PRECIPITATION PROCESSES IN A SUPERMARTENSITIC 13Cr6Ni2.5MoTi STEEL DURING QUALITY HEAT TREATMENT

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Abstract

The balance between strength and toughness of supermartensitic steels can be controlled by heat treatment parameters. Quality heat treatment usually consists of quenching and single or double tempering above the A_{c1} temperature. Such a treatment results in stabilization of reverted austenite in the tempered martensite. Tempering can also be accompanied by intensive precipitation processes, especially in high alloyed grades. A detailed TEM characterisation of precipitation processes in a 13Cr6Ni2.5MoTi supermartensitic steel proved that single tempering at temperatures of 600 °C and 690 °C was accompanied by precipitation of three minor phases: MX (TiX), $M_{23}C_6$ and Laves phase (Fe_2Mo type). Precipitation processes were more intensive at 690 °C. Volume fractions of MX and $M_{23}C_6$ phases were low. Laves phase precipitation was intensive and particles of this minor phase grew fast. However, thermodynamic calculations using the Thermocalc software suggest that Laves phase is not an equilibrium phase in the steel under consideration.

Keywords: Supermartensitic steels, precipitation, heat treatment.

1. INTRODUCTION

Low carbon supermartensitic 13 %Cr steels with 4-6 %Ni and 0-2.5 %Mo additions have been developed from the type AISI 420 steel for applications in the oil industry [1, 2]. Furthermore, 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 application of post weld heat treatment (PWHT) is either restricted or impossible. In order to achieve the necessary mechanical properties and corrosion resistance in the as-welded condition or after short time PWHT the carbon and nitrogen contents are reduced to extra low levels (< 0.01 %) and a small addition of titanium is added for grain growth control in the heat affected zone of welds [3]. They offer significantly better weldability, improved general corrosion resistance and some grades exhibit improved resistance to sulphide stress corrosion cracking. Quality heat treatment of supermartensitic steels usually consists of quenching and single or double tempering above the A_{c1} temperature, i.e. intercritical annealing [4, 5]. The A_{c1} temperature of these steels strongly depends on the nickel content. In high nickel grades the A_{c1} point can be close to 500 °C. If temperature of tempering exceeds the A_{c1} temperature only slightly, say by 40 °C, then austenite formed during tempering will be stable on cooling to ambient 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 (chemical stabilisation), strengthening of austenite by defects and small dimensions of austenite lamellae [4]. It has been proved that reverted austenite is stable during cooling down to -196 °C. However, plastic deformation can induce transformation of reverted austenite to martensite [1]. 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 “fresh” martensite will occur. This “fresh” martensite has to be tempered during second tempering at lower temperature [4]. It has been reported that double tempering can increase the fraction of reverted austenite in the final microstructure [6]. Tempering can also be accompanied by intensive precipitation of minor phases, especially in high alloyed grades [2, 4]. Precipitation might have an adverse effect on corrosion resistance

(sensitization) or mechanical properties (notch toughness) of supermartensitic steels [6, 7]. This paper deals with a detailed TEM characterisation of precipitation processes in a 13Cr6Ni2.5MoTi supermartensitic steel during single tempering of martensite at temperatures of 600 °C and 690 °C. Results of experimental studies are compared with thermodynamic calculations of equilibrium phases in this grade of supermartensitic steels.

2. EXPERIMENTAL MATERIALS AND TECHNIQUES

Investigations were carried out on the 13Cr6Ni2.5MoTi steel manufactured using EAF, VOD and LF technology. Experimental material was taken from a pipe Ø 324x16 mm in the as-rolled condition. Chemical composition of the steel investigated is shown in **Table 1**.

Table 1 Chemical composition of the steel, wt. %

C	Mn	Si	P	S	Cu	Ni	Cr	Mo	V	Ti
0.02	0.57	0.31	0.027	0.002	0.12	6.15	13.20	2.28	0.03	0.10

Temperatures of laboratory heat treatment corresponded to typical temperatures of commercial heat treatment: normalization annealing (970 °C), tempering at 600 °C, which makes it possible to stabilize about 30% of reverted austenite in the microstructure and tempering at 690 °C, which can be applied as the first step in double tempering procedure [4]. The thermal history of the specimens investigated was as follows:

1. ***Specimen A***: 970 °C/ 1 hour/ air,
2. ***Specimen B***: 970 °C/ 1 hour/ air + 600 °C/ 6 hours/ air,
3. ***Specimen C***: 970 °C/ 1 hour/ air + 690 °C/ 6 hours/ air.

Studies on minor phases were carried out using scanning and transmission electron microscopy. Carbon extraction replicas were used for TEM investigations. Identification of minor phases was carried out by a combination of electron diffraction (SAED) and X-ray microanalysis (EDX) techniques. The Thermocalc software and the database TCFE7 were used for calculations of equilibrium phases in the steel under consideration in the temperature interval from 400 - 1200 °C.

3. RESULTS

3.1 Specimen A

Microstructure of the Specimen A consisted of lath martensite with traces of δ-ferrite (< 1 %). **Fig. 1** shows primary MX particles which formed during solidification of steel. These particles often nucleated on alumina particles, see an arrow in **Fig. 1**. EDX spectrum of primary MX phase in **Fig. 2** proves that it is titanium nitride. Except for coarse MX particles extraction replicas revealed many fine particles in the Specimen A, **Fig. 3**. These particles were also identified as titanium rich MX particles. Spot diffraction pattern of this phase is shown in **Fig. 4**. Small MX particles were significantly enriched in molybdenum, which is typical for MX phase precipitating in martensite or ferrite. It can be speculated that small MX particles formed during production of pipes. Austenitizing temperature of 970 °C was too low for dissolution of both primary and secondary titanium rich MX particles. Fine secondary MX particles (ca 100 nm) inhibited austenite grain size growth. Chemical compositions of primary and secondary MX particles are summarized in **Table 2**.

Table 2 Chemical compositions of MX particles in the Specimen A, wt. %

Phase	Ti	Cr	Fe	Mo
prim. MX	97.3 ± 0.4	1.0 ± 0.1	1.7 ± 0.2	-
sec. MX	81.7 ± 5.5	2.8 ± 1.0	0.5 ± 0.2	15.0 ± 5.5

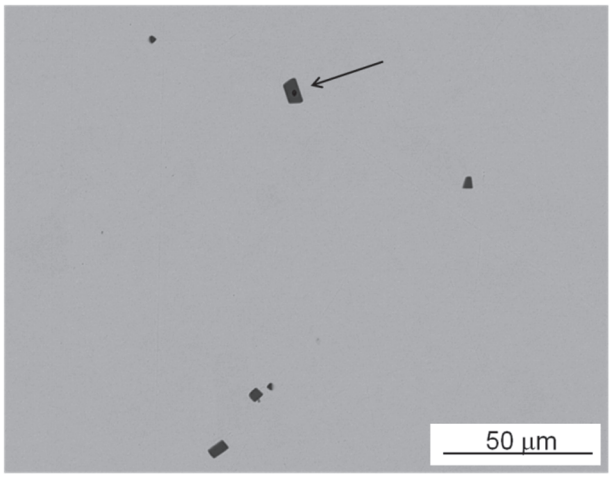


Fig. 1 Primary MX particles, Specimen A

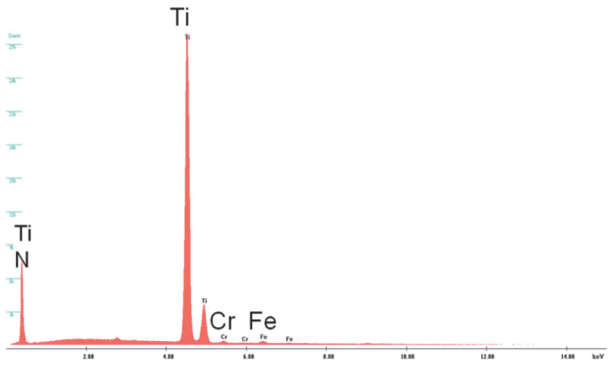


Fig. 2 EDX spectrum of primary MX phase

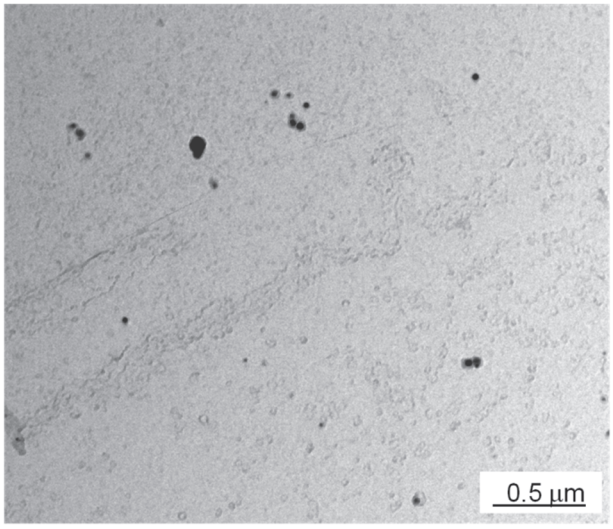


Fig. 3 Secondary MX particles, Specimen A

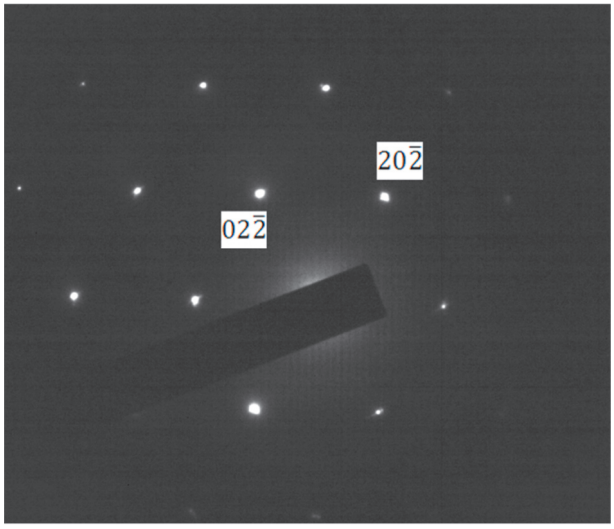
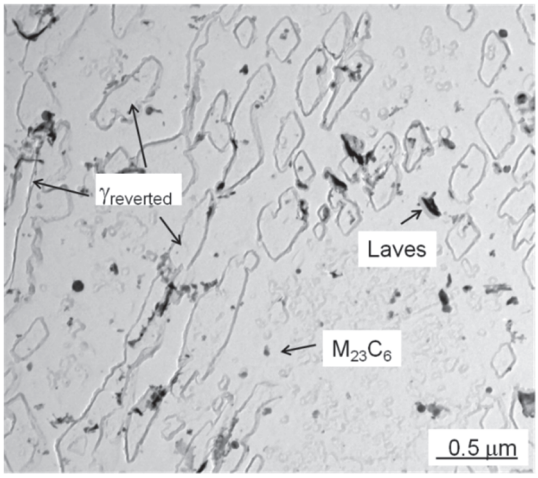


Fig. 4 Spot diffraction pattern of MX, zone axis [111]

3.2 Specimen B



Tempering of martensite at 600 °C resulted in the formation of lamellae of reverted austenite and precipitation of fine particles along prior austenite grain boundaries and along martensitic lath interfaces. Most austenite lamellae remained stable on cooling to ambient temperature. All austenitic lamellae inside one prior austenite grain had the identical crystallographic orientation. **Fig. 5** shows typical distribution of islands of reverted austenite in the tempered martensite and fine precipitates. A detailed TEM analysis revealed three minor phases: MX (TiX), $M_{23}C_6$ and Laves phase (Fe_2Mo type). Chemical compositions of all minor phases in the Specimen B are summarized in **Table 3**.

Fig. 5 Islands of reverted austenite and precipitation of minor phases in the

Table 3 Chemical compositions of minor phases in the Specimen B, wt. %

Phase	Si	Ti	Cr	Fe	Ni	Mo
$M_{23}C_6$	0.3 ± 0.1	-	57.3 ± 2.2	16.0 ± 0.8	1.5 ± 0.4	24.9 ± 3.1
Laves	3.6 ± 0.5	-	15.2 ± 2.5	26.0 ± 0.4	2.5 ± 0.3	52.7 ± 2.6
sec. MX		50.4 ± 5.8	8.1 ± 0.5	10.2 ± 3.0	-	31.4 ± 5.4

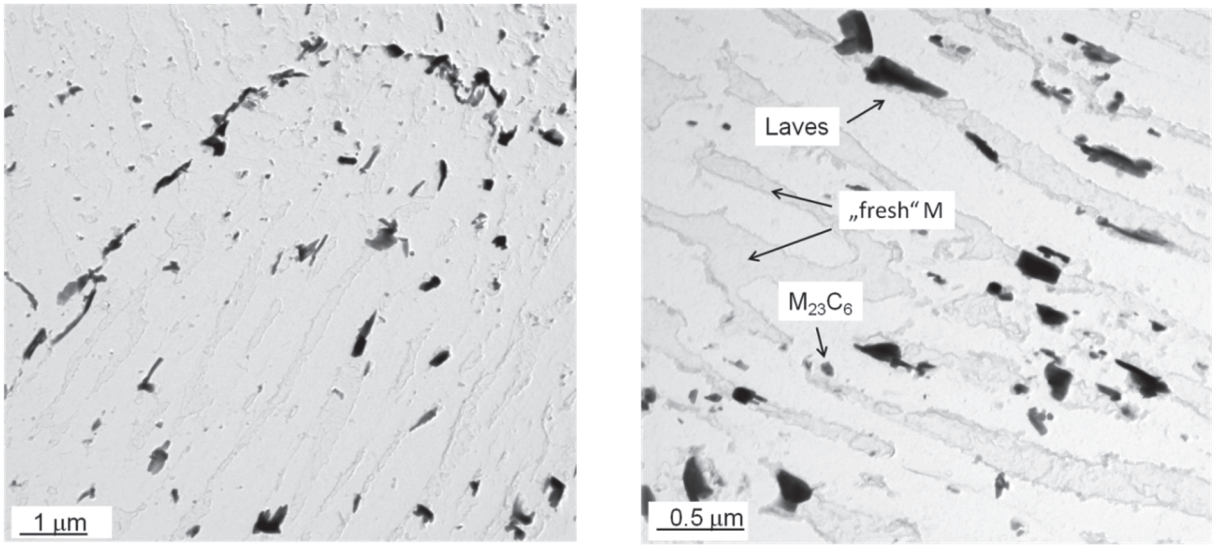
3.3 Specimen C

Tempering of martensite at 690 °C resulted in the formation of a high volume fraction of austenite. On cooling to room temperature most austenitic pools transformed back to "fresh" martensite. The fraction of stable reverted austenite in the microstructure of the 13Cr6Ni2.5MoTi steel after tempering at 690 °C is less than 5 % [4]. Distribution of "fresh" martensite in the specimen C is shown in **Figs. 6a, b**. Furthermore, tempering at 690 °C was accompanied by intensive precipitation processes. **Fig. 6a** shows a network of precipitates along a prior austenite grain boundary. Precipitation along "fresh" martensite/tempered martensite interfaces can be seen in **Fig. 6b**.

Table 4 Chemical compositions of minor phases in the Specimen C, wt. %

Phase	Si	Ti	Cr	Fe	Ni	Mo
$M_{23}C_6$	0.4 ± 0.2	-	56.5 ± 0.9	20.7 ± 1.5	1.4 ± 0.3	21.1 ± 1.2
Laves	2.3 ± 0.1	-	9.9 ± 0.5	32.2 ± 0.9	0.8 ± 0.1	54.6 ± 1.1
sec. MX	-	55.9 ± 6,4	4.7 ± 1,2	0.9 ± 0.6	-	38.4 ± 6.9

Investigations on minor phases revealed three phases: MX, $M_{23}C_6$ and Laves phase. Spot diffraction patterns of $M_{23}C_6$ and Laves phase are shown in **Figs. 7 and 8**, respectively. Diffraction patterns of Laves phase revealed pronounced "streaking" due to a number of defects on the basal plane (001), **Fig. 8**. Chemical compositions of minor phases, as determined by EDX, are summarized in **Table 4**. Precipitation during tempering at 690 °C was more intensive than that at 600 °C. Volume fractions of MX and $M_{23}C_6$ phases were low due to very low contents of both carbon and nitrogen in the steel investigated. Laves phase precipitation was intensive. Coarse particles which can be seen in **Fig. 6b** are mostly Laves phase particles.



a) b)

Fig. 6 Precipitation in the Specimen C, a) network of precipitates along a prior austenite grain boundary, b) precipitates along "fresh" martensite/ tempered martensite interfaces

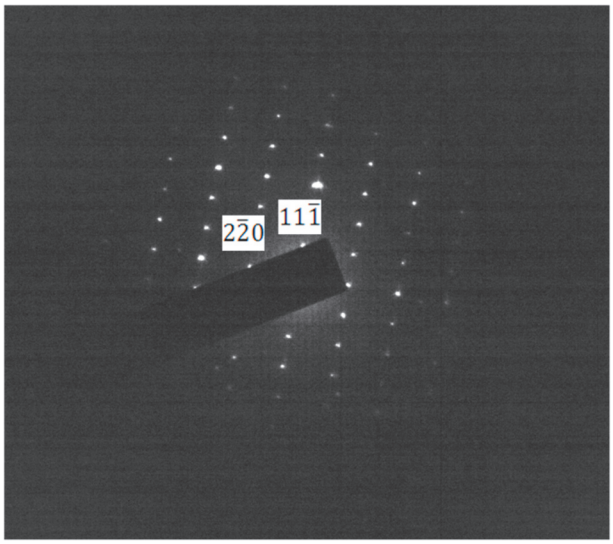


Fig. 7 SAED pattern of $M_{23}C_6$ phase, zone axis [112]

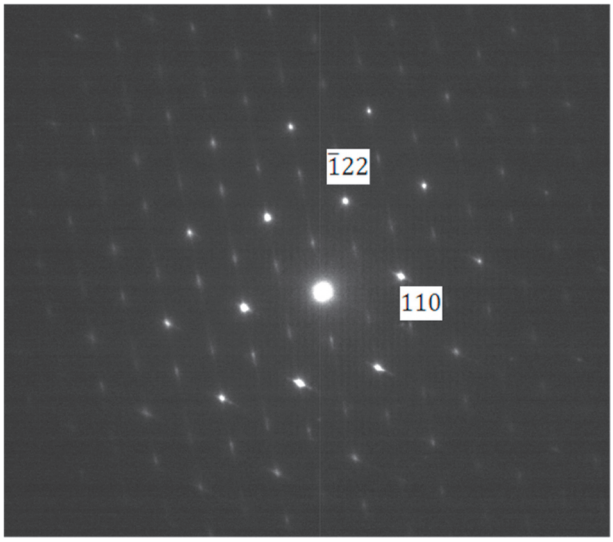


Fig. 8 SAED pattern of Fe_2Mo, zone axis [2-23]

4. DISCUSSION

A useful tool which can be used to predict how changes in alloy compositions can affect volume fractions and compositions of equilibrium phases in engineering materials is the Thermocalc software. This software calculates the stability, compositions and volume fractions of phases in any system by minimizing the Gibbs free energy, along with the requirement for conservation of mass. **Fig. 9** shows equilibrium phases in the steel investigated in the temperature interval from 400 to 1200 °C. In accordance with experimental results calculations predict that at 970 °C equilibrium microstructure will consist of austenite and a small volume fraction of MX phase. At temperatures of 600 °C and 690 °C following minor phases are predicted as equilibrium precipitates: MX, $M_{23}C_6$ and chi-phase.

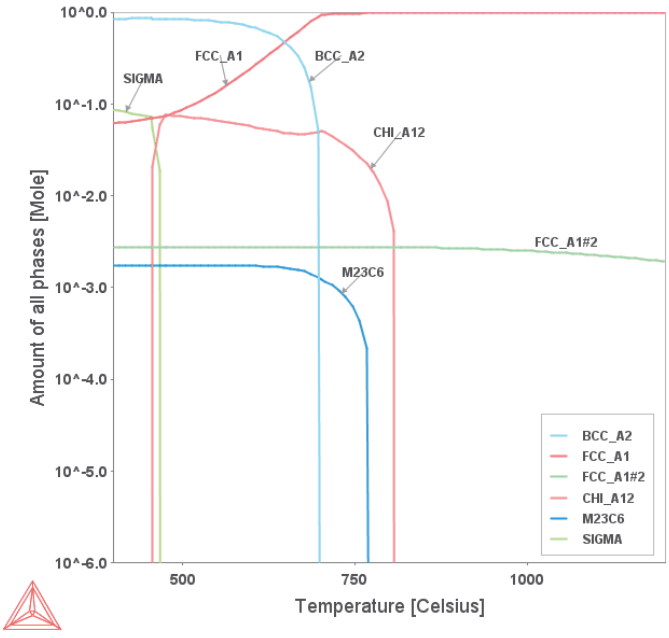


Fig. 9 Calculated amounts of equilibrium phases in the steel i13Cr6Ni2.5MoTi, database TCFE 7, FCC_A1: austenite, BCC_A2: ferrite, FCC_A1#2: MX phase

Chi-phase is an intermetallic phase with the BCC structure and the lattice parameter is a = 0.89 nm. As an example, chemical composition of chi-phase in UNS S31803 duplex stainless steel was determined as (in wt.%): 1 Si, 24 Cr, 2 Mn, 60 Fe, 4 Ni, 11Mo [8]. Tempering of the 13Cr6Ni2.5MoTi steel at 600 °C and 690°C was accompanied by intensive precipitation of an intermetallic phase which was, based on electron diffraction and EDX results, identified as Laves phase of Fe_2Mo type. Thermocalc can be used to predict what is possible thermodynamically, but it cannot predict the time dependence of the microstructure which depends on transformation kinetics. Calculations using TCFE 7 database classified Laves phase (Fe_2Mo) as a metastable phase in the steel investigated.

CONCLUSIONS

- Lath martensite formed during normalization annealing contained coarse primary and fine secondary TiX particles. Temperature of austenizing (970 °C) was not high enough to dissolve particles of this phase.
- Tempering of martensite at both 600 °C and 690 °C was accompanied by partial reverse transformation of martensite to austenite and intensive precipitation processes. Three minor phases were identified: MX, $M_{23}C_6$ and Laves phase (Fe_2Mo). Precipitation processes were more intensive at 690 °C. Volume fractions of MX and $M_{23}C_6$ phases were low. Laves phase precipitation was intensive and this minor phase formed the coarsest particles.
- Thermocalc calculations suggest that Fe_2Mo is a metastable phase in the steel under consideration. Reasons for its intensive precipitation during heat treatment probably lie in transformation kinetics.

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REFERENCES

[1] TOUSSAINT, P., DUFRANE, J. J. Advances in the Making and Base Material Properties of Supermartensitic Stainless Steels, In: Proc. *of Supermartensitic Stainless Steels 2002.* KCI Publishing BV, Brussels, 2002, 23 - 28.

[2] LADANOVA, E., SOLBERG, J.K. In: Proc. of *Supermartensitic Stainless Steels 200.* KCI Publishing BV, Brussels, 2002, 205 - 211.

[3] CARROUGE, D. *Welding of Supermartensitic Steels*. Ph.D. Thesis,TWI Institute, Abingdon, 2002.

[4] VODÁREK, V., TVRDÝ, M., KORČÁK, A. Heat Treatment of Supermartensitic Steels. *Inženieria Materialowa*, XXII, 5 (124), 2001, 939 - 941.

[5] BOJACK, A., ZHAO, L., MORRIS, P.F., SIETSMA, J. In situ Determination of Austenite and Martensite Formation in 13Cr6Ni2.5MoTi Supermartensitic Stainless Steel. *Materials Characterization*, 71, 2012, 77 - 86.

[6] Da SILVA, G.F., TAVARES, S.S.M., PARDAL, J.M., SILVA, M.R., de ABREU, H.F.G. Influence of heat treatments on toughness and sensitization of a Ti - alloyed supermartensitic stainless steel. *J. Mater. Sci.,* 46, 2011, 7737 - 7774.

[7] SONG, Y.Y., PING, D.H., YIN, F.X., LI, X.Y., LI, Y.Y. Microstructural Evolution and Low Temperature Impact Toughness of a Fe-13%Cr-4%Ni-Mo Martensitic Stainless Steel. *Mater. Sci. Eng., 527 A*, 2010, 614 - 618.

[8] ESCRIBA, D.M., MATERNA-MORRIS, E., PLAUT, R.L., PADILHA, A.F. Chi-phase Precipitation in a Duplex Stainless Steel. *Materials Characterization*, 60, 2009, 1214 - 1219.