Analysis of precipitates in heat treated thermo-mechanically processed steel with a high yield strength

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Abstract: The aim of this study was to analyse the precipitates and determine their impact on the structure of thermomechanically processed high strength S700MC steel. The tested samples were subjected to a heating process at temperatures from 100°C up to 1300°C with a 100°C step. The chemical composition analysis in the micro-areas of the samples, thin-film tests and quantitative measurements of carbonitride precipitates were performed. In order to describe the grain size, a method of calculating the number of grains cut through the measuring line was used. In order to determine the effect of heat treatment on strength and plastic properties, Charpy V-notch, Vickers hardness and static tensile tests were carried out. The study showed that S700MC steel is characterized by a non-equivalent, fine-grained bainitic-ferritic structure. The test showed a significant impact of heat treatment on the strength and plastic properties of S700MC steel.

1. Introduction

In recent years, there has been growing interest in the complexity and operational expectations for steel structures. These conditions can be met through the use of high strength steel with good plastic properties, corrosion resistance and also due to the way they are joined with the appropriate weldability. In the early 1960s, publications by Hall and Petch showed that in ferritic-pearlitic steels the fine ferrite grain causes a simultaneous increase in strength and a decrease of the brittle transition temperature of steel products. Since then, it is the most important metallurgical parameter in the production of structural steels. The production of high-strength steel, in addition to strong grain refinement, required the use of other steel strengthening mechanisms, i.e. precipitation strengthening. Therefore, in order to obtain the required material properties, the production of C-Mn structural steels with Nb, V, Ti alloy additions began which allowed to increase the yield strength up to 500MPa. These elements are micro-additives in steel, i.e. their concentration does not exceed 0.22%. Steels containing micro-additives are called microalloyed steels or high-strength low-alloy steels. In order to obtain the fine-grained structure, these steels are most often produced in a controlled rolling process followed by controlled cooling. The combination of these processes is called thermomechanical processing. The application of the described process and new metallurgical technologies allowed to obtain high strength steels while maintaining good plastic properties of the material. The use of thermomechanical treatment instead of conventional microstructure forming methods like normalizing heat treatment saves energy and allows to achieve greater grain refinement. Application of steel with high yield strength allow to produce of slimmer and lighter structure elements while maintaining the same load capacity and reducing welding time and costs. Technical and economic aspects have made...
these steels one of the basic structural materials. Therefore, improving the methods of their manufacture, analyzing precipitation processes during the production of these steels and during welding processes is extremely important from the point of view of the manufacture and construction of steel structures in the 21st century. Thermo-mechanical control process (TMCP) consists on continuous control of the temperature and deformation of manufactured steel products during rolling in order to obtain a material with high strength properties. During this treatment, two main effects are used: the impact of fine-grained structure on the increase of strength and plastic properties and limitation or delay of recrystallization due to the small amounts of alloying elements added to the material. Avoiding or limiting the recrystallization process is caused by micro-alloying elements, which also form secondary phases that inhibit the recovery process. Thanks to this, the austenite structure is characterized by strong grain refinement, high dislocation density and a significant number of crystals of new structural components directly from rolling temperature during a controlled cooling process. While the steel is cooled in the air, a fine grained ferrite with a small amount of perlite is obtained. When accelerated control cooling process is applied a fine grained polygonal or coniferous ferrite is obtained, while the pearlitic transformation is replaced by bainitic and partly martensitic transformation (depending on the temperature of the rolling end and cooling speed). Accelerated cooling after a controlled rolling process causes fragmentation of the ferrite grain and contributes to solid solution strengthening and precipitation hardening by dispersed particles. Steels produced in this way can reach a yield point of up to 700 MPa [1-30].

2. Materials and methodology
The tests were carried out on thermomechanically processed high-strength low-alloy S700MC steel of 10 mm thick. Chemical composition and properties of investigated material are shown in table 1.

Table 1. Actual chemical composition of 10 mm thick S700MC steel.

| Contents of chemical elements, % by weight |
|-------------------------------------------|
| C  | Mn | Si | S  | P  | Al |
| 0.056 | 1.68 | 0.16 | 0.005 | 0.01 | 0.027 |
| Nb | Ti | V  | N* | C* | Ce** |
| 0.044 | 0.12 | 0.006 | 72 | 0.33 |

* - N: content in ppm; nitrogen was identified using the high-temperature extraction method
** - C* – carbon equivalent

Total content of Nb, V and Ti should amount to a maximum of 0.22%

| Mechanical properties |
|-----------------------|
| Tensile strength $R_m$, MPa | Yield point $R_y$, MPa | Elongation $A_5$, % | Toughness, J/cm$^2$ (-20 °C) |
| 822 | 768 | 19 | 135 |

S700MC steel is characterized by non-equivalent, fine-grained bainitic-ferritic structure with a relatively low carbon equivalent (at the level of 0.33%), which should indicate its good weldability. The high strength properties of S700MC steel are obtained by a thermomechanical treatment process combined with the strengthening by micro-additives, such as Ti, Nb and a small amount of V. The total content of alloying micro-additives is 0.17 wt%, which does not exceed the permissible value of 0.22 wt% in steel with micro additives. S700MC steel has a very low carbon concentration (0.056 wt%), which may limit the impact of austenite transformation under the influence of welding thermal cycle which affects on the strength and plastic properties of welded joints.

2.1 Heat treatment
In order to determine the effect of temperature on the mechanical and plastic properties of S700MC steel, heat treatment was performed on investigated material. The samples of tested steel were heated at temperature ranges from 100°C to 1300°C with 100°C gradation. The heat treatment was carried out on
a 24-channel resistance annealing machine WO6524 with a rated power of 65 kVA designed by LMS S.C., equipped with temperature controllers P62. Each sample was placed on a separate heating mat, then the samples were insulated and heat treated. The time for soaking the samples was 1 hour and cooling process took place in the air. The method of individual identification of samples is shown in table 2.

**Table 2.** Designation of heat treated samples.

| Soaking temperature in accordance to sample Identification number [°C] | A   | B   | C   | D   | E   | F   | G   |
|---------------------------------------------------------------------|-----|-----|-----|-----|-----|-----|-----|
| A                                                                   | 100 | 200 | 300 | 400 | 500 | 600 | 700 |
| B                                                                   |     |     |     |     |     |     |     |
| C                                                                   | 800 | 900 | 1000| 1100| 1200| 1300|     |

2.2 Precipitates analysis

After the heat treatment process, each sample on cross-section was subjected to metallographic examination (etching – Nital). Additionally, the examinations were provided on the sample which after thermomechanical rolling was not heat treated and was marked with the symbol MR. Five microphotographs were taken on each specimen using a digital camera coupled with a light microscope at 1000x magnification. Microphotographs were taken near the corners of the sample and in its central part, as shown in figure 1.

![Figure 1. Scheme of areas where individual micrographs of samples were taken.](image)

Chemical composition researches in the micro-areas of the samples were performed on a Zeiss SUPRA 35 scanning electron microscope equipped with an EDS made by EDAX company which allows quantitative analysis of chemical elements present in the sample. The backscattered electrons (BSE) techniques of observation was used. Tests of thin films were performed on a High-resolution scanning transmission electron microscope (HRSTEM) Titan 80-300kV made by FEI, equipped with XFEG electron gun with Schottky field emission. Quantitative measurements of carbonitride precipitates were carried out on automatic image analyser – NiS – Elements BR 3.1. Using this analyser the number of carbonitride precipitates was calculated on all 5 images and other parameters such as area, circumference, length and width of obtained precipitates were also measured. Additionally, the percentage share of precipitates to the surface area on each microphotography was calculated. The percentage share of carbonitrides was calculated according to the following formula:

\[ A_X = \left( \frac{\sum_{i=1}^{n} a_i}{A} \right) \times 100\% \] (1)
where:

\[ A_A = \text{percentage share of carbonitrides on investigated area}, \]
\[ \sum_{i=1}^{n} a_i = \text{sum of carbonitrides area on observation area}, \]
\[ A = \text{observation area (microphotography area)}. \]

The grain size was measured on one selected microphotography of each sample in accordance with the international standard PN-EN ISO 643. In order to evaluate the grain size, the method of counting number of grains cut by the measuring line was used. The measuring line was a section of a straight line of equal length to the image placed on each sample at the same microregion. Counted number of grains “\(N\)” formed the basis for determining “\(NL\)” parameter, i.e. the average number of grains per measuring line length, which allowed to determine the parameter “\(l\)” (average chord lengths cut off by grains on measuring line). The calculation procedure is presented below.

Parameters definition:

\[ N \] – number of grains cut with measuring line,
\[ L \] - length of measurement line after division by magnification,
\[ N_\bar{} \] - average number of grains cut with a measuring line,
\[ L_T \] – actual length of measuring line.

Based on the above-mentioned parameters:

\[ NL = \frac{N}{L_T} \quad (2) \]

\(NL\) – average number of cut grains per unit of measuring line length.

Then the parameter \(NL\) was used to calculate the value “\(l\)”: \n
\[ l = \frac{1}{NL} \quad (3) \]

\(l\) – average chord lengths cut off by grains on a measuring line.

3. Results and discussion

3.1 Analysis of basic material

Chemical composition analysis of S700MC steel on Optical Emission Spectroscopy analyser (OES) confirmed compliance of chemical composition with the PN EN 10149-2 standard. In tested steel, the carbon concentration is 0.056% wt, titanium – 0.12% wt, niobium – 0.044% wt, vanadium – 0.006% wt. The sum of micro-additives responsible for strengthening mechanism does not exceed the maximum permissible concentration of 0.22% wt. Content of nitrogen (70 ppm) based on the high-temperature extraction process confirms compliance of investigated material with delivered material certificate. Studies of thin films on Transmission Electron Microscope have shown that the strengthening mechanism of S700MC steel is determined by precipitates \((\text{Ti, Nb})(\text{C, N})\) which size is of few to several nanometers. The precipitation hardening process is mainly caused by dispersion of a few nanometre precipitates, which are produced in ferrite during cooling of steel (figure 2). Particles larger than dozen nanometers do not make a significant contribution to the precipitation hardening however, they limit growth of recrystallized austenite grain, favouring the formation of fine-grained structure.

3.2 Microstructure analysis

Based on the heat-treatment test carried out on S700MC steel, it was found that in heating temperature range from 100 to 600°C the bainitic structure undergoes tempering and from 500°C the process of single grains recrystallization begins and strain hardening is reduced. After exceeding 800°C process
of complete recrystallization is observed and the proportion of ferrite in the structure increases. Further increase in temperature above 1000°C causes strong grain growth (figure 3). The microscopic tests confirmed high temperature stability of Ti(C,N) and (Ti,Nb)(C,N) precipitates.

Figure 2. TEM micrograph with the corresponding selected area diffraction pattern illustrating carbonitride (Ti,Nb)(C,N) with small spherical precipitates responsible for precipitation strengthening of S700MC steel: (a) Bright-field; (b) Dark field; (c, d) selected area diffraction pattern; (e) EDX spectrum
Material without heat treatment

Material with heat treatment at 100°C

Material with heat treatment at 200°C

Material with heat treatment at 300°C

Material with heat treatment at 400°C

Material with heat treatment at 500°C

Material with heat treatment at 600°C

Material with heat treatment at 700°C
3.3 Quantitative share of precipitates

Investigated precipitates had relatively large sizes, the average length of their cross sections $d_\ell$ ranged from 4.29 to 9.64 μm. The large size of carbonitride phases indicates that they had to be formed during steel production process at high temperatures. This is evidenced by their considerable size already in the MR sample that was not heat treated. The number of particles on the plane ranged from 22.1 up to 40 mm$^{-2}$. The percentage share of carbonitrides was in the range of 0.327–0.821%. Its highest value – 0.821% was registered for sample D heat treated at 400°C, while the lowest value was observed in sample G (0.340%) and H (0.327%) heat treated at 700 and 800°C. Distribution of this parameter is variable, i.e. it increases and decreases without a clear trend line. In samples from J to K, the percentage share of carbonitrides is at a similar level, table 3. The distribution of this parameter is shown in figure 4.
3.4 Grain size
The grain size was measured in accordance with international standard PN-EN ISO 643. For each sample the grain size was characterized by average chord lengths “l”, obtained results were in the range from 1.77 up to 15.4 μm, figure 5. Parameter of average chord lengths of samples MR to H remains at a relatively low level. The smallest grain size value of 1.77 μm was observed for sample H, heat-treated at 800°C. This is probably the result of the appearance of fine grains due to the austenite phase transformation. After reaching the smallest value of grain size in sample H, in subsequent samples heat treated at higher temperatures a sudden increase of this parameter was observed. This is due to the recrystallization phenomena and growth of austenite grains. The largest grain size was observed for samples L (8.06 μm) and M (15.40 μm) heat treated at 1200°C and 1300°C, respectively.

Table 3. Average precipitation lengths and number of particles on microphotography on each sample.

| Sample designation | Heating temperature to [°C] | Average length of precipitates d [μm] | Number of precipitates on investigated area Na [mm⁻²] |
|--------------------|-----------------------------|---------------------------------------|---------------------------------------------------|
| MR                 | n/a                         | 6.85                                  | 316.5                                             |
| A                  | 100                         | 6.91                                  | 271.3                                             |
| B                  | 200                         | 4.29                                  | 406.9                                             |
| C                  | 300                         | 7.08                                  | 361.7                                             |
| D                  | 400                         | 9.64                                  | 271.3                                             |
| E                  | 500                         | 6.00                                  | 316.5                                             |
| F                  | 600                         | 7.97                                  | 316.5                                             |
| G                  | 700                         | 4.81                                  | 316.5                                             |
| H                  | 800                         | 5.65                                  | 316.5                                             |
| I                  | 900                         | 4.58                                  | 406.9                                             |
| J                  | 1000                        | 9.29                                  | 226.1                                             |
| K                  | 1100                        | 5.50                                  | 271.3                                             |
| L                  | 1200                        | 7.30                                  | 226.1                                             |
| M                  | 1300                        | 6.52                                  | 316.5                                             |

Figure 4. Distribution of percentage share of carbonitrides.
4. Conclusions

S700MC steel is characterized by an unbalanced, fine-grained bainitic-ferritic structure. High strength properties of tested material are ensured by thermomechanical processing combined with strengthening process caused by micro-additives such as Ti, Nb. Precipitation hardening is mainly caused by the dispersion of few nanometers precipitates, which are formed in ferrite during cooling process. Microscopic studies showed the presence of large carbonitride precipitates, their average size ranged from 4.29 to 9.4 μm. The significant size of the carbonitride phases indicates that they had been formed during the production process of steel at high temperatures, due to the high diffusion coefficient of the elements that form the precipitates. The large size and small amount of carbonitride phases in the range from 226.1 to 406 mm² indicates that grain boundaries rarely encounter them during growth. Therefore, the micro-additives in S700MC steel are not fully used to control precipitation hardening process and grain growth. The increase of average chord lengths parameter in the temperature range from 900 to 1300°C is associated with recrystallization phenomena and grain growth. Recrystallization and subsequent grain growth could start at higher temperatures if there were more niobium dissolved in a solution or a higher amount of precipitates.

5. References

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