

## Article

# Tracing microalloy precipitation in Nb-Ti HSLA steel during austenite conditioning

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**Abstract:** Microalloying of low carbon steel with niobium (Nb) and titanium (Ti) is standardly applied in high-strength low-alloy (HSLA) steels enabling austenite conditioning during thermo-mechanical controlled processing (TMCP), which results in pronounced grain refinement in the finished steel. The metallurgical effects of microalloying elements are related solute drag and precipitate particle pinning, both acting on the austenite grain boundary thereby delaying or suppressing recrystallization of the deformed grain. In that respect it is important to better understand the precipitation kinetics as well as the precipitation sequence in a typical Nb-Ti-microalloyed steel. Various characterization methods have been utilized in this study for tracing microalloy precipitation after simulating different austenite TMCP conditions in a Gleeble apparatus. Atom probe tomography (APT), scanning transmission electron microscopy in a focused ion beam equipped scanning electron microscope (STEM-on-FIB) and electrical resistivity measurements provide complementary information on the precipitation status and are correlated with each other. It will be demonstrated that accurate electrical resistivity measurements can monitor the general consumption of solute microalloys (Nb) during hot working which was complemented by APT measurements of the steel matrix. On the other hand, STEM revealed that a large part of Nb-containing particles during hot working are co-precipitated with titanium during cooling from the austenitizing temperature. Precipitates that form during cooling or isothermal holding can be distinguished from strain-induced precipitates by corroborating STEM measurements with APT results. APT specifically allows obtaining detailed information about the chemical composition of precipitates as well as the distribution of elements inside the particle. Electrical resistivity measurement, on the contrary, provides macroscopic information on the progress of precipitation and can be calibrated by APT. The current paper highlights the complementarity of these methods and shows first results within the framework of a larger study on strain-induced precipitation.

**Keywords:** Niobium-Titanium microalloyed steel, Electrical resistivity, Atom probe tomography, Scanning electron microscopy

## 1. Introduction

The development of weldable low-carbon steels with high mechanical strength and good toughness is the basis for many modern applications in the structural, energy and automotive sectors. Key to this steel development is the use of microalloying in combination with thermo-mechanical controlled processing (TMCP) [1–4]. This concept of high-strength low-alloyed (HSLA) steels is being produced as strip and plate products covering a wide range of thicknesses and yield strength levels

up to 700 MPa. The involved strengthening mechanisms are in first place grain refinement followed by precipitation and dislocation strengthening. Grain refinement in combination with low carbon content is particularly effective in lowering the ductile-to-brittle transition temperature (DBTT) and increasing ductile plateau toughness.

Microalloying elements, in particular niobium and titanium, play a major role in achieving these strengthening mechanisms. Grain refinement in the final product starts with preventing excessive austenite coarsening during soaking treatment. Therefore, particles insoluble at that high temperature ( $> 1200\text{ }^{\circ}\text{C}$ ), typically consisting of TiN, are required [5]. Niobium ideally is brought into solution by the soaking treatment. It is the most efficient microalloying element for suppressing recrystallization during rolling at lower austenite temperature [6]. The obstruction of recrystallization is caused by solute drag of niobium atoms segregated to the austenite grain boundary as well as by grain boundary pinning after strain-induced precipitation of small Nb(C,N) particles [5,7]. Any niobium left in solid solution after austenite conditioning has further metallurgical effects that contribute to strengthening. Solute niobium delays the austenite-to-ferrite transformation provoking under-cooling and thus further grain refinement or in combination with accelerated cooling promoting transformation into bainite [8]. Depending on the finishing conditions solute niobium can also precipitate as ultra-fine particles in ferrite enhancing strength according to the Orowan-Ashby mechanism [9]. Therefore, it is of great importance to predict and to verify the solute and precipitate status of microalloying elements along the entire process route.

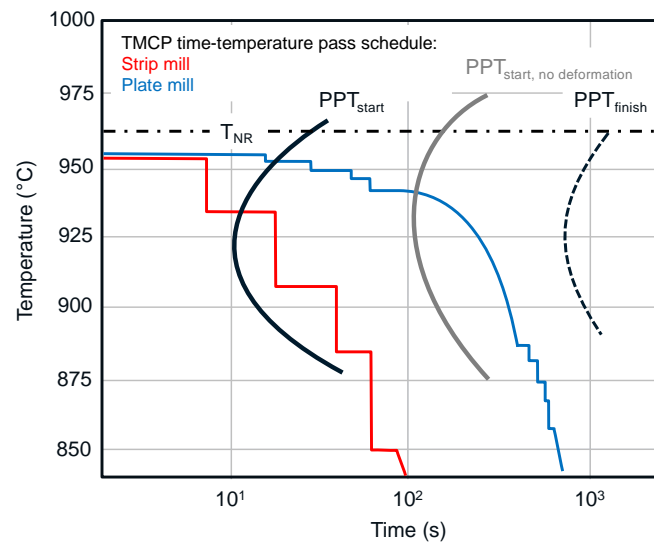
In Nb-Ti dual microalloyed steel a considerable fraction of the nominal titanium addition precipitates at the late stages of solidification caused by segregation of titanium and nitrogen to the residual melt. Any titanium that has not precipitated during solidification does so at temperatures below  $1200\text{ }^{\circ}\text{C}$ , even in undeformed austenite as detailed by Kunze et al. [10]. At higher austenite temperatures these precipitates nucleate on dislocations yielding particle rows or tapes where the particle diameters are in the 20 to 50 nm range. Below  $1000\text{ }^{\circ}\text{C}$  supersaturation becomes so high that nucleation of TiN can also take place in the matrix resulting in randomly distributed particles with sizes below 15 nm [10].

Niobium carbide has a quite good solubility in low-carbon steels. For industrially relevant carbon and nitrogen levels more than 0.1 wt% Nb can be dissolved at  $1200\text{ }^{\circ}\text{C}$  [11]. The niobium solubility diminishes with decreasing temperature to a value of around 0.01 wt% at  $900\text{ }^{\circ}\text{C}$ . Yet, sufficient supersaturation allowing spontaneous precipitation of NbC in the matrix is not being reached. However, heterogeneous nucleation of NbC on pre-existing TiN particles is possible. It has been found that up to 0.02 wt% niobium can be trapped in this way [12,13]. The amount of solute niobium effective for retarding recrystallization is therefore reduced [5,7,14]. This can be overcome by increasing the amount of niobium added to the steel. Higher niobium additions are also motivated by the increase of the temperature of non-recrystallization ( $T_{\text{NR}}$ ) enabling higher finish rolling temperatures and thus yielding better efficiencies in the mill [15,16].

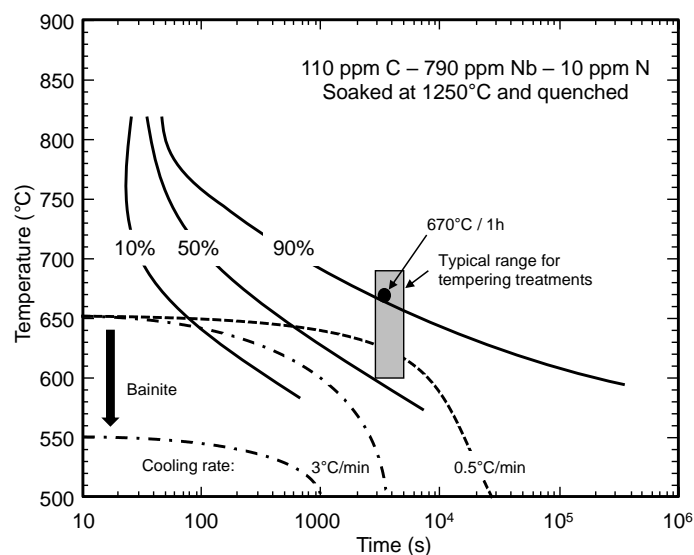
The precipitation of niobium at lower austenite temperatures, where solubility is sufficiently reduced and supersaturation occurs, is greatly facilitated by introducing deformation [11]. This is shown schematically in Figure 1. The precipitation kinetics reaches a maximum at temperatures between  $950$  and  $900\text{ }^{\circ}\text{C}$  [17,18]. Rolling in that temperature range induces simultaneous precipitation of NbC thereby strongly obstructing the recrystallization of deformed austenite grains. It is also obvious that rolling schedules practiced by hot strip mills result in a much lower amount of niobium precipitation than plate mill rolling schedules.

The niobium left in solute solution after rolling is available for precipitation during or after the phase transformation from austenite to ferrite. These NbC precipitates can nucleate as a consequence of partitioning and local supersaturation in the vicinity of the moving phase front known as interphase precipitation [19,20]. Spontaneous precipitation after phase transformation can occur by nucleation on dislocations or by a mechanism of replacing iron by niobium atoms in previously formed nano-cementite particles as described by Hin et al. [21]. The kinetics of spontaneous niobium precipitation in ferrite is also relatively slow under typical finishing conditions for plate and strip products (Figure 2) [22]. It is apparent that even under hot finishing conditions, niobium precipitation will not be complete. Colder finishing conditions promoting bainite formation largely prevent

niobium precipitation. Secondary heat treatment such as tempering, however, allows nearly complete precipitation [23].



**Figure 1:** Schematic of rolling pass schedules in the TMCP regime for strip and plate mills with respect to no-recrystallization temperature  $T_{NR}$  (dashed line) and precipitation (ppt) kinetics.



**Figure 2:** Kinetics of spontaneous NbC precipitation in ferrite in an experimental steel after solution annealing and quenching [22]; typical cooling curves and tempering conditions are indicated.

The optimum exploitation of niobium with regard to the before mentioned physical metallurgical effects demands a precise knowledge of the solute niobium status before and after hot deformation. Numerous studies exist on how to calculate the behavior of microalloying elements using thermodynamics, which was recently summarized [24]. Several techniques that either directly or indirectly measure the niobium in solution exist. Early work of LeBon et al. [25] used hardness testing to quantify the amount of niobium precipitated based on the assumption of a higher hardness being due to less niobium in solution. However, such measurements are liable to misinterpretation caused by competing effects on hardness.

Electrical resistivity measurements of alloys rely on the principle that solute precipitant elements are consumed while precipitation advances. As the iron matrix of the steel is more and more depleted of elements participating in precipitation, the resistivity of the steel drops because solute elements are stronger scattering centers for electrons in comparison to precipitates. Simoneau et al. [26] measured the electrical resistivity of niobium-microalloyed steels isothermally held at 900 °C for

different times and found a good correlation with different precipitation stages. Park et al. [27] estimated the dissolution temperature of a Nb-microalloyed steel to be the point where the electrical resistivity reached a plateau and verified it by using transmission electron microscopy (TEM) replica. Jung et al. [28,29] also used this technique to investigate the precipitation in a thermo-mechanically processed Nb-Ti-V microalloyed steel with and without deformation. By applying the lever rule to the resistivity curve, they could show that the precipitation mole fraction increases earlier when the sample is pre-strained. These reported results rely on the fact that the upper and lower limit of the electrical resistivity are tied to the total dissolution or precipitation of niobium, respectively. However, for (Nb,Ti)(C,N) steels, the maximum amount of niobium in solution is generally less than the nominal amount due to the above-mentioned reasons. Therefore, in that case, the electrical resistivity curves need to be calibrated on the actual amount of niobium in solution.

One common technique to assess the amount of solute niobium is the extraction of precipitates by dissolving the metallic matrix in acid and the subsequently filtering the precipitates from the solution. Measurement of both filter and filtrate yields the niobium precipitated and in solid solution, respectively [16,30]. This method ensures a very easy and statistically significant measurement. However, it cannot be excluded that small precipitates either pass through the filter or partially dissolve during the extraction and thereby bias the analysis of solute niobium concentration.

A feasible alternative is given by atom probe tomography (APT), which detects all elements with the same sensitivity and a spatial resolution in the sub-nanometer range [31]. Therefore, the technique applies especially well to investigation of segregation lines or nanometer-sized precipitates. Furthermore, APT can also measure the chemical composition of the matrix excluding even the smallest precipitates or clusters into the composition calculation [32], contrary to other spectroscopy techniques. APT was used to characterize (Nb,Ti)(C,N) particles formed during hot-rolling [33–37]. Nöhner et al. investigated the influence of deformation level [33] while Kostryzhev and Pereloma et al. investigated the influence of the deformation temperature [34,35] on the precipitation of (Nb,Ti)(C,N) in low-alloyed steels. Due to the small analysis volume of APT measurements, quantitative data of the precipitation number density or size distribution must be treated with caution. (S)TEM characterization, which is often used to obtain counting statistics, is liable to misinterpretation because of the user-dependent production of the thin foil or carbon replica. Besides, user-dependently there might be a range of precipitate sizes that will be not detected by either APT nor TEM as shown in the case of Kostryzhev et al. [35], which might be also due to the loss of smallest precipitates during excessive etching when producing the replica.

Accordingly, the correlation and calibration of electrical resistivity measurements with the APT analysis of precipitates and matrix offers a high potential for obtaining meaningful quantitative data for the precipitation kinetics of (Nb,Ti)(C,N) and to establish a guideline for the heat treatments during steel processing.

In this work, APT is used to detect and differentiate precipitates that form during various TMCP stages, in combination with scanning transmission electron microscopy (STEM-on-FIB). Furthermore, the amount of solute niobium measured by APT for different processing stages is correlated with the electrical resistivity method. It will be shown that both, deformation level and temperature during hot working, can be distinguished based on electrical resistivity. Finally, the composition of precipitates formed at lower austenite temperature as well as after transformation to ferrite is characterized with APT.

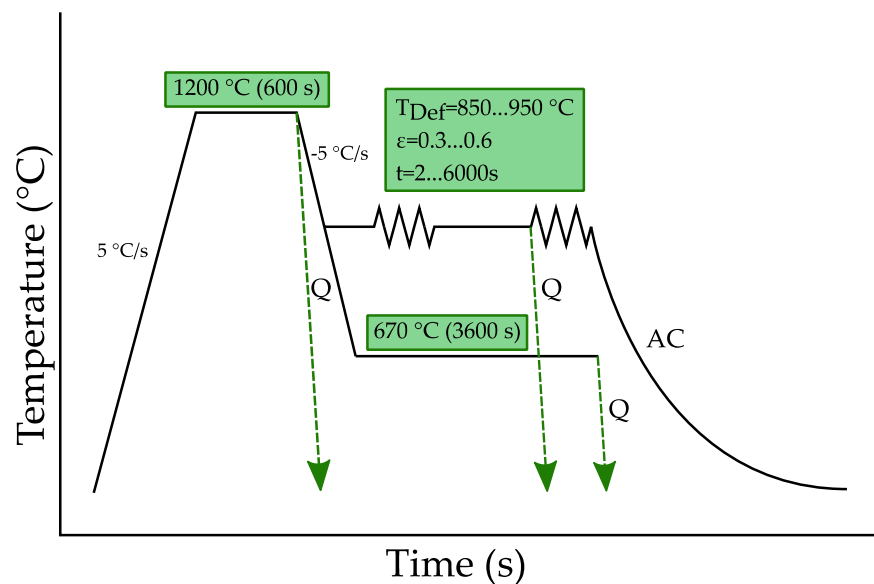
## 2. Materials and Methods

The current study has been conducted on a laboratory melt of a Nb and Ti dual-microalloyed steel according to composition listed in Table 1. Similar compositions are in industrial use for advanced linepipe or structural steel grades being produced either as plate or hot-rolled strip. The weight percent ratio of titanium and nitrogen in this analysis has a value of 3.4 corresponding almost exactly to an atomic Ti:N ratio of 1:1.

**Table 1:** Steel composition.

Element	C	Si	Mn	P	Cr	Mo	Ni	Cu	Al	N	Nb	Ti
wt %	0.042	0.32	1.69	0.012	0.036	0.021	0.195	0.215	0.033	0.005	0.085	0.017

Cylinders of as-cast material were cut into a dimension of 16 mm length and 8 mm diameter. The sample cylinders were then thermo-mechanically processed in a Gleeble 3800 simulator (Dynamic Systems Inc., USA), using a hot-compression module with compressed helium gas as quenching medium. A schematic of the different heat-treatment simulations is shown in Figure 3. It consisted of an austenitizing stage at 1200 °C for 10 minutes. Samples were then cooled down to the deformation temperatures of 950 °C, 900 °C and 850 °C, respectively, with a rate of 5 °C/s. Double-hit compression tests ( $\epsilon = 0.3 + 0.3$ ) with variable inter-pass time (2 – 100 s) were performed to determine the recrystallization-stop temperature and to reveal the softening stasis. Single-hit compression tests ( $\epsilon = 0.3$  or  $\epsilon = 0.6$ ) and subsequent isothermal holding periods ranging from 2 to 6000 s followed by quenching were performed to characterize strain-induced precipitation. Additional samples were directly quenched from temperatures of 1200 °C and 950 °C without deformation, whereas one sample was held isothermally at 670 °C for 1 hour after cooling down from 1200 °C, and then quenched. These treatments aimed at characterizing the precipitation status before austenite deformation as well as after austenite-to-ferrite transformation.



**Figure 3.** Schematic of the simulated heat treatments. Samples were characterized quenched (Q) from austenitization temperature or cooled down to deformation temperature  $T_{Def} = 950, 900$  and  $850$  °C with varying strain  $\epsilon$ , holding times  $t$  and quenching/second compression to measure the softening, and air cooling (AC). Also, samples quenched from austenitization temperature were aged at  $670$  °C for 1 hour and quenched.

For each TMCP-stage described above, cylindrical samples were machined for electrical resistivity measurements by cutting cylinders of length 10 mm and diameter 5.6 mm from the thermo-mechanically deformed samples. The rather short length is due to constraints originating from the maximum cylinder length which could be treated in the Gleeble compression module without buckling. The setup for measuring the electrical resistivity was a 4-point measurement, as described in early works of Simoneau et al. [26]. The voltage drop within fixed potential points on the sample is proportional to the internal resistivity. Oxides or contaminations with organic residue will greatly increase the resistivity and produce erroneous values. Therefore, before measuring, the samples were further ground with 1200 grid sandpaper and cleaned with isopropyl alcohol to establish the most optimal surface conditions. The temperature was  $23$  °C for all measurements.

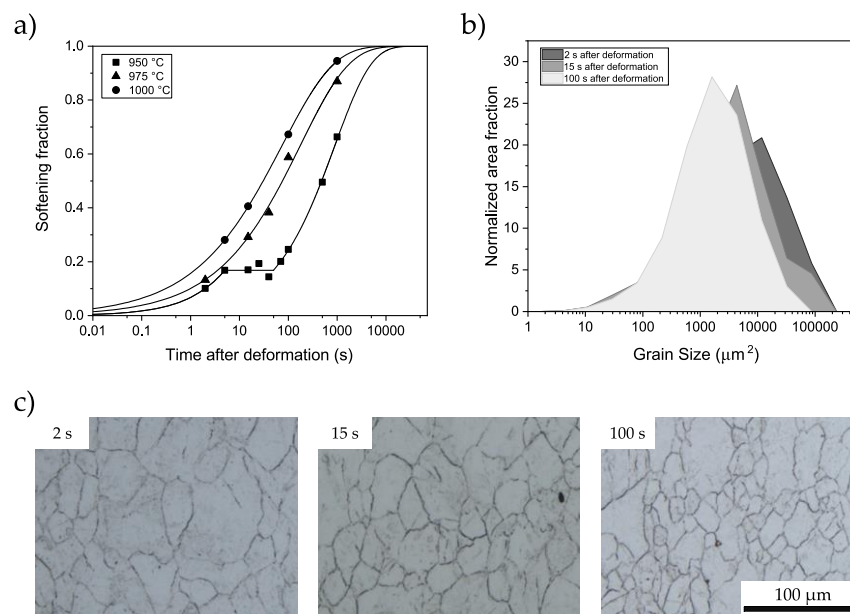


For selected samples, cylinders were also cut along the length and the samples were prepared for metallography, carbon replica technique and APT by polishing with 6, 3 and 1  $\mu\text{m}$  diamond suspension and a final oxide polishing using silica slurry (0.05  $\mu\text{m}$ ). For all investigations, sample sections in the half-length and quarter-width were investigated because at this position the local strain was calculated to be approximately equal to the nominal strain during compression. Metallography for assessing the prior austenite grain structure was conducted using hot aqueous supersaturated picric acid and images were taken with a light optical microscope Leica DM6000 (Leica Microsystems, Germany). Carbon replica were prepared by using a 2% Nital etching after carbon coating and investigated in STEM-on-FIB (Helios Nanolab™ 600, Thermo Fisher Inc., USA, formerly FEI Company, USA).

APT was done using a LEAP3000X HR (Cameca Inc, USA) with voltage pulsing mode. APT analyzes specimen volumes of about  $80 \times 80 \times 200 \text{ nm}^3$  (usually tens of millions of atoms). The instrumental details are described elsewhere [31]. The specimens were prepared using the conventional lift-out technique in the FIB-SEM dual station (Helios Nanolab™ 600, Thermo Fisher Inc., USA, formerly FEI Company, USA) [38]. A final low voltage milling at 2 kV was performed to minimize the gallium induced damage. APT measurements were at 15 % pulse fraction, temperature of around 60 K, pressure lower than  $1.33 \times 10^{-8} \text{ Pa}$ , frequency of 200 kHz and evaporation rate of 5 atoms per 1000 pulses. All APT data reconstruction was done within the software IVAS 3.6.14 (Cameca Inc, USA). For composition measurements, it was distinguished between precipitates and steel matrix. Precipitates were analyzed using a constant iso-concentration surface with 1 at% Nb., which gave best visual representation of the precipitate surfaces. Small clusters were analyzed using the maximum separation method [39], whereas the steel matrix composition was measured using precipitation/cluster or grain boundary/segregation-free volume of at least 1,000,000 atoms.

### 3. Results

Based on double-hit compression tests in the Gleeble apparatus and evaluation of respective softening behavior (Figure 4a), the recrystallization stop temperature  $T_{\text{NR}}$  of laboratory steel was estimated to around 960 °C. Representative microstructures for all deformation temperatures were developed to reveal the prior austenite structure (Figure 4c). The mean austenite grain size decreases and the number of grains increases with longer inter-pass times between compression hits (Figure 4b and Table 2).



**Figure 4.** **a)** Softening behavior of austenite after Gleeble double-hit deformation, **b)** austenite grain size distribution as a function of the inter-pass time between two deformation hits derived from **c)** light-optical metallography of the respective prior austenite microstructures.

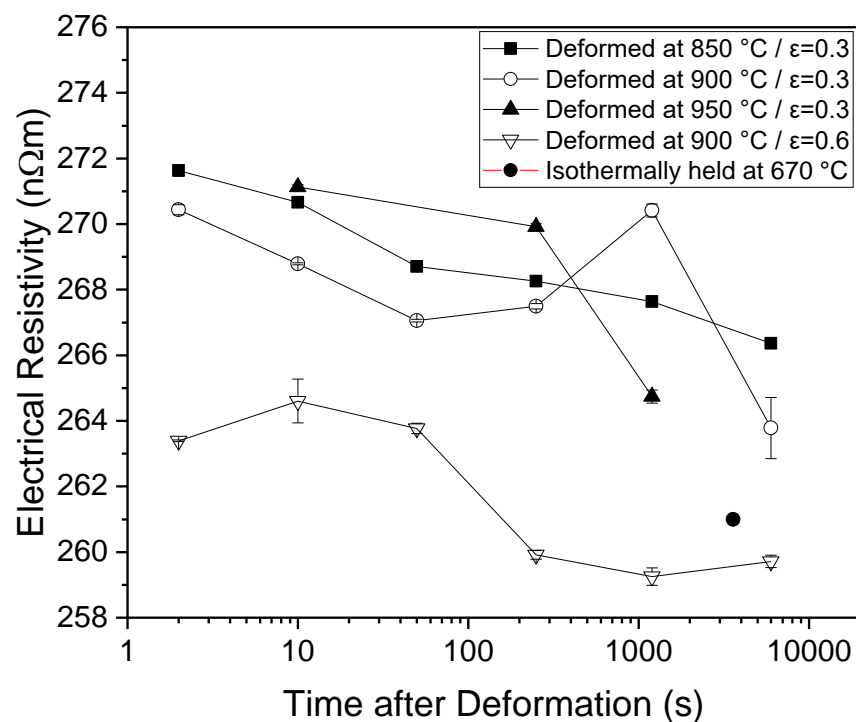
**Table 2.** Evaluation of mean austenite grain size and grain count in a 500x500  $\mu\text{m}^2$  area.

Inter-pass time	Mean PAG size ( $\mu\text{m}^2$ )	Number of grains
2 s	587.41	4144
15 s	464.85	5121
100 s	400.82	5634

### 3.1. Electrical resistivity measurements

The electrical resistivity behavior as function of the time elapsed after deformation is shown in Figure 5 for the temperatures 850, 900 and 950 °C. For all temperatures, there was an almost steady decrease of resistivity after deformation which slowed over time (note the logarithmic time axis). Directly after the deformation, the resistivity is around 272 and 270 n $\Omega\text{m}$  for samples deformed at 850 and 900 °C, respectively, and goes down to 266 and 264 n $\Omega\text{m}$  after 6000 seconds. The resistivity of the samples deformed at 900 °C was mostly lower than for 850 °C with an offset of roughly 1 n $\Omega\text{m}$ . For 950 °C, the resistivity dropped significantly at 1200 seconds after being higher than 850 °C and 900 °C for shorter holding times. The strong resistivity increase of the sample deformed at 900 °C and held for 1200 °C was reproduced in many different measurements and was assumed to be related to a faulty sample production in Gleeble. When the deformation is increased to  $\epsilon = 0.6$ , compared to  $\epsilon = 0.3$ , the resistivity was significantly lower even for short holding times, and then dropped finally to resistivity values of roughly 259 n $\Omega\text{m}$ . Just above that value, with 261 n $\Omega\text{m}$ , lies the electrical resistivity of the sample that was isothermally held at 670 °C for 1 hour.

For these measurements to provide a quantitative understanding of the evolution of precipitation, calibration on the solute niobium is necessary. This can be achieved by using atom probe tomography, as will be shown in section 3.3.

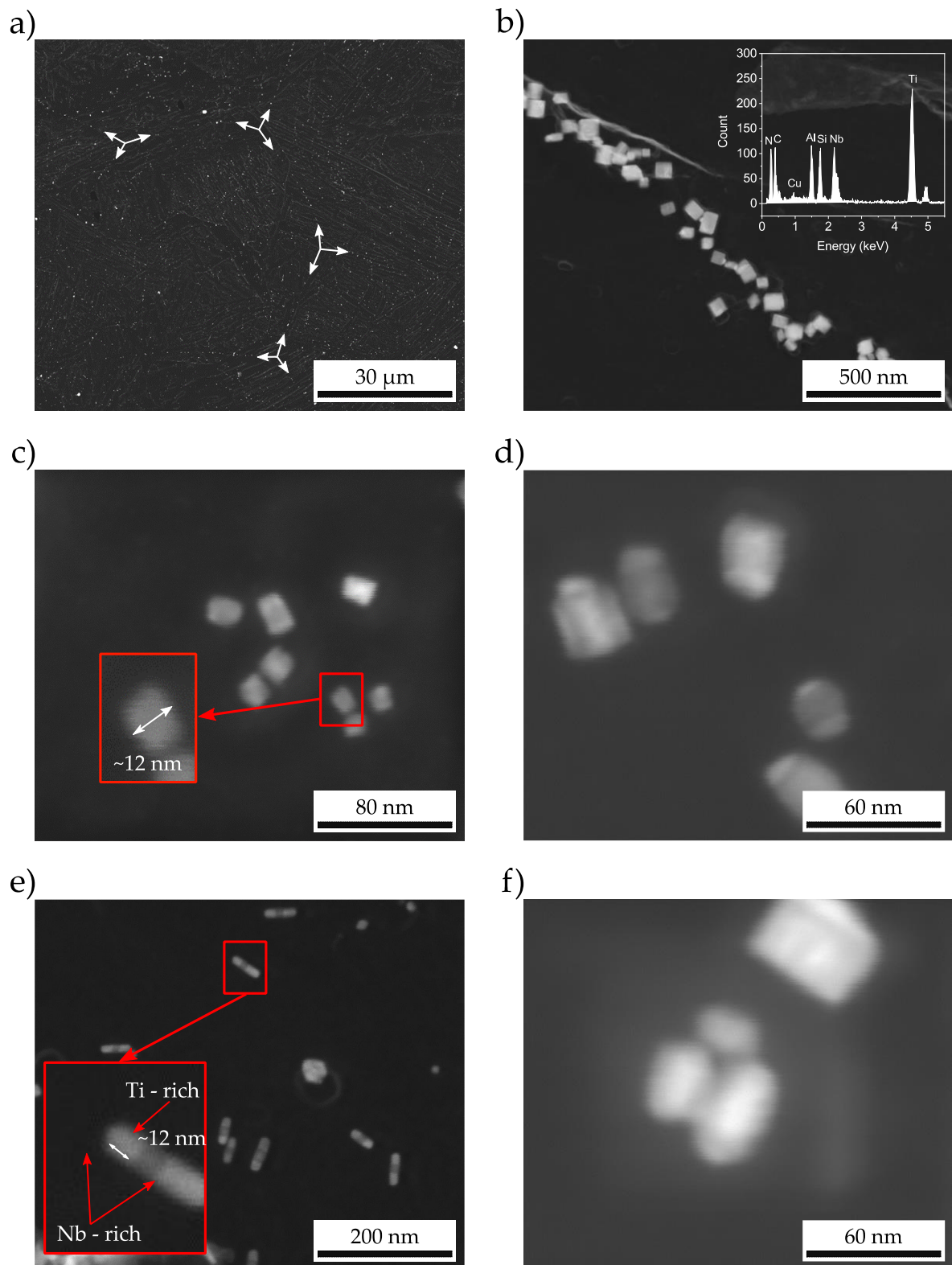
**Figure 5.** Evolution of electrical resistivity with time after deformation for samples deformed at 850 °C, 900 °C and 950 °C with  $\epsilon = 0.3$  and  $\epsilon = 0.6$  and after isothermal holding at 670 °C for 1 hour.

### 3.2. Precipitate characterization by STEM

Precipitation at different treatment stages was investigated by producing carbon replica samples and analyzing them using STEM-on-FIB. Samples directly quenched from 1200 °C revealed precipitates that did not dissolve during soaking treatment. Those quenched from 950 °C indicate whether additional precipitates have formed during the cooling phase from soaking temperature. Analyzing the same condition after deformation by a strain of  $\epsilon = 0.6$  and a holding time of 200 s and 1200 s revealed newly formed strain-induced precipitates.

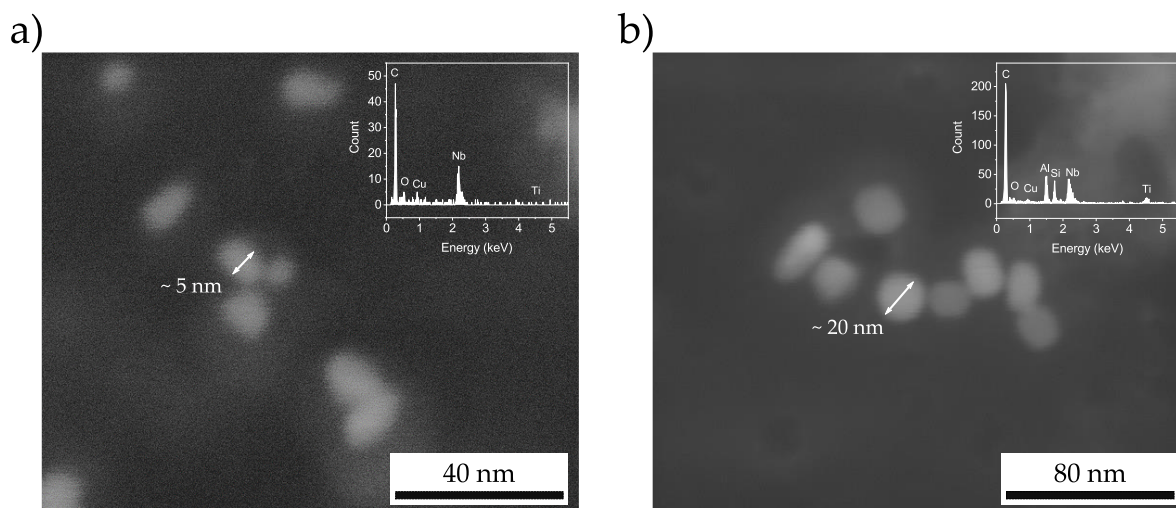
Figure 6a shows the precipitate population of a sample cooled down to 950 °C after soaking at 1200 °C followed by quenching. One can observe particles decorating the prior austenite grain boundary (indicated by white arrows), particle clusters inside the austenite grain and more randomly distributed particles. The stage after soaking at 1200 °C comprises aligned clusters of cube-shaped particles having sizes of up to 80 nm that have not dissolved. Energy dispersive x-ray spectroscopy (EDS) identified the particle composition as being Nb-rich TiN (Figure 6b). Al, Si and Cu elemental signals had their origin in the STEM setup. The particle clusters likely originate from casting and did not dissolve during soaking. A fraction of smaller cube-shaped particles with a size of around 12 nm, appears to be rather pure TiN (Figure 6c). Also, these particles must have existed before the soaking treatment. Similar-sized particles are found carrying a Nb-rich layer on two opposing sides (Figure 6d) that seems to have nucleated on pre-existing TiN cubes. For part of these compound particles the Nb-rich layer has grown to larger dimension (Figure 6e). However, the Nb-rich layer appears to grow only along one direction on opposite sides of the TiN core. It is feasible that niobium co-precipitates on the pre-existing particle after soaking. Finally, bean-shaped particles were found showing niobium and titanium peaks in the EDS spectrum, yet not comprising a core-shell morphology (Figure 6f). All these particle species were also found in the various hot-deformed and held samples.





**Figure 6.** STEM images of carbon replica of precipitates present after quenching from 950 °C. **a)** Grain boundaries visible through line-like precipitation of **b)** large (approx. 80 nm), cube-shaped precipitates which EDS identifies as Nb-rich TiN. **c)** More homogeneously distributed in the grain interior are TiN of smaller size (< 15 nm) as well as **d)** TiN with heterogeneously nucleated Nb-rich caps, which **e)** also can be larger. **f)** Nb- or Ti-rich Nb (or Ti)(C,N) were found with a homogeneously looking atom distribution.

After applying deformation, the precipitate population observed by STEM was strongly augmented by a large amount of small precipitates which were homogeneously distributed inside the grains. Figure 7 shows their size and distribution exemplarily on the sample deformed at 950 °C with a strain of  $\varepsilon = 0.3$ . The size of precipitates is in the range of 5 to 20 nm depending on the holding period after the compression hit, which was 200 s and 1200 s, respectively. EDS shows, that the precipitates are free or nearly free of Ti even after long holding times.



**Figure 7:** STEM image and EDS spectra of precipitates that have formed after hot deformation at 950 °C,  $\varepsilon = 0.3$ , and holding for **a)** 200 and **b)** 1200 seconds.

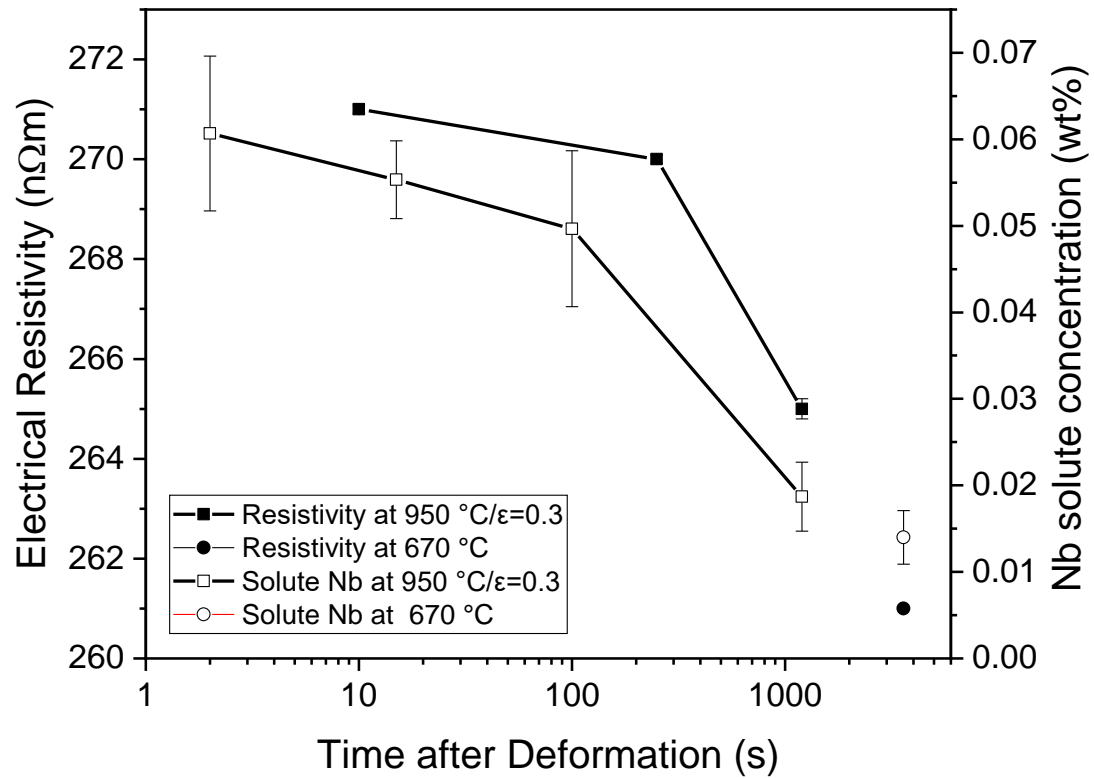
### 3.3. APT analysis of precipitates and solute niobium status

Along with the very precise analysis of precipitates, the precipitate-free material volume bears valuable information as it allows determining the amount of niobium dissolved in the steel matrix. This allows the characterization of the solute depletion after precipitation in the larger neighborhood. Figure 8 compares the decreasing mass fraction of solute niobium measured by APT in the steel matrix with the electrical resistivity as function of the time elapsed after deformation (950 °C,  $\varepsilon = 0.3$  and 670 °C isothermally held for 1 hour). For the deformed sample, the APT analysis revealed an initial solute niobium content of  $0.061 \pm 0.009$  wt%, whereas the steel nominally contains 0.085 wt% niobium (Table 1). This indicates that the difference of around 0.024 wt% niobium precipitated before the deformation treatment. For the applied temperature-deformation condition, solute niobium is depleted to  $0.019 \pm 0.004$  wt% after a holding time of 1200 seconds. Thus approximately 70 % of the initially dissolved niobium precipitated as deformation-induced particles. In the case of the sample isothermally held at 670 °C for 1 hour, the concentration of solute niobium is  $0.014 \pm 0.003$  wt% which is 16.5 % of nominal concentration or, taking the measured initial amount in the deformed sample, 23 %. In the precipitation/segregation-free areas, the other carbide forming elements -titanium, carbon and nitrogen- were not detected in the mass spectra of the APT measurements, because they were either below the detection limit (the background of the APT measurements was around 10 atoms), or, in the case of nitrogen, silicon, which has a much higher concentration in the steel, overlaps with the peaks in the mass spectrum.

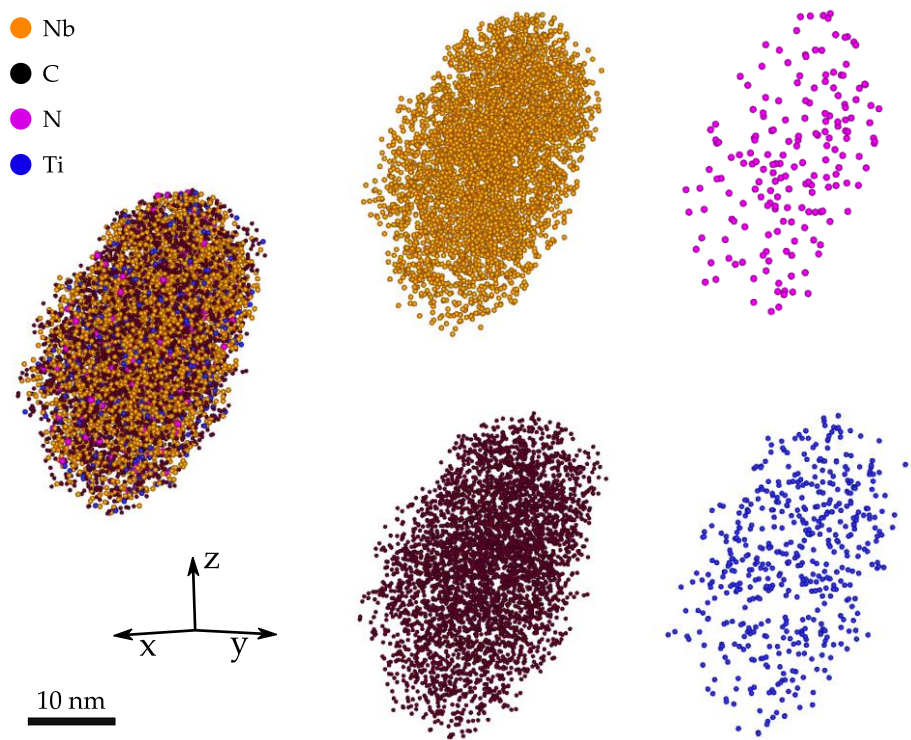
Overlaying the data from electrical resistivity measurements shows a good correlation with the APT data (Figure 8).

In addition to the matrix measurements, homogeneous precipitates were analyzed by APT in samples deformed at lower austenite temperature (850 °C,  $\varepsilon = 0.6$ , quenched after holding for 200 seconds), which have a bean-shaped morphology (Figure 9). Their morphology fits best to the precipitates shown in Figure 6f, indicating that these precipitates also existed in the samples that were not deformed but directly quenched from high austenite temperature. Their existence is rather interesting, since the understanding of particles having a heterogeneous TiN-core-Nb(C,N)-shell morphology is quite established. As visible in Figure 9, the particle predominantly consists of carbon

and niobium as well as smaller fractions of titanium and nitrogen. The elemental distribution in this particle is homogeneous and its composition is given in Table 3. The amount of niobium and titanium is nearly the same than the amount of carbon and nitrogen so that the particle can be considered being a stoichiometric (Nb,Ti)(C,N) precipitate.



**Figure 8:** APT evaluation of solute Nb in the steel matrix and correlation with electrical resistivity measurements.

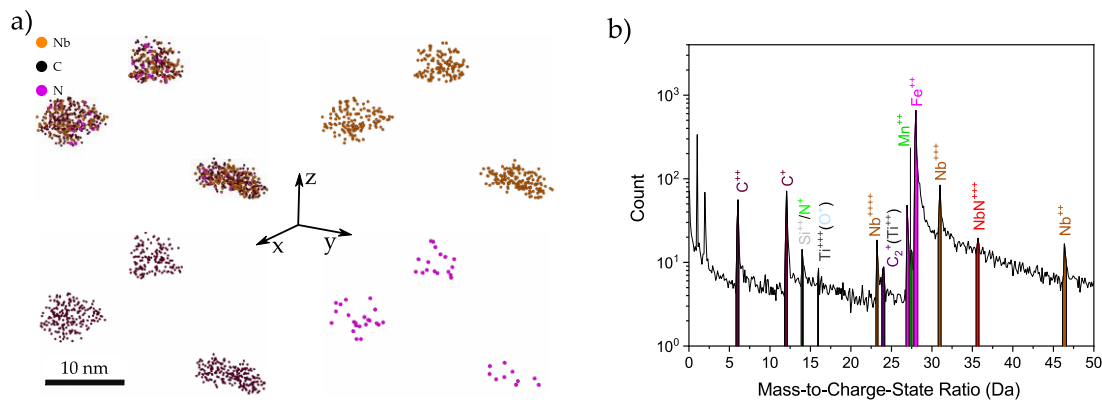


**Figure 9:** APT analysis of bean-shaped particle similar to those in Figure 6f, but measured in sample deformed at lower austenite temperature and higher strain (850 °C,  $\epsilon=0.6$ ) and quenched after holding for 200 seconds. Niobium, carbon, titanium and nitrogen atoms are shown.

**Table 3.** Elemental composition of APT-measured, bean-shaped particle in Figure 9.

Element	Nb	C	Ti	N
Atom count	4582	4400	480	177
Rel. at%	47.5	45.6	5.0	1.7

As shown above, after applying strain, the precipitate population observed by STEM was strongly augmented by a large number of small particles (Figure 7). In the sample deformed with higher strain of  $\epsilon=0.6$  at 850 °C, APT could detect small precipitates which are represented in Figure 10a. Carbon and niobium are indeed the dominant elements in these precipitates, while only a small fraction of nitrogen and practically no titanium is found. Their composition is given in Table 4. The APT measured mass-to-charge ratio peaks of  $^{12}\text{C}^{2+}$  and  $^{12}\text{C}^{+}/^{12}\text{C}_2^{2+}$  both contain significantly more atoms than the combined niobium atoms contained in the peaks at 23.3 Da ( $^{93}\text{Nb}^{4+}$ ), 30.9 Da ( $^{93}\text{Nb}^{3+}$ ) and 46.5 Da ( $^{93}\text{Nb}^{2+}$ ), and the ( $^{93}\text{Nb}^{14}\text{N}$ ) $^{3+}$  (Figure 10b). The peak at 24 Da can correspond either to carbon or titanium. Since no  $\text{Ti}^{2+}$  isotopes at 23, 23.5, 24.5 and 25 Da are present, the peak at 24 Da was assigned to  $^{12}\text{C}_2^{2+}$ . Although it is not possible to assure that all the counts at this peak correspond unambiguously to carbon, these counts represent only 5 percent of the particle composition. Adding up all carbon counts, the Nb/C ratio is only 1.2:2. Yet, if the nitrogen counts are considered as well, the ratio of niobium to interstitial atoms is approaching 1:2. The chemistry of the precipitates is thus sub-stoichiometric (Table 4).



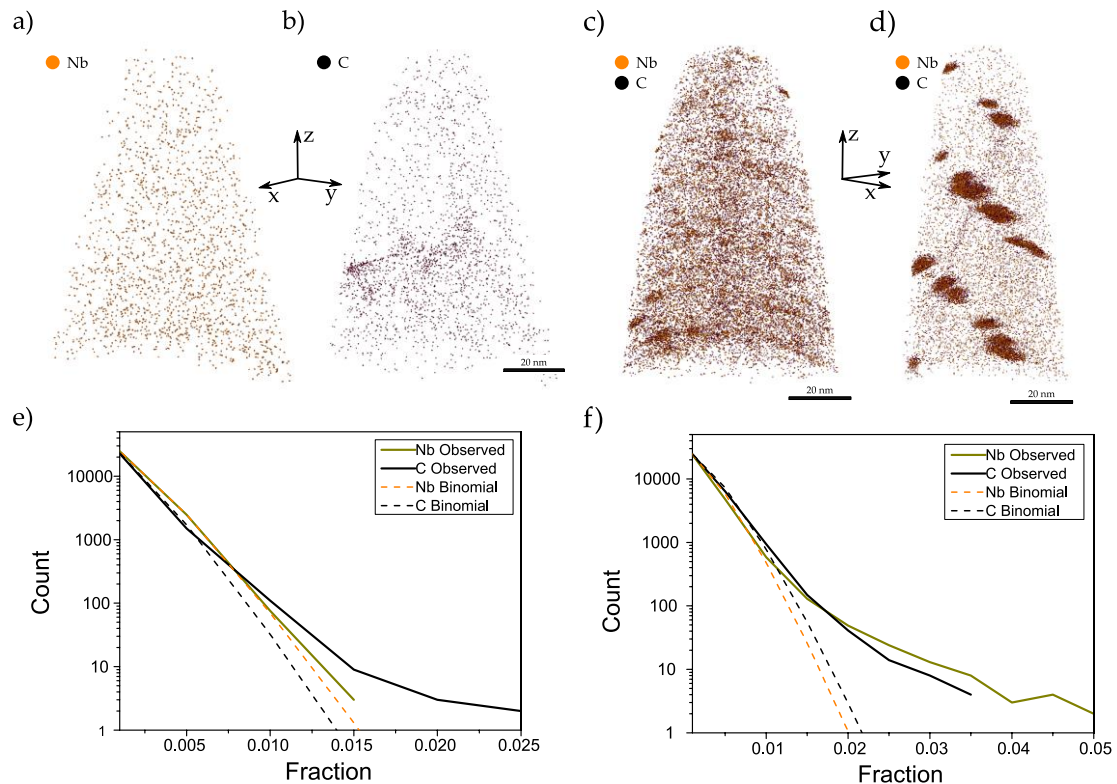
**Figure 10:** APT analysis of precipitates formed after deformation at lower austenite temperature and higher strain (850 °C,  $\epsilon = 0.6$ ) and holding for 200 seconds. **a)** Atom distribution map with niobium, carbon and nitrogen shown; **b)** mass-to-charge ratio peak analysis.

**Table 4.** Elemental composition of precipitates measured by APT in Figure 10.

Element	Nb	C	Ti	N
Atom count	410	688	/	74
Rel. at%	35.0	58.7	/	6.3

In samples deformed at 950 °C and quenched after short holding times up to 1200 seconds, carbon clusters were observed as shown in Figure 11b, whereas the atom map of niobium (Figure 11a) indicates no obvious clustering in any of the cases (ten or more measurements for each holding time 2, 15, 100 and 1200 seconds, analogue to the APT analysis shown in Figure 8). To rule out early stages of clustering, the distribution of the carbon and niobium atoms in the APT reconstructions was compared to a random distribution (frequency distribution analysis, binning 200 ions, Figure 11e). It can be seen that in the particular case of the atom maps of Figure 11a and 11b, only carbon is exhibiting a small deviation of 0.5 to 1 at% from the random distribution for a small number of clusters (Figure 11b) while niobium appears to be randomly distributed throughout the volume (Figure 11a). No precipitates as detected in STEM (Figure 7) were detected by APT.





**Figure 11: a,b,e)** APT analysis of a sample deformed at 950 °C and short holding time of 2 seconds. **a)** Niobium atom map, **b)** carbon atom map and **e)** nearest neighbor distribution of niobium and carbon observed in sample (solid lines) vs. random distribution (dashed lines). **c,d,f)** Isothermal holding at 670 °C for 1 hour on samples soaked at 1200 °C lead to **c)** pronounced clustering or **d)** to interphase precipitation. **f)** Nearest neighbor distribution analysis of the dataset reconstructed in **c)** shows strong deviation of the observed niobium and carbon distribution (solid lines) compared to their random distribution (dashed lines).

Finally, APT analysis was performed on the sample that was isothermally held at 670 °C after soaking at 1200 °C and cooling without deformation. It is reasonable to assume that the precipitation in this sample will be similar to that present in the sample cooled to 850 °C and subsequently quenched. In absence of strain-induced precipitation a substantial amount of solute niobium is thus still present at the austenite-to-ferrite transformation when the niobium solubility drastically decreases. Figure 11c and 11d depicts two reconstructions showing only niobium and carbon from samples after the isothermal holding period. The atom map in Figure 11c contains short range clustering of niobium and carbon with sizes of 0.5 to 2 nm (after the maximum separation algorithm [39] with the clustering atom species niobium and carbon:  $d_{\max} = 1.2$  nm,  $N_{\min} = 10$  atoms, erosion of 1.2 nm). The nearest neighbor distribution shows a deviation from randomness (Figure 11f) for both carbon and niobium. In another ferrite grain of the same sample (Figure 11d) precipitates of typically less than 10 nm size have developed and the matrix is depleted from carbon and niobium although a residual amount of both is still in solution. The precipitates are aligned in arrays and comprise an aspect ratio that is more pronounced for the larger particles. This alignment of particles is a typical feature of interphase precipitation, which occurs during the austenite-to-ferrite transformation [19,20,40]. For areas exhibiting interphase precipitation (such as that in Figure 11d), a solute amount of niobium of  $0.018 \pm 0.002$  wt% was measured in the surrounding matrix, whereas for areas containing clusters (such as that in Figure 11c), the solute amount can be only estimated because of the rather diffuse boundary between NbC clusters and the steel matrix. In an exaggerated generous definition of a cluster – using a minimum cluster size of only 4 atoms – the remaining volume still contained  $0.005 \pm 0.002$  wt% of niobium according to peak decomposition. This corresponds well to



the data provided in Figure 2, where 90 % of niobium is calculated to be precipitated after a similar heat treatment of a comparable steel. In the as-cast state of the steel melt used in the reported work, interphase precipitation analogue to Figure 11d was found, but with the difference, that the matrix was almost completely depleted of niobium with only  $0.002 \pm 0.002$  wt%.

The composition of both cases in Figure 11c and 11d are given in Table 5. For the cluster composition, we regarded clusters larger than 20 atoms detected, which would mean a count of roughly 60 atoms (when the assumed detector efficiency of 37 % is used this would be, for example, a round nano-precipitate of one atomic layer and 2 nm diameter as found by Breen et al. [41]). The precipitates and clusters have very similar compositions and are stoichiometric.

**Table 5.** Elemental composition of interphase precipitates (IP) and clusters of samples which went through the austenite-to-ferrite transformation at 670 °C for 1 hour (Figure 11c and 11d).

Element	Nb	C	Ti	N
<b>IP</b>				
<b>(Figure 11d)</b>				
<b>Atom count</b>	752	846	54	7
<b>Rel. at%</b>	45.3	51.0	3.3	0.4
<b>Clusters</b>				
<b>(Figure 11c)</b>				
<b>Atom count</b>	7708	8566	405	190
<b>Rel. at%</b>	45.7	50.8	2.4	1.1

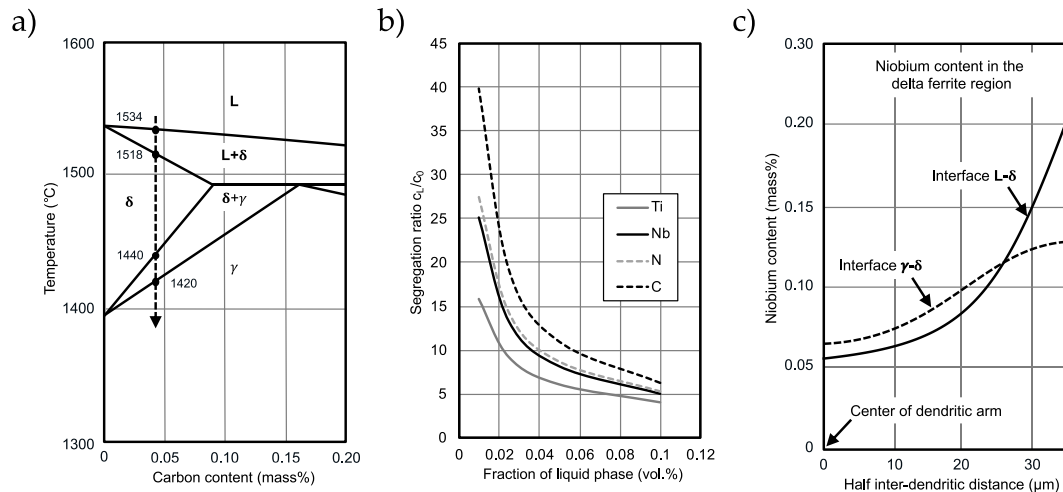
## 4. Discussion

### 4.1. Precipitation behavior before TMCP treatment

The types of precipitates observed and their evolution with simulated processing are generally in agreement with the results of other publications in literature. Cube-shaped TiN particles typically containing a smaller fraction of niobium are already present at high austenite temperature ( $> 1200^\circ\text{C}$ ). The spatial arrangement of these particles and their proximity suggest that these have been formed in residual liquid pools of the late solidification phase. Titanium, niobium, nitrogen and carbon, all strongly segregate to the liquid phase as the amount of solidified delta-ferrite increases. The local supersaturation with titanium and nitrogen can become so high that spontaneous precipitation occurs. The severity of segregation is controlled by the distribution coefficient of the element and may result in local supersaturation exceeding the solubility limit. The segregation ratio,  $c_L/c_0$ , of the relevant elements titanium, niobium, nitrogen, and carbon was calculated as function of the remaining liquid volume fraction,  $f_L$ , with progressing solidification using Scheil's equation [42] and published distribution coefficients ( $k_{\text{Ti}} = 0.4$ ,  $k_{\text{Nb}} = 0.3$ ,  $k_{\text{N}} = 0.28$  and  $k_{\text{C}} = 0.2$ , compiled by Morita and Tanaka [43]) according to:

$$\frac{c_L}{c_0} = f_L^{k-1} \quad (1)$$

Figure 12b demonstrates the segregation ratio of the four elements as function of the remaining liquid volume fraction. According to Kunze et al., TiN can precipitate in liquid steel if the supersaturation product of both elements exceeds the limit solubility by a factor of approximately 10. For steels having near-stoichiometric titanium and nitrogen content as considered in the present study, this condition is fulfilled when the volume fraction of liquid phase is becoming less than 5 vol%. Niobium has a higher segregation ratio in the residual liquid phase than titanium. Nevertheless, supersaturation levels necessary for spontaneous precipitation are not reached. However, type II dendritic precipitates can nucleate on titanium-rich nitride particles at the very final stage of the inter-dendritic liquid, or alternatively, on delta-ferrite phase boundaries as described in detail by Chen et al. [44]. The precipitates have a cored structure and are unstable at higher austenite temperature where niobium carbide re-dissolves leaving behind a string of small insoluble titanium-rich particles.



**Figure 12:** a) Solidification scenario in the delta-ferrite range of the binary Fe-C diagram (equilibrium transformation temperatures for carbon content of 0.04%); b) calculated segregation ratios as function of the residual liquid share; c) homogenization of unequal niobium distribution after solidification by fast diffusion in delta-ferrite as function of the secondary dendrite arm spacing.

Upon full solidification the significantly unequal distribution of solute microalloys between the center of a secondary dendrite and the last liquid periphery is quickly diminished by fast diffusion of these atoms in the delta-ferrite (Figure 12c). Short secondary dendrite arm spacings exhibit a quite equalized concentration profile at the transformation to austenite.

TiN is practically insoluble in austenite so that any remaining solute titanium is expected to precipitate upon further down-cooling. Such particles nucleate at dislocations and austenite grain boundaries. Considering the degree of solute titanium depletion and the diffusion range, these particles are expected to have a relatively small size in the range of 10 to 20 nm.

At the simulated reheating temperature of 1200 °C, niobium for the current alloy composition has a solubility of 0.27 wt% (based on a commonly accepted solubility product  $\log [Nb] \times [C] = -7900/T + 3.42$  [45]). An estimation of the dissolution kinetics predicts that particle sizes in the order of 1 μm could dissolve within the 10 minutes of soaking treatment simulated. Therefore, it is concluded that the NbC caps are growing onto TiN cubes during down-cooling from soaking temperature to a lower austenite temperature. The fact, that the NbC caps grow unidirectionally to opposite sides suggests that the TiN particle is located at a dislocation or grain boundary providing fast diffusion of niobium and carbon in this direction.

According to EDS measurements in Figure 6b, the precipitates that form above the deformation temperature incorporate a considerable amount of niobium. The APT measurements of the steel matrix (950 °C /  $\varepsilon = 0.3$ ) confirm this (Figure 8a), as the concentrations lie approx. at 0.06 wt% even 2 seconds after deformation, whereas the nominal bulk composition is around 0.085 wt%. This would mean, that more than 1/4 of the added niobium is already precipitated, either on prior precipitated TiN or TiCN, and lost for later strain-induced precipitation or precipitation strengthening. This was also found by Hegetschweiler et al. [14], who used particle extraction methods. On the contrary, in niobium microalloyed steels without titanium, all niobium can be brought back into solution, as was shown by an APT study by Palmiere et al. [32].

#### 4.2. Precipitation behavior during TMCP treatment

The electrical resistivity method allows to follow the evolution of strain-induced precipitation. The drop of resistivity can be explained by the nucleation and/or growth of precipitates and the subsequent consumption of solute niobium, and consequently, less scattering of electrons. According to the results of the different temperatures in Figure 5, the samples deformed at 900 °C have the lowest resistivity in general, which also corresponds to the well-accepted fact that precipitation start and finish happen much earlier in that temperature range (Figure 2). According to the resistivity data,

the consumption of niobium for precipitation is multiple times faster than for 850 °C. However, the difference between samples of different deformation temperatures but same deformation grade ( $\varepsilon = 0.3$ ) is relatively low compared with an increased deformation (900 °C/ $\varepsilon = 0.6$ ). As deformation induces dislocations, the dominating effect for solute niobium and carbon consumption is due to strain-induced precipitation. The strong decrease could be either due to a higher nucleation rate or an increased niobium diffusion along the dislocation core (pipe diffusion), both consuming niobium and carbon faster. In principle, the deformation degree seems to have the stronger effect as compared to the deformation temperature itself, which was also found by Jung et al. [29]. The cooling rate from austenitizing temperature down to deformation temperature was 5 °C/s and therefore the difference in total TMCP time for the different temperatures was only 10 seconds between each other. Because of that, the influence of precipitates formed or grown during cooling on the difference of resistivity should be negligible in this discussion. In Figure 8, the dropping niobium concentration in the steel matrix, although only analyzed in detail for the sample deformed at 950 °C, correlates well with the downward trend of the electrical resistivity with increasing holding time after deformation. Theoretically, the other carbide-forming elements titanium, carbon and nitrogen also increase the resistivity when in solid solution, however, their quantification in the steel matrix was not possible. For the counts in the mass spectrum belonging to titanium (Figure 10b), the matrix spectrum neither had visible peaks at 16 Da, nor at 24 Da. With the background of roughly 10 atoms this means that for all measurements the solute titanium amount must be lower than 5 ppm (for comparison, the amount of 0.002 wt% solute niobium which was measured in the as-cast sample with visible peaks equals 200 atoms in an APT measurement of 10,000,000 atoms which is well above the background noise). Since even at the austenite-to-ferrite transformation temperature titanium could be found in precipitates, a small amount must have still been in solution. Likewise, no carbon (with the exception of the carbon atmospheres, and occasional lath boundaries or retained austenite islands) was detected in the matrix. For nitrogen, the quantification is additionally complicated by the overlap of the nitrogen peak at 14 Da with silicon, that has a much larger abundance in the sampled steel. As it will be discussed later, when addressing potential errors of the resistivity measurements, carbon and nitrogen influence might actually be ruled out.

The big family of precipitates that form during TMCP of Nb-Ti-microalloyed HSLA steels makes it challenging to fully distinguish them with (S)TEM alone. Adding APT to the characterization toolbox brings about the ability to characterize the chemistry of single precipitates with the highest resolving power available to date and without interfering with the precipitate environment. For example, the bean-shaped precipitates with homogeneous niobium and titanium atom distribution in Figure 9 had a size and morphology that could be both, the STEM-characterized precipitates present at soaking (Figure 6f) or after deformation (Figure 7). However, APT reveals the composition of the precipitate to contain also small fractions of titanium (Table 3), whereas the careful comparison of precipitates after deformation and austenite-to-ferrite transformation (Figure 10, Table 4, and Figure 11c and 11d, Table 5, respectively) shows that strain-induced precipitation contains no titanium with regard to the detection limits of the APT. Characterization of the precipitate in Figure 9 on the basis of (S)TEM could erroneously identify it as the product of deformation, which would overestimate the growth kinetics of strain-induced precipitates for the investigated deformation temperature (note that this Ti-containing precipitate was found after a holding time of 200 seconds, whereas even at 950 °C, only after 1200 seconds can strain-induced precipitates reach such a size (Figure 7)). Despite a very precise chemical quantification of the big and small (Nb,Ti)(C,N) precipitates, small size deviations are possible due to APT-related artifacts. The so-called local magnification effect [46] appears when precipitates have a very different evaporation field compared to the matrix. In this special case, (Nb,Ti)(C,N) showed a high evaporation field of around 55-60 V/nm for pure NbC. In the steel matrix with an evaporation field of 33 V/nm the reconstructed precipitates would therefore appear larger than they are. Although a direct size comparison of APT and STEM-measured precipitates is not possible, the medium-sized and homogeneous (Nb,Ti)(C,N) precipitates found in STEM for samples quenched from the soaking temperature (Figure 6f) fall in range with the APT-measured precipitate in Figure 9.

A more plausible explanation for the origin of the precipitate in Figure 9 is that it formed during the casting. If these precipitates do not dissolve during reheating, they will still be present in the samples quenched from higher austenite deformation temperature after austenitizing at 1200 °C (Figure 6f), as well as in all other deformed samples. As it was shown for the Ti-containing small precipitates in the samples transformed isothermally into ferrite (Figure 11c and 11d), titanium is still in solution at the austenite-to-ferrite transformation temperature. The bigger (Nb,Ti)(C,N) precipitates might be therefore the outcome of the coarsening of clusters such as displayed in Figure 11c. Many preliminary works on the co-microalloying of niobium and titanium consider the higher temperature stability of (Nb,Ti)(C,N) precipitates to be the reason of their presence even after soaking at high austenite temperatures [5,7].

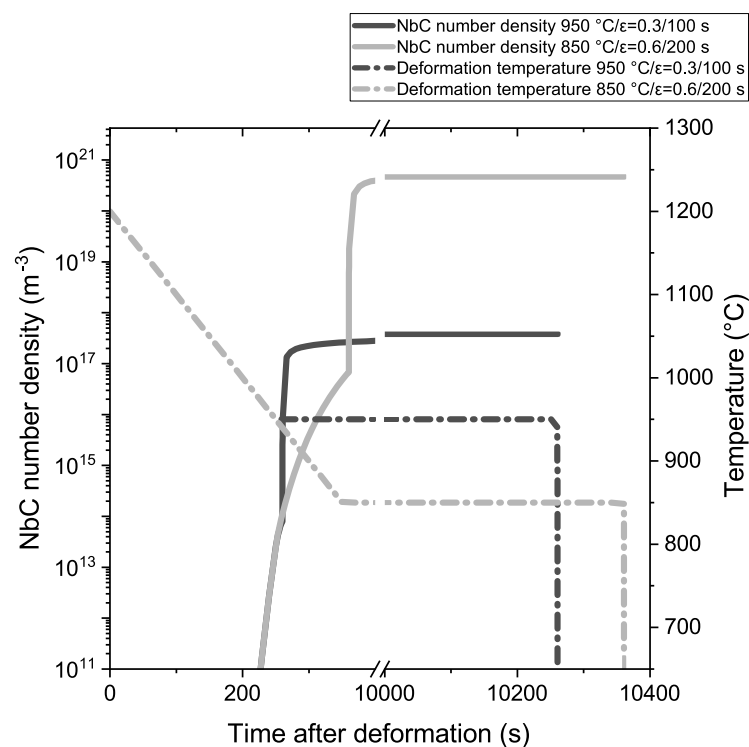
When applying deformation, STEM images show a sharp increase in very small precipitates which grew over holding time (Figure 7). Likewise, APT results depict small precipitates in the sample deformed with  $\varepsilon = 0.6$  strain at 850 °C and found them to be free or nearly free of titanium but with an over-stoichiometric amount of carbon (Figure 10 and Table 4).

In the sample deformed at 950 °C with  $\varepsilon = 0.3$  strain, no precipitates were detected by APT although their existence and coarsening are visible in STEM (Figure 7). MatCalc simulations were conducted (Figure 13) to investigate what density of precipitates can be expected after deformation in the higher and lower austenite temperature. According to simulation the precipitation density increases a factor of  $10^3$  when lowering deformation temperature from 950 °C to 850 °C and increasing total strain from  $\varepsilon = 0.3$  to  $\varepsilon = 0.6$ . The number density of  $10^{17}/\text{m}^3$  in the case of 950 °C/30 % would approximately mean the detection of one particle every 8000 measurements (taking an average volume of one APT measurement as a cone with diameter 80 nm at base and 200 nm length), whereas for the case 850 °C /  $\varepsilon = 0.6$ , an average of one detection every six measurements was predicted. This lies in the range of the experimental findings for these cases. Furthermore, compared to the influence of deformation temperature, the drop of electrical resistivity was much higher with a higher deformation of  $\varepsilon = 0.6$  compared to  $\varepsilon = 0.3$  at a deformation temperature of 900 °C. The sharper drop of resistivity is therefore well reflected by the increased detectability of NbC in APT. Together with the APT measurements, it is concluded that the measured effect is strain-induced precipitation. The strain induced NbC had a non-stoichiometric composition with the carbon content being almost 1.5 times larger than the niobium concentration. A previous investigation using APT discussed the hypothesis of a deficiency of carbon detection in carbides [48] which is contrary to the findings of the present report. Besides, if these precipitates are strain-induced, then it is conceivable that the carbon surplus comes from its segregation along dislocations which precede the precipitate formation. Carbon atmospheres as possible precursors were detected in almost every APT measurement of the samples deformed at 950 °C, and many of them show line-like features like in Figure 11b. The carbon enrichments are therefore assumed to be Cottrell atmospheres, to which niobium with a much slower diffusion rate diffuses in a later stage to form precipitates. When deformation increases, more dislocations are produced facilitating the diffusion along the dislocation core. Therefore, the particle detection statistics during APT experiments corroborates the suggestion that the precipitates found are indeed strain-induced. The existence of metastable NbC precipitates was already discussed earlier by Danoix et al. [49] and the detected Nb(C,N) in the sample subjected to a higher deformation provides evidence of their existence.

Kostyryzhnev et al. [35] proposed early stages of precipitation in the form of clusters (in the range of 30 to 60 atoms) during austenite deformation. No evidence of such a clustering was found in this work. The atom maps of deformed and then quenched samples did not show any visible clustering of niobium or titanium except the already discussed precipitates in the sample 850 °C /  $\varepsilon = 0.6$ . In Figure 11, the atom distribution of the sample deformed at 950 °C /  $\varepsilon = 0.3$  and the sample held at 670 °C for 1 hour were compared. In the latter case, Figure 11f displays a marked deviation of niobium and carbon distribution from random, which is also visibly clustered in the atom map of Figure 11c. In contrast, sample 950 °C /  $\varepsilon = 0.3$  has no visible niobium clustering (Figure 11a), while the carbon clustering in Figure 11b shows a Cottrell atmosphere as discussed above. It is therefore concluded that strain-induced precipitation during deformation in the higher austenite temperature regime is challenging to trace with APT alone due to the low particle density. An ongoing project is

developing a method to increase the precipitate yield in APT measurements by their extraction and re-encapsulation in a suitable matrix material. It is envisioned that by this methodology, precipitates of any heat treatment can be measured with sufficient yield.

The correlation of APT results with the electrical resistivity shows that bulk measurements can successfully describe the precipitation sequence occurring at the atomic scale. As specific resistance measurements are quite challenging, the sources of error need to be addressed. The electrical resistivity relies on the precise measurement of the current that flows through the sample, the voltage drop over the sample, and the precise knowledge of the relative position of the potential points. The latter aspect is especially important for the currently used Gleeble setup. The hot-deformed samples were relatively short to prevent buckling. The total increment of resistivity drop from dissolved to fully precipitated accounts only for less than 10 % of the total resistivity range. Because the distance of the potential relates goes linearly to the resistivity, a misplacement of several hundreds of microns in the present setup can introduce errors that make the distinction between different holding times less clear. This translates into the rather large error bars for each of the data points. Future experiments with larger samples may help to reduce the error in the measurement of the distance of the potential points. Another aspect worth mentioning is the assumption that the other elements in the sampled steel do not change their atomic distribution in the different heat treatment stages investigated. This approximation is probably correct for most elements, such as Mn, Cu, Si and Ni, which did not show any sign of segregation or taking part in the precipitation process. Regarding carbon and nitrogen which actively take part in the precipitation process, tempering at low temperature was conducted in prior work to bring all solute carbon and nitrogen to lath or grain boundaries [26,28,29]. However, more recent experimental data suggest that even under heat treatment conditions severely obstructing diffusion – such as quenching – there is sufficient time for interstitial atoms to diffuse to bainite or martensite lath boundaries or prior austenite grain boundaries in large quantity [50,51], or, as in some cases, to dislocations (Figure 11b). Therefore, the matrix is depleted of those elements which was also confirmed by APT measurements, and consequently their influence on changes of the electrical resistivity was assumed to be negligible.



**Figure 13:** Simulation of the development of precipitate number density over time for compression with a total deformation of  $\varepsilon = 0.3$  at 950 °C and  $\varepsilon = 0.6$  at 850 °C.



#### 4.3. Precipitation during austenite-to-ferrite transformation

When isothermally held at 670 °C for 1 hour, APT measured a high density of (Nb,Ti)(C,N) precipitates. In some ferrite grains, very fine clusters with sizes even below 1 nm were found whereas in other grains an ordered arrangement of bigger (5-10 nm) precipitates typical for interphase precipitation appeared. These two phenomena coexist in the same heat treatment (Figure 11c and 11d). The interphase precipitation proceeds over the moving ferrite grain front into the austenite and when a certain level of supersaturation is reached, the solute niobium precipitates along the whole front. However, some grains might transform too quickly for interphase precipitation to follow, or the grain orientation is not favorable [20].

The interphase precipitates had a similar composition as the medium-sized (Nb,Ti)(C,N) (Table 3 and 5, respectively). Interphase precipitation was also observed in as-cast samples, likewise, containing titanium. As these small (Nb,Ti)(C,N) precipitates were not present in the hot-deformed and quenched samples, they must have either totally dissolved again during soaking or coarsened to larger particles, similar to the one shown in Figure 9. The Gibbs-Thompson effect predicts solubilities almost twice as high for small precipitates compared to larger ones as found in the samples quenched from austenitizing temperature [52]. Therefore, smaller (Nb,Ti)(C,N) precipitates could have completely re-dissolved, whereas bigger precipitates did not dissolve during re-heating. The residual solute amount of niobium after the isothermal holding phase was measured to be approximately  $0.014 \pm 0.003$  wt%. Considering that  $0.061 \pm 0.009$  wt% niobium was re-dissolved after soaking and thus was available for precipitation during isothermal holding, the fraction of precipitation is approximately 77 %. This is close to the value that would be expected according to the kinetics shown in Figure 2 and is also well reflected in the electrical resistivity measurements.

## 5. Conclusions

Multi-scale characterization methods were used to quantify the precipitation status of niobium during austenite conditioning in a typical Nb-Ti microalloyed high-strength low-alloy steel, namely electrical resistivity, STEM and APT measurements. These methods provide complementary information on nucleation, growth, spatial distribution and chemical composition of Nb(C,N) precipitates. The reported results show that the electrical resistivity method can efficiently monitor the progress of precipitation for different TMCP conditions. Measuring the average amount of solute niobium in the steel matrix by APT allows to calibrate the electrical resistivity method. Such measurements also demonstrated that, in Nb-Ti dual microalloyed steel, part of the niobium is bound in mixed Ti,Nb(C,N) particles that do not dissolve during typical soaking treatment.

All characterization methods used in this study confirmed that the degree of deformation is dominating over temperature with regard to precipitate nucleation during TMCP treatment, which is in agreement with established knowledge.

APT allows a detailed chemical characterization of particles as compared to electron microscopy. It was demonstrated that precipitates being present before the deformation stage can be distinguished from strain-induced precipitates, thus preventing erroneous estimations of growth kinetics. In this context, current typical restrictions on the detectability and precise size estimation of precipitates will be addressed in future work through an extraction and re-encapsulation methodology. APT is able to show the formation of atom clusters in the nucleation stage of particles. During TMCP treatment applied in this study only weak clustering of carbon could be detected, yet no significant clustering of niobium was seen. However, after quenching and isothermal holding in the ferrite phase the formation of niobium-carbon clusters was evident.

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