Characterization of the effect of cryogenic treatment on the tempering behavior of a secondary hardening high Co-Ni steel

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Abstract. For high Co-Ni steels sub-zero treatments are conducted to reduce the retained austenite phase fraction for obtaining excellent fracture toughness properties, but in general, cryogenic treatment has a great impact on the microstructural evolution of steels during tempering. Hence, the aim of this work was to analyze the influence of cryogenic treatments on the microstructural evolution of high Co-Ni steels, including carbide precipitation kinetics and austenite phase fraction evolution, during heating to elevated temperatures. In order to study the formation properties of carbides, the heating processes of cryogenically and non-cryogenically treated specimens were analyzed by dilatometer measurements. Furthermore, for determining the evolution of austenite phase fraction and hardness due to tempering, dilatometer investigations were combined with X-ray diffraction analyses and hardness measurements. It is revealed that sub-zero treated samples exhibit much stronger carbide precipitation signals. This was ascribed to the lower phase fraction of retained austenite, as more carbon is available for carbide precipitation.

1. Introduction
For tool steels, the application of a cryogenic treatment during the heat treatment, i.e. before tempering, has a massive impact on mechanical and microstructural properties such as enhancement of wear resistance and hardness, reduction of retained austenite phase fraction and refinement of carbide structure [1, 2, 3, 4, 5]. Nevertheless, a cryogenic treatment is also applied before tempering of the martensitic high Co-Ni steel Aermet® 100 for obtaining excellent toughness properties. Generally, high Co-Ni steels contain retained austenite, which is present after quenching from austenitization, and reverted austenite, which forms during tempering [6, 7]. As retained austenite in Aermet® 100 would lower toughness values because of its low stability, a sub-zero treatment is conducted to reduce the retained austenite content [6, 7, 8]. However, the effect of cryogenic treatment on carbide precipitation kinetics in high Co-Ni steels has not been precisely characterized so far.

Hence, this work presents experimental results on the influence of sub-zero treatments on the carbide precipitation kinetics and the austenite evolution during tempering of a high Co-Ni steel. The microstructural evolution during heating was characterized by dilatometer investigations on specimens, which were quenched to room temperature or cryogenically treated. Furthermore,
X-ray diffraction (XRD) analyses and hardness measurements in combination with dilatometer investigations were conducted to determine the austenite phase fraction and the hardness after various tempering treatments. It is shown that cryogenically treated samples present a more pronounced carbide precipitation reaction during heating compared to the non-cryogenically treated samples. It could be revealed that the austenite phase fraction affects the precipitation kinetics, causing further microstructural differences between cryogenically and non-cryogenically treated samples.

2. Experimental

The used material in this work was a high Co-Ni steel with 11 wt.% Ni, 13.5 wt.% Co, 2.9 wt.% Cr, 1.2 wt.% Mo and 0.22 wt.% C. The material was forged to round bars with a diameter of 200 mm and austenitized in a vacuum furnace at 885°C for 1 h and cooled to room temperature with 10°C/ min. Half of the samples were cryogenically treated (CT) in a freezing unit at −73°C for 1 h.

Dilatometer investigations were carried out by using a DIL 805A dilatometer from TA Instruments (formerly BAEHR). The samples for dilatometer investigations had a diameter of 4 mm and a length of 10 mm. The differential length change signals from the dilatometer measurements were obtained by deriving the relative length change with respect of time. CT and non-CT samples were heated (1st run) in the dilatometer to a maximum temperature of 620°C with 20°C/ min and immediately cooled to room temperature (20°C/ min) and additionally reheated (2nd run) with the same parameters. Heating parameters were chosen in a way that no significant reverted austenite formation occurs.

Austenite phase fraction and hardness measurements were carried out on CT and non-CT samples with a diameter of 10 mm and a length of 15 mm, which were heated in the dilatometer with 20°C/ min to various temperatures up to 620°C and immediately cooled to room temperature with 100°C/ min. XRD measurements for austenite phase fraction determination were performed by using a D8 Discover diffractometer from Bruker AXS. Cr-Kα radiation with a wavelength of 2.29 Å was used for measurements and for a quantitative determination of phase fractions the Rietveld method was applied [9]. The absolute inaccuracy of phase fraction determination was about 1-2 %. Transmission electron microscopy (TEM) investigations were carried out on a Philips CM12 microscope. Samples were conventionally prepared by grinding to a thickness of 80 µm and a subsequent electro polishing procedure.

3. Results

3.1. Characterization of the evolution of austenite

To study the evolution of austenite content due to tempering, austenite phase fraction measurements were carried out on CT and on non-CT samples before heating and after heating to 200°C, 400°C, 500°C and 580°C and immediately cooling to room temperature. The results are shown in Fig. 1. The austenite content of the non-CT sample without tempering is approximately 6.5 %. By performing a cryogenic treatment the austenite content decreases to 3.5 %. After heating the cryogenically treated samples to different temperatures, the austenite phase fraction does not change significantly, whereas heating of the non-cryogenically treated samples beyond 400°C leads to a marked decrease of austenite content to about 4.5 %. For analyzing this decrease of phase content more precisely, the relative length change curves, obtained from dilatometer experiments, were studied. Fig. 2 depicts the dilatometer cooling curves of the non-cryogenically treated samples after tempering to 400°C, 500°C or 580°C. A distinct phase transformation can be observed for the samples, which were annealed to 500°C and 580°C, as indicated by the volume increase during cooling compared to the sample, which was annealed to 400°C. Since the phase transformation is accompanied with a volume increase, it is attributed to a transformation of austenite into a bcc phase, e.g. martensite. Furthermore, these dilatometer investigations also
reveal that the reduction of austenite content of the non-CT samples occurs during cooling from the tempering treatment.

For characterizing the retained austenite more precisely, TEM investigations were carried out. Fig. 3 shows a TEM bright-field image of the microstructure of the investigated steel. The material exhibits a martensitic matrix after austenitizing and quenching to room temperature. Retained austenite films are present along martensite lath boundaries, as indicated by the arrows. It is estimated that austenite films have a thickness between 3 nm (detection limit) and 40 nm.

**Figure 1.** Austenite phase fraction of cryogenically and non-cryogenically treated samples after heating in the dilatometer to various temperatures up to 580°C (heating rate: 20°C/ min) and cooling down to room temperature (cooling rate: 100°C/ min). The non-cryogenically treated samples exhibit a decrease of austenite phase fraction, when tempering is conducted beyond 400°C.

**Figure 2.** Relative length change of dilatometer cooling curves after heating of non-CT samples to 400°C, 500°C or 580°C and subsequent cooling (100°C/ min). A transformation of austenite occurs during cooling for the non-CT samples, which were annealed to 500°C or 580°C. For a better comparability, the curves were shifted along the y-axis. Therefore, no scaling of the y-axis is shown.

**Figure 3.** TEM bright-field image of the martensitic microstructure after austenitizing at 885°C for 1 h and quenching to room temperature. Retained austenite is present at martensite lath boundaries, as marked by the arrows.
3.2. Detailed analyses of the tempering behavior

For a detailed characterization of the processes, taking place during tempering of CT and non-CT samples, dilatometer analyses were conducted. In Fig. 4 the relative length change during heating of CT and non-CT samples is plotted as a function of temperature. Generally, the heating curves of both conditions exhibit differences. The most significant difference is observed in the range between 250°C-350°C, as CT samples exhibit a more pronounced deviation from the linear expansion. For a more precise characterization of the phenomena, which occur during heating, the derivatives of the relative length change curves were calculated as depicted in Fig. 5. These curves show three main reactions, which are indicated by the numbers 1 - 3, respectively. The first effect during heating in the range between 100°C and 200°C may be attributed to transition carbide precipitation, as this process generally occurs in the temperature range between 80°C and 200°C and causes a reduction of volume \[10, 11, 12\]. The second effect, which also causes a reduction of volume, occurs in the temperature regime between 250°C and 400°C and can be assigned to cementite precipitation \[10, 11, 12\].

There are distinct differences between CT and non-CT samples regarding cementite precipitation properties, as precipitation is more enhanced for CT samples. This is also observed for the processes, which start at temperatures above 450°C - 500°C. These processes are ascribed to secondary hardening carbide precipitation, because the formation of these carbides generally proceeds in this temperature range and would cause an increase of length \[6, 10, 13, 14, 15\].

The dilatometer curves of both conditions do not show any increase of length in the range between 200°C and 350°C, which is typical for austenite transition into ferrite and carbides or bainite \[10, 11, 12, 16, 17\]. Hence, it is suggested that austenite stays stable and no austenite transformation occurs during heating. This is also supported by austenite phase fraction measurements, where no reduction of austenite phase fraction occurs up to temperatures of 400°C.

**Figure 4.** Relative length change curves of dilatometer heating experiments of cryogenically and non-cryogenically treated samples. The heating rate was 20°C/ min. Generally, the curves of CT and non-CT conditions exhibit a different behavior, which is indicated by the lower expansion for CT compared to non-CT samples during heating.

**Figure 5.** The derivatives of the relative length change curves obtained from dilatometer heating experiments of the 1st and the 2nd run of CT and non-CT samples. The heating rate was 20°C/ min. The effect 1 can be attributed to transition carbide precipitation, the effect 2 to cementite precipitation and the effect 3 is ascribed to secondary hardening carbide formation.
For correlating the results of the dilatometer analyses, hardness measurements were carried out after various tempering treatments. The results are shown in Fig. 6. It is revealed that the hardness of the CT samples is higher compared to the non-CT samples after tempering up to temperatures of 500°C. After tempering beyond temperatures of 500°C the hardness of CT and non-CT conditions is the same. A decrease of hardness values for both conditions can be observed between 200°C and 400°C (process 2, shown in Fig. 6), which corresponds, according to dilatometer analyses, to the region of cementite precipitation. Additionally, the raise of hardness, which occurs for CT and non-CT samples in excess of 400°C can be attributed to secondary hardening carbide formation, which supports the results from dilatometer analyses.

![Figure 6. Hardness measurements of the CT and non-CT samples after heating (20°C/min) to various temperatures up to 620°C and cooling to room temperature (100°C/min). The reduction of hardness can be related to cementite formation (2). The large increase of hardness (3) is caused by the formation of secondary hardening carbides.](image)

4. Discussion

The influence of cryogenic treatments on the microstructural evolution during heating was analyzed. It is identified that CT compared to non-CT samples exhibit a more intense cementite formation between 250°C and 400°C and more pronounced secondary hardening carbide precipitation above temperatures of 450°C - 500°C.

By XRD measurements, the austenite phase fraction of the cryogenically treated sample without tempering was determined with approximately 3.5 %. Due to tempering, the austenite content of the CT samples does not change significantly. Hence, it is suggested that for the CT samples neither austenite formation nor austenite transition occurs during tempering. This is also in accordance with the dilatometer heating and cooling (not shown here) curves, as they do not show any indication for austenite transformation. Conversely, the austenite phase fraction of the non-CT samples, which is about 3 % higher compared to the CT samples after tempering up to temperatures of 400°C, decreases due to tempering at higher temperatures. This decrease of the austenite phase fraction is identified to occur during cooling by dilatometer investigations.

As the transformation of austenite is accompanied with an increase of volume, it is expected that austenite transforms into a bcc phase, e.g. martensite.

The lower hardness values of the non-CT compared to the CT conditions after tempering up to temperatures of 500°C can be ascribed to the higher austenite phase fraction of non-CT samples. Since the austenite of non-CT samples partially transforms upon cooling after tempering above temperatures of 500°C into martensite, the hardness values of the non-CT and CT conditions are comparable, as also the austenite phase fraction is in the same range.

The decrease of hardness between 200°C and 400°C can be attributed to a reduction of carbon content in martensite. This reduction of carbon content is a result of carbon segregation to lattice defects, e.g. dislocations, which is followed by the formation of carbides such as cementite. However, the reduction of carbon in martensite causes a decrease of tetragonality, which is accompanied with a stress relief in martensite. This process causes a reduction of
hardness, whereas the formation of cementite principally produces an increase of hardness. As the increase of hardness produced by cementite formation is to neglect compared to the hardness reduction due to the relief of stresses in martensite, the hardness decreases in the temperature range between 200°C and 400°C.

Furthermore, it is observed that the decrease of hardness in the temperature range between 200°C and 400°C is as high for CT samples as for non-CT samples. As carbon diffusion out of martensite causes this hardness decrease, it is assumed that for CT and non-CT conditions an equal reduction of carbon content in martensite occurs. In contrast to that, it is observed by dilatometer analyses that the cementite precipitation reaction for CT samples is more intense, indicating that more carbon is available for cementite formation in CT samples as in non-CT samples. Since it is suggested that a significant amount of carbon may also diffuse into austenite, the lower austenite phase fraction of CT samples compared to non-CT samples (in the temperature range between 200°C and 400°C) is probably the reason for the higher availability of carbon for cementite precipitation in CT samples. Generally, austenite has a higher solubility for carbon than martensite. Therefore, carbon is easier to diffuse from the supersaturated martensite into austenite. As non-CT samples exhibit two times as much austenite as CT samples in this temperature region, also the amount of carbon which can dissolve in austenite is twice as much. By assuming a maximum carbon enrichment in austenite of 2 wt.% [18, 19, 20], the non-CT samples can dissolve 0.12 wt.%, whereas the CT samples are only able to dissolve 0.06 wt.% of carbon in austenite. Consequently, less carbon is available for forming cementite in the non-CT samples, resulting in a smaller reaction peak for cementite formation.

The increase of hardness beyond temperatures of 400°C is assigned to be a result of secondary hardening carbide precipitation, which may also be influenced by the preceding precipitation processes. Thus, the carbide precipitation reaction in the CT samples is more intense, which was also determined by dilatometer analyses. Alterations in the carbide structure due to cryogenic treatment are also described by Das and Huang et al. [1, 4].

Secondary hardening carbide precipitation near or at the interface between retained austenite and martensite would cause a reduction of carbon content in austenite. Generally, this reduction leads to a decrease of the stability of austenite [21]. Conversely, cryogenic treatment would cause an enhancement of the stability of austenite, as it is explained in the following. It is expected that the thickness of retained austenite particles varies, as estimated by Fig. 3. Waitz et al. [22] reported that larger austenitic particles exhibit a lower stability. As cryogenic treatment causes a partially transformation of retained austenite, it is estimated that due to the cryogenic treatment a transformation of the larger, less stable austenitic regions takes place. As a result, for CT samples the less stable austenitic particles have already transformed during the cryogenic treatment. Hence, no transformation of austenite occurs during cooling of the CT samples after heating to temperatures beyond 400°C. Conversely, during cooling of the non-CT samples some austenite transforms, proving its lower stability. This transformation of austenite into martensite, produces an increase of hardness for the non-CT samples, which overlaps with the increase of hardness due to secondary hardening carbide precipitation. Hence, no comparison between CT and non-CT samples regarding the hardness increase due to formation of secondary carbides can be carried out.
5. Conclusion

The investigations on the effect of cryogenic treatment on the microstructural evolution during tempering of a high Co-Ni steel leads to the following conclusions:

- Cryogenic treatment causes a reduction of austenite phase fraction. This reduction is probably accompanied with a stabilization of austenite, as the less stable austenitic regions transform during the cryogenic treatment. Conversely, tempering causes a destabilization of austenite because of carbon reduction in austenite due to secondary hardening carbide formation. As a result of these opposing processes, the austenite of the CT samples does not transform due to the stabilization of austenite by the cryogenic treatment. In contrast, the austenite of the non-CT samples transforms upon cooling when tempering is conducted beyond 400°C, i.e. in the temperature range of secondary hardening carbide precipitation.
- Due to the higher austenite content of the non-CT samples during tempering in the temperature range between 200°C and 400°C, a higher amount of carbon can be dissolved in austenite. Thus, less carbon is present in martensite, causing a reduction of the intensity of the cementite precipitation reaction compared to the CT samples.
- The precipitation of secondary hardening carbides may also be influenced by the preceding precipitation processes. As a result, the CT samples also exhibit a more pronounced secondary hardening carbide precipitation.

References
[1] Das D, Sarkar R, Dutta A K and Ray K K 2010 Mat. Sci. Eng. A 528 589–603
[2] Zhirafar S, Rezaeian A and Pugh M 2007 J. Mater. Process. Tech. 186 298–303
[3] Molinari A, Pellizzeri M, Gialanella S, Straffelini G and Stiasny K H 2001 J. Mater. Process. Tech. 118 350–355
[4] Huang J, Zhu Y, Liao X, Beyerlein I, Bourke M and Mitchell T 2003 Mat. Sci. Eng. A 339 241–244
[5] Stratton P F 2007 Mat. Sci. Eng. A 449–451 809–812
[6] Ayer R and Machmeier P M 1993 Metall. Trans. A 24 1943–1955
[7] Sato K 2002 Ph.D. thesis University of California, Berkeley
[8] Haidemenopoulos G N 1988 Ph.D. thesis Massachusetts Institute of Technology
[9] Young A 2002 The Rietveld Method (Oxford University Press)
[10] Speich G R and Leslie W C 1972 Metall. Trans. 3 1043–1054
[11] Morra P V, Böttger A J and Mittemeijer E J 2001 J. Therm. Anal. Calorim. 64 905–914
[12] Waterschoot T, Verbeken K and De Cooman, B C 2006 ISIJ International 46 138–146
[13] Bala P, Pacyna J and Krawczyk J 2007 Archives of Materials Science and Engineering 28 517–524
[14] Bala P, Pacyna J and Krawczyk J 2007 Journal of Achievements in Materials and Manufacturing Engineering 22 15–18
[15] Thehing K E 1978 Steel and its heat treatment (Butterworth Co Publishers Ltd)
[16] Pacyna J 2011 Journal of Achievements in Materials and Manufacturing Engineering 46 7–17
[17] Cheng L, Brakman C M, Korevaar B M and Mittemeijer E J 1988 Metall. Trans. A 19 2415–2426
[18] Garcia-Mateo C, Caballero F G, Miller M K and Jimenez J A 2012 J. Mater. Sci. 47 1004–1010
[19] Speer J, Matlock D K, De Cooman, B C and Schrot J G 2003 Acta. Mater. 51 2611–2622
[20] Wang J and Van Der Zwaag, Sybrand 2001 Metall. Trans. A 32 1527–1539
[21] Lerchbacher C, Zinner S and Leitner H 2012 Metall. Mater. Trans. A 43A 4989–4998
[22] Waitz T, Antretter T, Fischer F D and Karntalher H P 2008 Mater. Sci. Technol. 24(8) 934–940