HEAT TREATMENT OF A 13Cr-6Ni-2.5Mo-Ti SUPERMARTENSITIC STEEL

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ABSTRACT

Low carbon supermartensitic 13%Cr steels with 4-6%Ni and 0-2.5%Mo additions have been developed from type AISI 420 steels for applications in the oil industry. They offer significantly better weldability, improved general corrosion resistance, particularly in carbon dioxide environments, and some grades exhibit improved resistance to sulphide stress corrosion cracking. In this paper results of detailed investigations on a 13Cr-6Ni-2.5Mo-Ti steel after quenching and double tempering are presented. Microstructural studies were carried out using optical microscopy, transmission electron microscopy and X-ray diffractometry. The results prove that formation of austenite during tempering at both 690 and 620°C is accompanied by intensive precipitation of Fe_2Mo Laves phase particles.

KEYWORDS

Supermartensitic steels, heat treatment, double tempering, reverted austenite, Laves phase, tensile properties, impact toughness.

INTRODUCTION

Martensitic stainless steels , type AISI 420 with 13%Cr and 0.2%C, have been widely used for many years in the oil industry. Demands for improved weldability and corrosion resistance, particularly in moderately sour environments, have lead to the development of a group of materials broadly described as "*Supermartensitic Stainless Steels*"[1-5]. They offer significantly better general corrosion resistance than type 420 steels, especially in environments containing carbon dioxide at temperatures up to about 200°C. Furthermore, some grades show resistance to sulphide stress cracking (SSC) at levels up to an H_2S partial pressure of about 0.1 bar. They are considered to be an economic alternative to 22%Cr duplex stainless steels.

Supermartensitic 13%Cr steels contain less than 0.02% of carbon, 4-6% of nickel and molybdenum in the range 0.5-2.5% [1,2]. Some grades contain copper up to 1.5% and controlled nitrogen additions up to about 0.1%. Special grades have been developed for field welding where the use of PWHT is either restricted or impossible. In order to achieve the necessary mechanical properties and corrosion resistance in the as-welded condition or after limited time PWHT the carbon and nitrogen contents are reduced to extra low levels (< 0.01%) and a small amount of titanium is added for grain growth control in the HAZ [2].

It is worth noting that chemical composition of newly developed supermartensitic stainless steels is very close to composition of 13%Cr, 4-6%Ni, 0-0.5%Mo steels which have been widely used for the construction of hydraulic turbines and components of hydraulic pumps for several decades [6-9]. Vítkovice started to utilise VOD process for production of these steel grades with a very low carbon content (< 0.03%) as one of the first steelmaking companies [7, 10].

The balance between strength and toughness of 13%Cr, 4-6%Ni (Mo) steels can be controlled by heat treatment. Tempering of martensite above the A_{c1} temperature results in a mixture of tempered martensite and reverted austenite which is regarded as the optimum microstructure. The A_{c1} temperature of these steels depends strongly on nickel content. In high nickel grades the A_{c1} point can be as low as 500-550°C. If during tempering the A_{c1} temperature is exceeded only slightly, say by 40°C, than austenite formed will be stable on cooling to room temperature. The stabilisation of this reverted austenite in the microstructure has been attributed to a combination of several mechanisms: an enrichment of austenite in carbon, nitrogen and nickel, strengthening of austenite by defects and small dimensions of austenite lamellae [11]. It has been proved that reverted austenite is stable during cooling down to - 196°C [9,11]. However, plastic deformation can induce transformation of reverted austenite to martensite [11]. At tempering temperatures further above the A_{c1} point, the austenite fraction is increased and on cooling to room temperature partial or complete transformation of austenite to new martensite will occur, Fig. 1. This untempered martensite has to be tempered during second tempering at lower temperature.
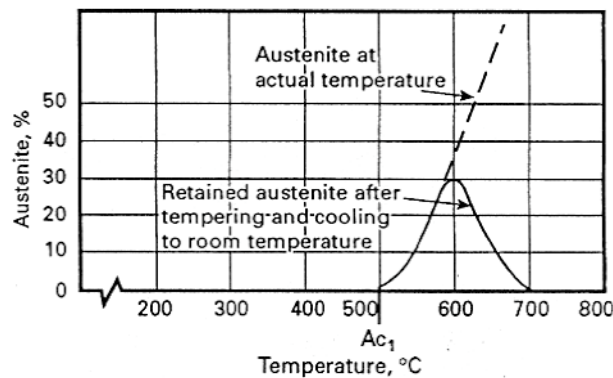

Fig. 1 Formation of austenite during tempering of 13%Cr – 6%Ni steels [6]

Quality heat treatment of supermartensitic steels usually consists of quenching and single or double tempering which make it possible to achieve required properties for basic three major strength levels API X80, X95 and X110. For some of the older steels tempering parameters are recommended by NACE and EN 10088 standards [1]. However, for each particular steel the optimum tempering regime has to be determined experimentally.

MATERIAL AND EXPERIMENTAL PROCEDURES

Studies were performed on a 13Cr-6Ni-2.5Mo-Ti steel produced in VÍTKOVICE using EAF, VOD and LF technology. Experimental material was cut from a preliminary forging. Chemical composition of the steel is shown in Table 1.

Table 1. Chemical composition of the steel, wt. %

C	Mn	Si	P	S	Ni	Cr	Mo	V	Ti	Al	N
0.02	0.56	0.30	0.03	0.001	6.17	13.0	2.40	0.03	0.10	0.02	0.01

In the frame of heat treatment optimisation the effect of tempering in the temperature range 580-690°C on the tensile properties, impact toughness and microstructure was investigated [12]. Experimental results were used for a proposal of single and double tempering regimes with respect to specified properties for individual strength grades.

In this paper results of investigations on the test material of the strength grade X80 are discussed. Experimental material was heat treated as follows:

970°C/1 hour/air + 690°C/6 hours/air + 620°C/6 hours/air.

Mechanical properties were evaluated by hardness measurements, tensile and Charpy impact tests. Microstructural studies were carried out by using optical microscopy, transmission electron microscopy and X-ray diffractometry. Electron microscopy investigations were performed on a JEM 200CX microscope using both carbon extraction replicas and thin foils. Thin foils were prepared by twin jet electropolishing in a solution of 5%$HClO_4$ in acetic glacial acid at room temperature and a voltage of 80V.

RESULTS AND DISCUSSION

In Table 2 results of hardness evaluation and austenite fraction measurements after individual steps of the quality heat treatment are shown.

Table 2. Evaluation of hardness and austenite fractions during heat treatment

Heat Treatment	HV30	% of Austenite
Quenching (Q)	305±6	<2
Q + 690	290±5	4
Q + 690 + 620	262±5	15

Results of tensile and Charpy impact tests on the test material after the quality heat treatment are shown in Table 3. The experimental results meet requirements of API standard for the X80 strength grade.

Table 3. Tensile properties and impact energy at room temperature

$R_p0.2$ [MPa]	R_m [MPa]	A [%]	Z [%]	KCV [Jcm^{-2}]
607	849	17	57	157

Chemical composition of supermartensitic steels is balanced in order to avoid formation of high amounts of δ-ferrite during austenitization. Microstructural investigations on the test material after 970°C solution treatment followed by air cooling revealed a very small amount of δ-ferrite (<1%) in lath martensite. As evident from Table 2 the fraction of retained austenite in the microstructure was very low. Furthermore, primary Ti(C,N) particles were randomly distributed throughout the martensitic matrix.

During tempering at 690°C formation of austenite was accompanied by precipitation processes. As the temperature of tempering was high above the A_{c1} point most of austenite islands were unstable and during subsequent air cooling transformed to new martensite, Fig. 2. The fraction of reverted austenite in the microstructure after cooling was only ~4%, see Table 2. Precipitation processes took place along prior austenite grain boundaries and also in the martensitic matrix.. An example of intergranular precipitation is shown in Fig. 3. Precipitates were identified using selective electron diffraction and EDX analysis as Fe_2Mo Laves phase. An EDX spectrum of this phase is shown in Fig. 4.
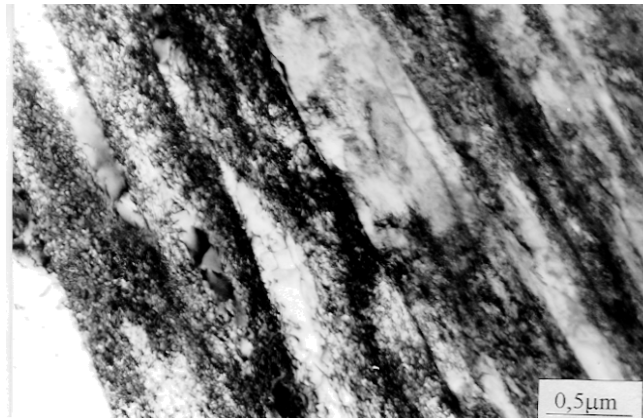

Fig. 2 Mixture of tempered and new martensite, HT: Q + 690

Fig. 3 Precipitates along prior austenite
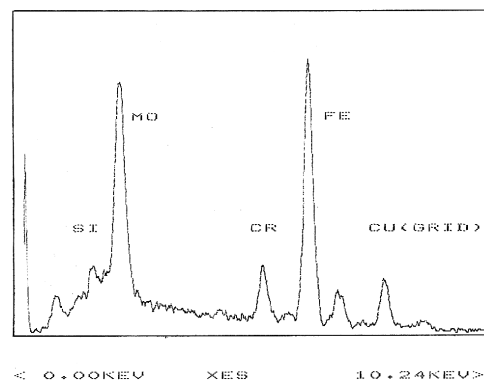   grain boundary,   HT: Q + 690

Fig. 4 EDX spectrum of Fe_2Mo
     Laves phase

Second tempering at lower temperature (620°C) resulted in stabilisation of ~15% of reverted austenite in the final microstructure. Lamellae of austenite formed predominantly alongmartensite lath boundaries. As can be seen in Figs. 5a,b all particles of austenite inside an original austenite grain had the same crystallographic orientation. Tempering at 620°C intensified processes of precipitation of Fe_2Mo Laves phase particles along prior austenite grain boundaries and in the martensitic matrix. A discontinuous network of Laves phase particles along prior austenite grain boundary is shown in Fig. 6.
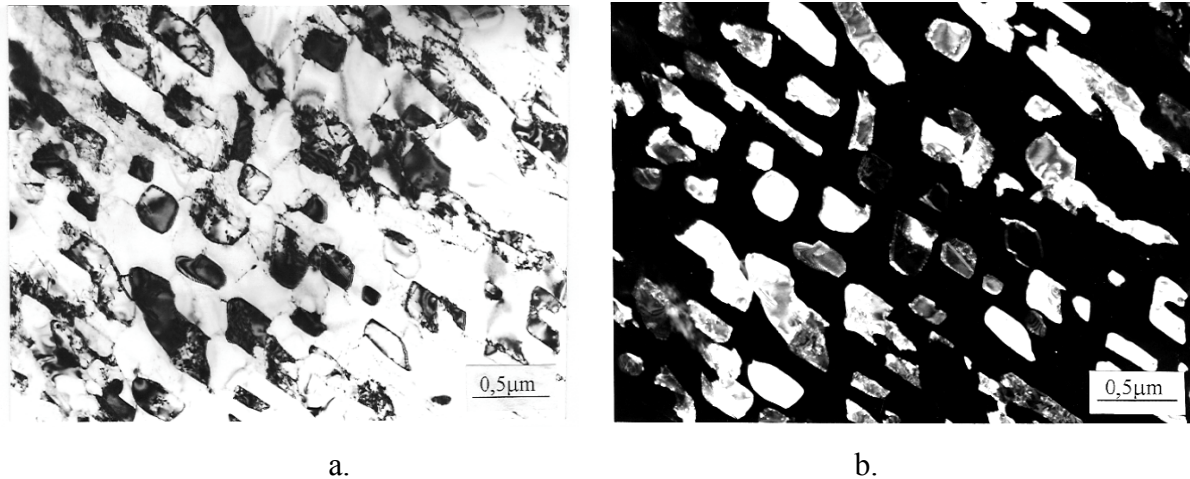

a.   b.

Fig. 5 Reversed austenite in tempered martensite, HT: Q + 690 + 620,

  a. bright field image,

  b. dark field image taken by using 200_γ reflection.

Precipitation of Fe_2Mo Laves phase during tempering is a consequence of a high molybdenum content in the steel investigated. Precipitation of this phase has never been observed in older 13%Cr,4-6%Ni containing up to ~0.5%Mo [6,7,11]. Further work is required to clarify the effect of Laves phase on mechanical and corrosion properties of newly developed supermartensitic steels.
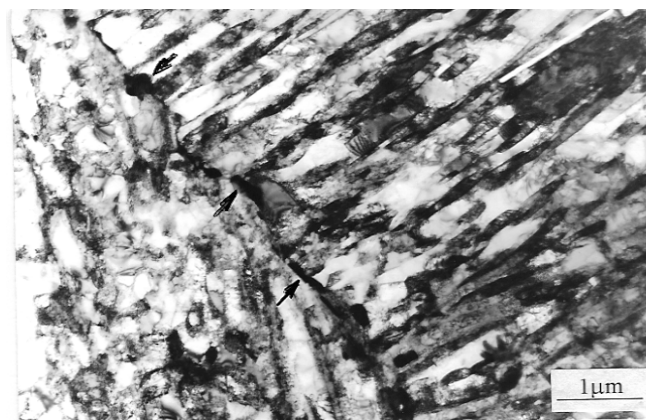

Fig. 6 Precipitation of Laves phase particles (arrows) along prior austenite grain boundary,

  HT: Q +690 + 620

CONCLUSIONS

The results of investigations on the 13Cr-6Ni-2.5Mo-Ti steel after quenching and double tempering can be summarised as follows:

1. Double tempering of martensite at 690 and 620°C enables to achieve the strength properties required for the strength grade API X80. The final microstructure is a mixture of tempered martensite and reverted austenite.

2. Formation of austenite during tempering at both temperatures is accompanied by intensive precipitation of Fe_2Mo Laves phase. Precipitation of Laves phase is a consequence of a high molybdenum content in the steel investigated.

3. Further work is required to clarify the effect of Laves phase precipitation on mechanical and corrosion properties of newly developed supermartensitic steels.

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