

SOLVUS TEMPERATURE OF MODIFIED Z-PHASE IN AISI316LN+V+NB STEELHOLEŠINSKÝ Jan¹, VODÁREK Vlastimil², SOJKA Jaroslav², SOZAŇSKA Maria³¹ArcelorMittal Ostrava a.s., Ostrava, Czech Republic, EU, jan.holesinsky@arcelormittal.com²VSB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Ostrava, Czech Republic, EU, vlastimil.vodarek@vsb.cz³Institute of Materials Science, Silesian University of Technology, Katowice, Poland, EU**Abstract**

Creep resistance of steels in the field of dislocation creep strongly depends on both thermodynamic and dimensional stability of minor phases. Precipitation of many minor phases in heat resistant steels is now very well documented. But it is not true in the case of some interstitial minor phases in nitrogen-bearing steels. For example, a limited amount of information is available about precipitation of a complex nitride (Nb,V)CrN, so called modified Z-phase, in austenitic steels. This paper deals with the studies on precipitation behaviour of the modified Z-phase in an AISI 316LN steel with vanadium and niobium additions. Thermodynamic equilibrium phases for the steel investigated were calculated using the ThermoCalc software. Furthermore, laboratory annealing of specimens was carried out in the temperature interval from 550 to 1250 °C for times 1, 20 and 50 h. Kinetics of precipitation of the modified Z-phase in the austenitic matrix was fast. Precipitation of this minor phase was observed in the temperature range of 750 - 1050 °C. The solvus temperature corresponded well with the results of thermodynamic calculations. The solvus temperature of the modified Z-phase in the steel investigated was determined to be about 250 °C lower than that calculated for NbCrN type of Z-phase in the AISI 316LN + 0.1Nb austenitic steel.

Keywords: Modified Z-phase, AISI 316LN+V+Nb steel, thermodynamic calculation, solvus temperature

1. INTRODUCTION

Z-phase, a complex NbCrN nitride, was firstly detected in niobium-bearing austenitic steels in 1950's [1]. Z-phase is seldom reported, even in alloys liable to form it on creep/aging. This could be a result of its composition and its general features of formation, which are not very different from those of MX precipitates. It has the tetragonal unit cell of dimensions $a = 0.3037$ nm, $c = 0.7391$ nm [2]. The metal atom arrangement is characterized by double layers of similar atoms alternating along the c axis of the unit cell to give an AABBAABB... sequence. In austenitic steels particles of this phase in the shape of short rods usually form from the solid solution. The kinetics of Z-phase precipitation is generally fast [1, 3]. The solvus temperature of NbCrN nitrides in austenitic steels was reported to be between 1250 and 1350 °C, depending on the steel composition [1]. Fine Z-phase particles in austenitic heat resistant steels have frequently been credited with beneficial strengthening effects during creep [3].

In martensitic (9-12) %Cr steels niobium in the Z-phase has been found to be partially substituted by vanadium and this results in a reduction of the tetragonal unit cell of this modified Z-phase ((Nb,V)CrN): $a = 0.286$ nm and $c = 0.739$ nm [4]. A lot of effort has been devoted to investigations on nucleation and fast growth of this phase in martensitic (9-12) %Cr steels [5]. The modified Z-phase is generally regarded as a harmful minor phase in these steel grades. However, a lack of information exists about precipitation behaviour of the modified Z-phase in austenitic steels containing both niobium and vanadium additions. Particles with the chemical composition corresponding to (Nb,V)CrN phase were observed after isothermal annealing at 750 °C/1170 h in an austenitic 18Cr-12Ni-VNb steel in [6]. These particles were not reported as Z-phase because their crystal structure corresponded to FCC NaCl structure. Karlsson et al. [6] speculated that the particles with the FCC

crystal structure could be a precursor of Z-phase. This paper deals with the solvus temperature and early stages of precipitation of the modified Z-phase in the AISI 316LN steel with niobium and vanadium additions.

2. EXPERIMENTAL MATERIAL AND TECHNIQUES

Studies were carried out on a laboratory heat. Chemical composition of the steel investigated is shown in **Table 1**. Elements marked in red were not taken into account for thermodynamic calculations.

Table 1 Chemical composition of the AISI 316LN+V+Nb steel, wt. %

C	S	Mn	Si	P	Cr	Ni	Mo	V	Nb	N
0.03	0.007	1.44	0.59	0.017	18.10	12.50	2.44	0.25	0.11	0.16

Preliminary heat treatment of forged rods consisted of solution annealing at 1300 °C/0.5 h followed by quenching in water. Next, annealing of test specimens was carried out in the temperature interval from 550 to 1250 °C for 1, 20 or 50 h, followed by water quenching. Matrix of annealing regimes is summarized in **Table 2**.

Table 2 Heat treatment regimes of specimens

Temperature [°C]	Annealing time [h]		
	1	20	50
	Sample ID	Sample ID	Sample ID
1250	A	I	J
1150	B	K	L
1050	C	M	N
950	D	O	P
850	E	R	S
750	F	T	U
650	G	V	W
550	H	X	Z

Minor phase identification in specimens of the austenitic steel was carried out using carbon extraction replicas. Studies were performed on a transmission electron microscope JEOL JEM 2100, equipped with an EDX analyser JEOL JED-2300T. Identification of minor phases was carried out using a combination of EDX and selected area electron diffraction (SAED). The criterion applied for identification of the modified Z-phase was: 40 at.% < [Fe] + [Cr] < 70 at.% [5]. Interstitial elements were not taken into account during semi-quantitative analyses. Results of semi-quantitative EDX analyses were always normalized to 100 %.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic simulations of modified Z-phase stability

The modelling of solvus temperature of the modified Z-phase in the AISI 316LN + V + Nb steel was carried out using ThermoCalc software and TCFE7 or Steel 16 databases. **Figure 1** shows predicted dependence of amount of phases on temperature. It should be stressed out that the TCFE7 database underestimates stability of Laves phase in molybdenum-bearing steels. The results predict that the modified Z-phase is stable up to the temperature of 1055 °C. At temperatures above 1050 °C MX phase (FCC) is regarded as the stable phase. Using the STEEL16 database the solvus temperature of the modified Z-phase was calculated as 1035 °C, i.e. 20 °C lower than that calculated using the TCFE7 database [7]. Calculations on the solvus temperature of

NbCrN type of Z-phase in the AISI 316LN + 0.1Nb steel predicted temperature of 1290 °C. The solvus temperature of the „original“ Z-phase (NbCrN) was simulated to be ca 250 °C higher than that of the modified Z-phase in the AISI 316LN + V + Nb steel [7].

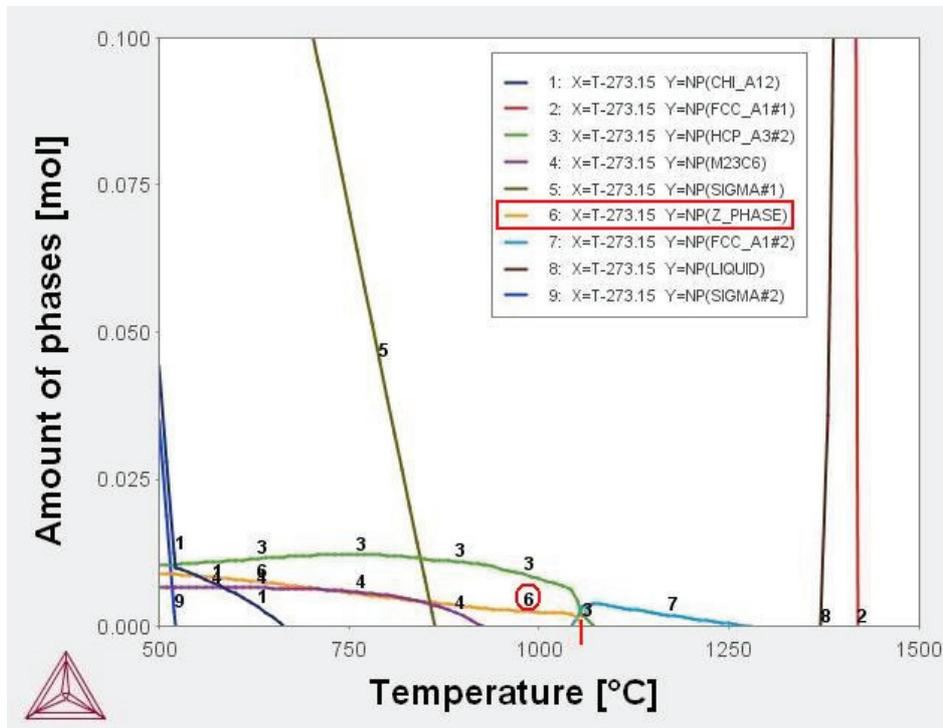


Figure 1 Dependence of amount of phases on temperature, AISI 316LN+V+Nb steel, TCFE7 database, where: 1=chi phase, 2=austenite, 3=Cr₂N, 4=M₂₃C₆, 5=sigma phase, 6=Z-phase, 7=MX phase, 8=liquid, ferrite suppressed

3.2. Experimental determination of the solvus temperature

Experimental investigations revealed that only two minor phases formed during annealing regimes specified in the **Table 2**: MX and the modified Z-phase. It indicated that due to kinetic reasons equilibrium state was not achieved. Both minor phases formed needles and that is why morphology of precipitates could not be used for reliable discrimination between these phases. Needle-like precipitation of MX phase in austenitic steels was also observed by Thorvaldsson [8]. Both phases contained a variable ratio of chromium, niobium and vanadium. Precipitation of the modified Z-phase was identified in specimens annealed in the temperature interval from 750 to 1050 °C for 20 or 50 h. Precipitation in the specimen U (750 °C/50 h) is shown in **Figure 2a**. Modified Z-phase particles reached up to 200 nm in length. At temperatures of 850 and 950 °C annealing for 1 h was sufficient for precipitation of this phase. At annealing temperatures lower than 750 °C precipitation of neither modified Z-phase nor MX was observed even after annealing for 50 h [7].

Heavy precipitation along austenite grain boundaries, twin boundaries and also inside austenitic grains was observed after annealing 850 °C/1 h (specimen E), **Figure 2b**. Similar character of precipitation was **observed** also in the specimen D (950 °C/1 h), **Figure 3a**. In both specimens most precipitates corresponded to MX phase, as evident from the ring diffraction pattern in **Figure 2c**. Particles of modified Z-phase in the specimen E mostly formed needles up to 100 nm in length and several nanometres in width. Many particles of MX phase did not reach 50 nm in length. Dimensions of Z-phase particles increased with both annealing temperature above 850 °C and the time of annealing. The size of the coarsest MX particles was comparable with that of Z-phase particles. After annealing 850 °C/50 h the length of typical Z-phase needles was 200 - 500 nm. Precipitation of the modified Z-phase in the specimen C (1050 °C/1 h) was not identified. Needle - like particles

in this specimen, see **Figure 3b**, were identified using a combination of EDX and SAED as MX phase (insert in **Figure 3b**). However, after longer durations at 1050 °C particles of Z-phase were present. Significant coarsening of the modified Z-phase needles was observed after annealing 1050 °C/20 h - some needles exceeded 2 µm in length and reached several tens of nanometres in width, see **Figure 4a**. Dimensional stability of the modified Z-phase particles in the austenitic steel investigated seems to be lower than that of the “original” NbCrN Z-phase. Results of EDX analyses on the modified Z-phase and MX particles in the specimen M (1050 °C/20 h) are summarised in **Table 3**. Furthermore, calculated equilibrium composition of the modified Z-phase for 1050 °C is included. As evident, the predicted composition of the modified Z-phase agreed well with experimental results.

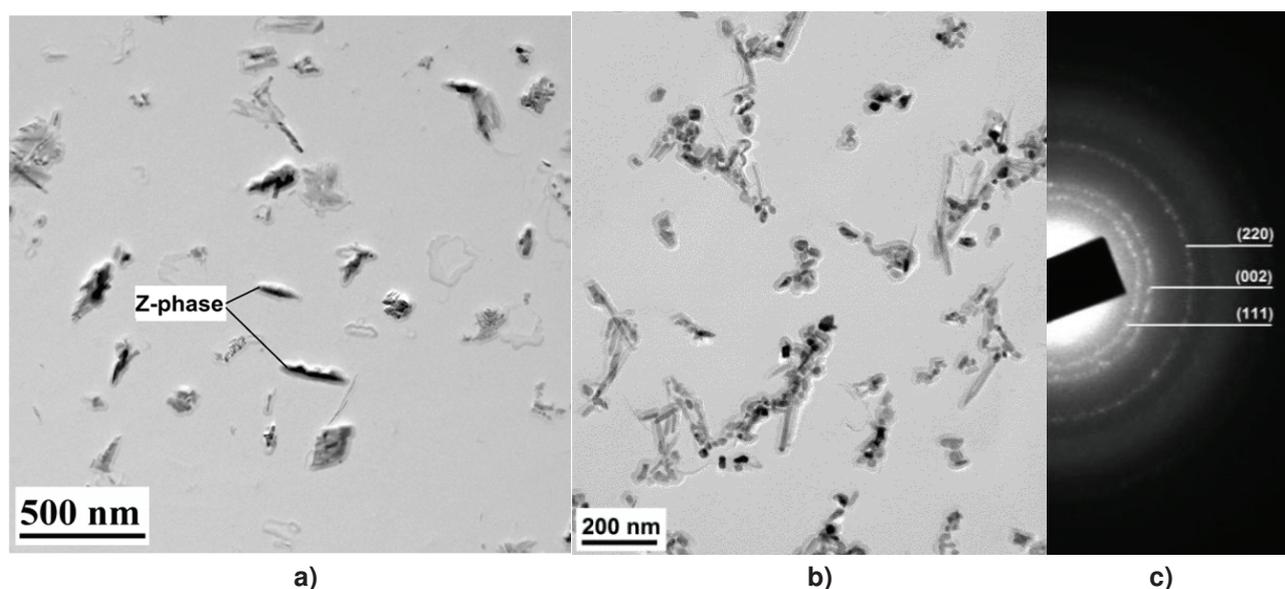


Figure 2 (a) Precipitation in the specimen U (750 °C/50 h), (b) precipitation in the specimen E (850 °C/1 h), (c) ring diffraction pattern of MX phase

Table 3 Results of EDX analyses of the modified Z-phase and MX phase in the specimen M (1050 °C/20 h) and calculated equilibrium composition of the modified Z-phase for 1050 °C, at. %

Element	Mod. Z-phase		MX
	EDX	Thermocalc	EDX
Cr	35.7 ± 3.6	43.2	12.5 ± 0.9
Fe	4.7 ± 0.3	6.8	-
Mo	2.7 ± 1.0	2.4	-
Nb	44.0 ± 4.4	30.0	46.7 ± 1.6
V	12.8 ± 1.7	17.6	40.7 ± 1.6

Note: results represent average values of 10 analyses and corresponding standard deviations

Diffraction patterns recorded on particles with chemical composition corresponding to the modified Z-phase were consistent with the tetragonal unit cell of $a = 0.286$ nm and $c = 0.739$ nm. An FCC precursor of the tetragonal modified Z-phase was not proved. However, in some diffraction patterns, obtained on particles formed during annealing at 850 °C for 1 h, “streaking” along $[001]^*z$ direction was observed. It indicated that there were defects along the c axis of the elementary unit cell. These defects were probably related to limited diffusivity of solute atoms during the formation of the double layer structure AABBAABB... of the modified Z-

phase. In diffraction patterns, recorded on particles of this phase formed at 1050 °C, such diffraction effects were not observed.

Fine particles, reaching several tens of nanometres, were observed in the specimen annealed at 1150 °C for 1 h. The size of these particles after annealing at 1150 °C for 50 h exceeded 0.5 µm, **Figure 4b**. Both fine and coarse particles were identified as MX phase. They formed along austenite grain boundaries, twin boundaries and also intragranularly.

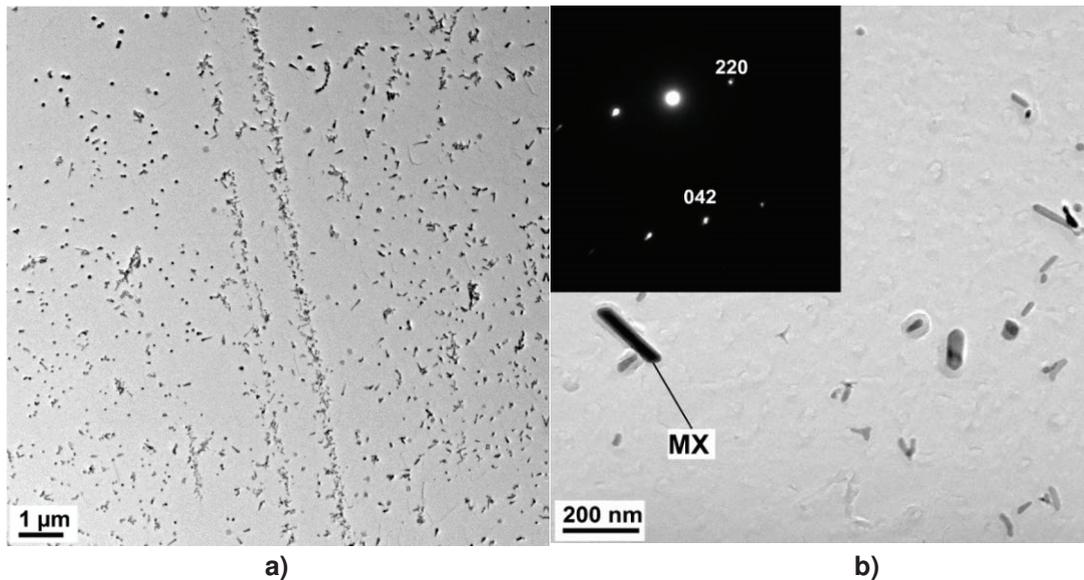


Figure 3 (a) Precipitation in the specimen D (950 °C/1 h), (b) MX particles in the specimen C (1050 °C/1 h), insert: spot diffraction pattern of MX with zone axis $[0\bar{1}4]_{MX}$

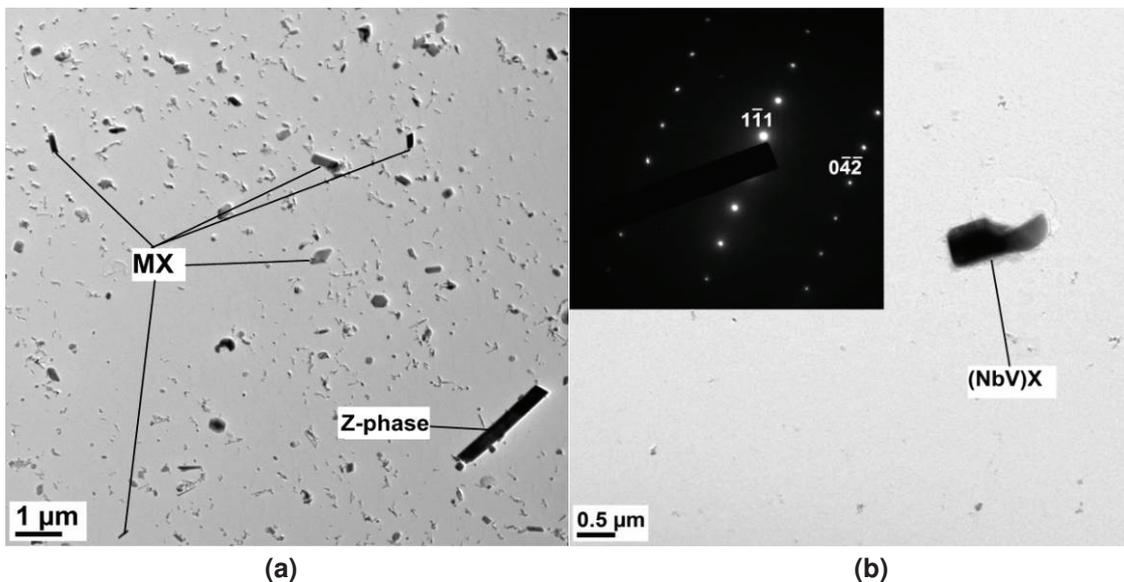


Figure 4 (a) Precipitation in the specimen M (1050 °C/20 h), (b) MX particle in the specimen L (1150 °C/50 h), zone axis $[\bar{3}12]_{MX}$

Particles with chemical composition corresponding to the modified Z-phase were not detected in any sample annealed at 1150 or 1250 °C. Diffraction studies on minor phase particles in specimens annealed at 1150 °C proved that only MX phase was present, see insert in **Figure 4b**. Annealing temperature of 1250 °C was above

the solvus temperature for MX phase. That is why neither Z-phase nor MX particles were observed in specimens annealed at this temperature.

CONCLUSIONS

The most important results obtained during studies on the solvus temperature of the modified Z-phase ((Nb,V)CrN) in the austenitic AISI 316LN + V + Nb steel are as follows:

- Precipitation of the modified Z-phase was experimentally observed in the temperature interval from 750 to 1050 °C. The solvus temperature of 1050 °C was in a good agreement with thermodynamic calculations using the TCFE 7 or STEEL 16 databases.
- The kinetics of precipitation of this minor phase was fast. Particles of modified Z-phase were identified after 1 h annealing at annealing temperatures of 850 and 950 °C. Results of diffraction studies on the particles of this phase confirmed the existence of the tetragonal unit phase already after short annealing times. However, “streaking” along $[001]_z$ direction suggested that there were defects along the c axis of the elementary unit cell. These defects were probably related to limited diffusivity of solute atoms during the formation of the double layer structure AABBAABB... of the modified Z-phase. In diffraction patterns recorded on particles of this phase precipitated at 1050 °C such diffraction effects were not observed.
- The solvus temperature of the modified Z-phase was about 250 °C lower than that of the “original” Z-phase (NbCrN) in the AISI 316LN + 0.1Nb steel.

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