cooling. Moli-Sanches [11] ascribed higher hydrogen mobility in the AISI 4135 treated at 680 °C instead of 540 °C to higher dislocation density and hydrogen trapping.

Nowadays, development of the steel 42CrMo4 similar to the AISI 4135 is targeted on maximal strength with simultaneously high toughness and favorable corrosion resistance in a sour environment [12]. This is also the aim of the presented work.

Experimental approach

For experiments the steel AISI 4135 after hot reversed extrusion from billet and subsequent reversed hot rolling to the thickness of 10.2 mm including ACP was used in order to find a way for reaching higher mechanical properties of the pressure steel cylinders. Three heats (AISI 4135) manufactured under the same conditions were used. Average chemical compositions corresponded to (in wt. %): 0.36 C, 0.84 Mn, 0.27 Si, 1.13 Cr, 0.21 Mo, 0.012 P, 0.004 S, 0.073 V, 0.0113 N and were in accord with the AISI 4135 steel. Three heat treatment modes were applied. The HT1 was based on the heating at 700 °C, fast cooling in quenching bath (QB) and tempering at 470 °C. The HT2 consisted of a controlled cooling process (CCP) based on heating to the austenitic zone (γ-zone) with subsequent fast air cooling to the intercritical zone (IZ). Afterwards, fast cooling in QB to the temperature T just above the martensite start (M_S) followed with air cooling to 40 °C under the M_S and cooling (QB) to the room temperature with tempering at 470 °C/air. Further, the heating to γ-zone followed by air cooling to the IZ with fast cooling (QB) to 200 °C above the M_S and air cooling to 90 °C above the M_S followed by QB cooling to the room T with tempering at 470 °C/air represented the HT3 mode. Fig. 1 shows scheme of three used heat treatment modes.

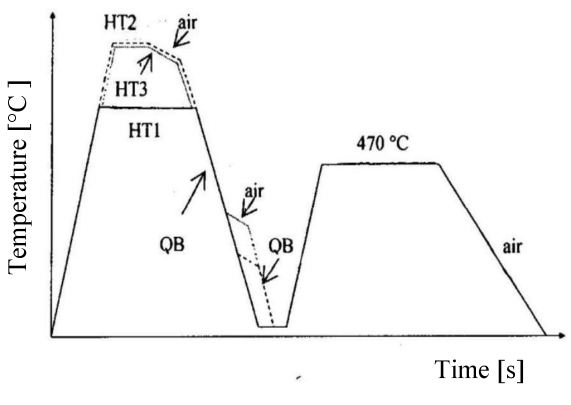

Fig. 1 Scheme of three used experimental heat treatment modes
Obr. 1 Schéma tří použitých experimentálních způsobů tepelného zpracování

Testing of mechanical properties was an integral part of the solution. The yield stress and tensile strength (*YS*, *TS*), elongation (*El*), Brinell´s hardness (HBW) and notch toughness (*CNV*) parameters were established. Testing of *YS*, *TS* and *El.* was realized by use of the Zwick/Roell Z 250 machine (EN ISO 6892-1). The *HBW* was measured using the M4U750 hardness testing machine (EN ISO 6506-1) and *CNV* was tested by use of the RKP 450 Charpy Impact Testing Machine (ISO 148-1) at -50 °C. Metallographic evaluation was carried out using a light microscope Neophot 21 (purity - ČSN ISO 4967, microstructure analysis, the grain size ($G\gamma$) - ASTM E 112). For micro-fractography transverse *CVN* samples were used (SEM JEOL JSM-6490).

Results and discussion

Results of all tested mechanical properties are summarized in table 1. The lowest levels of strength and *CVN* properties were found in case of the HT1. In both testing directions, *CVN* values showed an insignificant difference of 3 J·cm^{-2}. After HT2 application tensile properties were lying between the HT1 and HT3 values, however balanced CVN values in both testing directions were significantly higher than in cases of HT1 and HT3. Resulting *El* and *HBW* values fully correspond to the increasing trend of tensile properties as it can be seen in table 1, where microstructure and grain sizes $G\gamma$ are included.

Tab. 1 Found mechanical properties and grain size $G\gamma$ after application of three heat treatment modes
Tab. 1 Zjištěné mechanické vlastnosti a velikost zrna $G\gamma$ po aplikaci tří způsobů tepelného zpracování

Variant of heat treatment	HT1	HT2	HT3
YS [MPa]	676	1 120	1 272
TS [MPa]	824	1 257	1 397
El [%]	17.6	14.5	9.8
CNV_{trans}/CVN_{long} [J·cm^{-2}]	22/19	34/35	23/22
HBW (2.5/187.5) [-]	248	402	424
$G\gamma$ [grade]	10	11	8

The non-metallic inclusions evaluation of all three heats revealed a considerably high level of purity. Fine sulphides were detected (HT3) of the 1.1 grade. Aluminates were not observed, silicates were in the range from 0 to 0.5 and fine oxides from 0.1 to 0.8. The most favorable and balanced values of tensile properties and *CVN* in both directions of testing could be ascribed to the HT2 with the finest grain size $G\gamma$. Microstructure was evaluated from the areas close to the inner surface of the semi-product of HPSC. The reason for this choice of place is the most commonly used heat treatment of cylinders in closed state. Namely, there is no access of quenching medium to the inner surface of cylinders. This causes heating of the inner and slightly under the inner surface area of the cylinder by trapped gases for a longer time than the outer surface, where the cooling rate is much faster due to direct contact with the quenching medium. This results in more noticeable segregation banding in the inner under surface area due to longer times for possible segregation processes. Microstructure after the application of HT1 predominantly revealed bainite partially mixed with ferrite, low portion of acicular ferrite (AF) and pearlite - see Fig. 2a, b. This was also reason for the fact that tensile strength after the HT1 was by 34 % lower in comparison with the HT2. Microstructure after the HT1 is similar to the microstructure after the slow air cooling after the hot forming temperatures of reverse rolling, which allowed significant segregation of elements, such as Cr, Mo, and C to the segregation bands [13], which are moderately thick and of continuous character as shown in Fig. 2a-d.

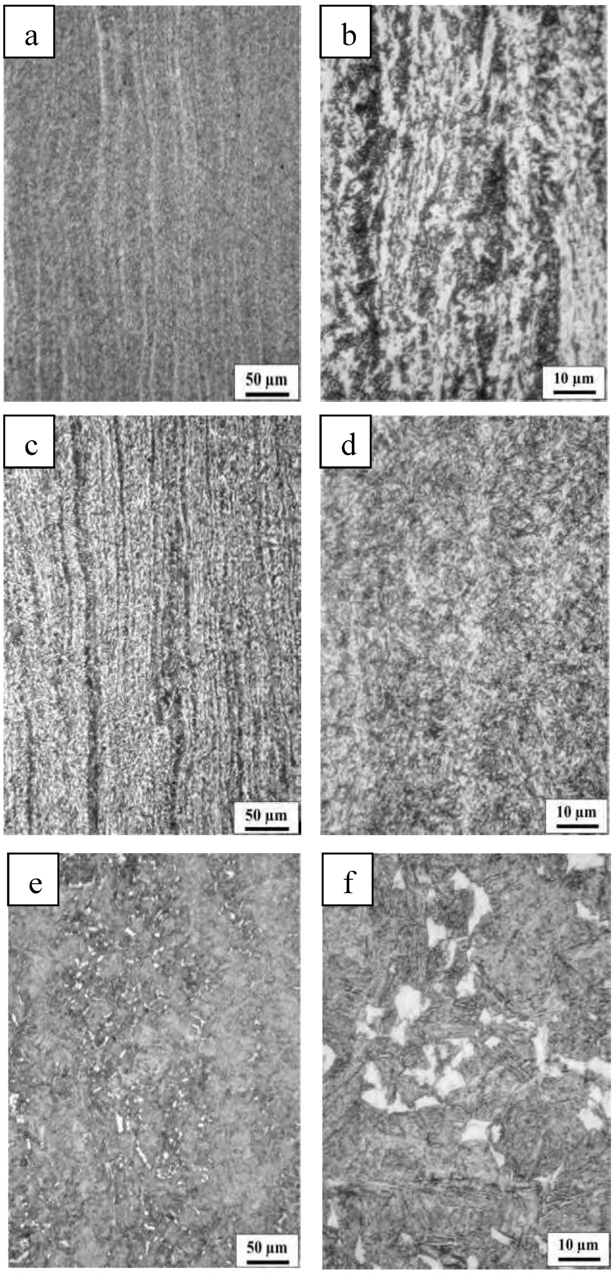

Fig. 2 Microstructure image in general view and in detail after the a), b) HT1, c), d) HT2 and e), f) HT3
Obr. 2 Zobrazení mikrostruktury v celkovém pohledu a detailu po a), b) HT1, c), d) HT2 a e), f) HT3

Heating at 700 °C was approx. 25 °C under the Ac_1 due to deficient heating temperature, and the austenitization process was not achieved. Resulting coarse microstructure (grade 10) contained numerous carbide particles, which precipitated during the tempering process. Significantly banded microstructure, which originated during the process of forming and subsequent cooling, was not reduced due to low heating temperature. Resulting tensile properties fully correspond to the microstructure and the differences of *CVN* values (table 1), in which testing directions are consistent with the segregation banding in microstructure. Fig. 2c and 2d represent finer morphology obtained after application of HT2 with significantly reduced segregation bands (thinner and discontinuous). This corresponds to the highly balanced *CVN* results in both testing directions, as well as highly balanced strength parameters (table 1). Microstructure consists of fine tempered martensite, acicular ferrite and low bainite in small portion. The phase of acicular ferrite was obtained by cooling in air from the fully austenitic zone to the IZ, which was able to suppress harmful segregation banding [14]. Presented oxi-sulfidic inclusions supported acicular ferrite nucleation, and Mo in steel modified its shape [14 - 16]. Subsequent fast cooling in the QB to the temperature just above the M_S ensured restriction of segregation processes to the minimum according to the resulting reduced banded microstructure. Cooling in air to the temperature of 40 °C resulted in partial low bainite transformation and the martensitic microstructure was gained by the subsequent quenching in QB.

Fig. 2e-2f shows the microstructure after application of the HT3. This microstructure is formed by tempered martensite, acicular and polygonal ferrite. After application of both HT2 and HT3, the acicular phase was obtained due to the rolling from full γ-zone to the IZ, and segregation banding was considerably eliminated, however, cooling in air from 200 to 90 °C above the M_S before cooling in QB, caused an undesirable extended polygonal ferrite formation, which disrupted the microstructure homogeneity, and from the point of view of mechanical properties it caused e.g. sulphide stress cracking resistance. This phenomenon appeared due to the long-lasting cooling in air from 200 to 90 °C with the contribution of hot gases trapped inside the heat treated cylinder, which were continuously heating the inner and under inner surface area of material. Restriction of noticeable segregation banding was directly reflected in the balanced *CVN* values in both testing directions, as shown in table 1.

The martensitic transformation occurred as a result of fast cooling in the QB from the temperature of 90 °C above M_S to the room temperature. By the subsequent tempering, primarily tempered martensitic phase and the precipitation of carbides particles in martensite and low bainite was formed, as it was observed after application of the HT2. The reached higher *YS* and *TS* levels resulted from higher quenching temperature used to realize the quenching as compared with the HT2 mode. The observed coarser grain size $G\gamma$ might have probably caused a decrease of the CVN and elongation values, together with higher level of tensile properties. As Fig. 3 shows it, the fractured CVN specimens showed coarser cleavage character (HT1, HT3) and/or quasi-cleavage facets, with ductile ridges (HT2). Their occurrence was sporadic and found ridges were very thin. The reason for the disproportional values of CVN in transverse and longitudinal testing direction (table 1) is continual thicker banding. This observed fracture surface corresponds to the achieved mixed microstructure of low bainite, pearlite and acicular ferrite and it also confirms the lowest achieved CVN values (table 1) correlating with [6].

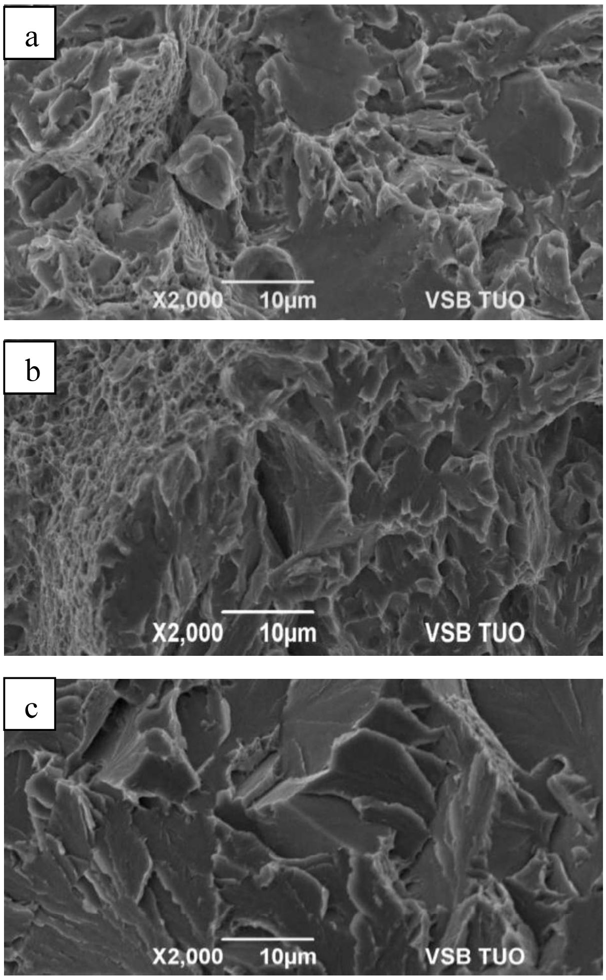

Fig. 3 Fracture surface of CVN specimen after a) HT1, b) HT2, c) HT3
Obr. 3 Lomová plocha vzorků KCV po a) HT1, b) HT2, c) HT3

Fracture surface of specimens after application of the HT2 revealed similar character of fracture surfaces as in case of the HT1, however cleavage and/or quasi-cleavage facets were significantly finer and more even, corresponding to the found grain size (table 1), partially decorated with thin ductile ridges, and also thicker and longer ductile ridges were observed (see Fig. 3c). This was the cause of the increased *CVN* values. Finer microstructure and partial elimination of unfavourable segregation banding of the HT2 microstructure unlike the HT1, contributed to balanced tensile properties and *CVN* levels.

Fig. 3 demonstrates the fracture surface of the CVN specimen after application of the HT3. In this case the fracture surface showed rather trans-crystalline cleavage character with creeks detected in some facets. In given case the facets were the coarsest. Ductile ridges were observed sporadically and were thin and short. This morphology fully corresponds to the lowest grain size of the used HT2 compared to the other two used treatments with finer grain size. Fracture surface character also corresponds to the highest tensile properties showing the lowest elongation value.

Conclusions

The paper summarizes the results of mechanical properties, metallographic and fractographic observations of three different heat treatment modes of the steel AISI 4135. The best achieved results of mechanical properties from the point of view of tensile properties vs. balanced and high *CVN* in two testing directions were seen in case of the HT2, where the segregation banding in microstructure was significantly restricted in comparison with the HT1 and HT3 modes. Microstructure obtained by the HT2 mode revealed slightly discontinuous segregation banding and its elimination would be possible by increasing the cooling rate from the austenitic zone to intercritical ones. The subsequent time and tempering temperature should be increased in order to moderately increase the values of elongation and *CVN* at the cost of a moderate TS decrease to approx. 1200 MPa. This experimental procedure proved that the most influencing factor for achievement of high tensile properties, and as high values of *CVN* as possible, is the grain size as it was reported in [6].

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Hightech povrchy prostřednictvím čárového laseru

Stahlmarkt *4/2015*

Pásová ocel by mohla být v budoucnu lépe chráněna proti korozi. Ve společném projektu ThyssenKrupp Steel Europe, Fraunhofer Institut IWS a specializované firmy na tvarování laserovým paprskem LIMO se testuje nová laserová technologe, která u povrchu pásu výrazně zvyšuje odolnost proti korozi. Funkcionalizace povrchů a povlaků je jedna z klíčových technologií 21. století. Pro výzkumné práce dalo spolkové ministerstvo pro vzdělání a výzkum v Německu 34 mil. € celkem na 12 projektů. Část z toho jde do projektu „Povrchově funkcionalizované ocelové pásové materiály prostřednictvím povrchového zpracování laserem v kontinuálním procesu výroby širokých pásů“, který byl zahájen v roce 2014. Lepší ochrana proti korozi by měla být dosažena prostřednictvím legování, resp. přetavení vhodných povrchových vrstev, které jsou naneseny na povrch pásu v průběhu výrobního procesu. Přitom jsou systémy vrstev homogenně nataveny laserem přes celou šířku pásu. U této technologie se s výhodou využívá jevu, že energie je vnášena jen v oblasti povrchu a ne do prohřívání celého pásu.

Směnný kurz způsobuje potíže na německém trhu s ušlechtilou ocelí

Stahl Aktuell *7. 4. 2015*

Že cena niklu na londýnském Metal Exchange krátce před koncem března spadla na nejnižší stav za posledních devět let, zajímá německé obchodníky s ušlechtilou ocelí jen okrajově. Ani skutečnost, že EU uvalila na výrobky z ušlechtilé ploché oceli z Číny a Tchaj-wanu nemravně vysoká antidumpingová cla, nikoho příliš nevzrušuje. Kdo ale používá materiál ve formě komoditních výrobků z Asie, trpí i nadále pod účinky propadu hodnoty eura. Obchodníci z Asie chtějí vidět víc peněz, protože sami nakupují v dolarech. Zda je možné toto zvýšení ceny převést na konečné zákazníky, není ovšem zdaleka jasné. Na odvětvovém veletrhu „Fastener Fair“ ve Stuttgartu byl vývoj směnného kurzu převládajícím tématem. Jedinou útěchou je, že tento vývoj dopadá na všechny stejně. Téměř nikdo z německých zpracovatelů se nezajistil proti změnám kurzu. Odhlédneme-li od vývoje směnného kurzu, probíhá ovšem obchod s ušlechtilou ocelí v Německu klidně. Střednědobě budou ale evropští podnikatelé v branži z antidumpingových opatření EU profitovat.