

IN-SITU MEASUREMENTS OF RESIDUAL STRESSES OF CHROMIUM-ALLOYED STEELS DURING A NITRIDING PROCESS¹

Doris Günther²
Ricardo Cumino³

Abstract

Residual stresses can be determined in-situ during a nitriding process with a special nitriding equipment mounted on a conventional X-ray diffractometer. During nitriding compressive residual stresses are formed in the compound layer as well as in the diffusion zone. Residual stresses in the γ' -nitride compound layer at nitriding temperature are caused by the amount of the nitrogen/carbon atoms and alloying elements of the sample. Residual stresses generated in the compound layer during cooling are predominantly caused by thermal expansion misfits. The residual stress state at a given nitriding temperature is mainly influenced by the steel grade. The cooling process can be regarded to be the most important step concerning the generation of residual stresses in the compound layer of carbon steels. In opposition to this fact the residual stresses in the diffusion zone are mainly generated at the nitriding temperature and are not changing during cooling. This is important for the non-alloyed steels and was already discussed in an earlier paper [1]. The residual stresses in the diffusion zone as well as in the compound layer of chromium-alloyed steels were formed during the nitriding and the cooling process. The compressive residual stress values in the diffusion zone are decreasing during nitriding. This behaviour is caused by the chromium content of the material and the formation of precipitates.

Key words: Nitriding; Residual stresses; Chromium-alloyed steels; Compound layer; Diffusion zone; In-situ; X-ray measurements

Technical Contribution to the 61st International Congress of the ABM, January 24-27th 2006, Rio de Janeiro – RJ – Brazil.

Dr.-Ing. Doris Günther; Schaeffler KG; Herzogenaurach; Germany

Dipl.-Ing. Ricardo Cumino; Schaeffler Brasil Ltda.; Sorocaba; Brazil

1 Nomenclature

λ	Wavelength [nm]	ε	phase ε -Fe ₂₋₃ N
2θ	Bragg angle [°]	γ'	phase γ' -Fe ₄ N
ψ	angle of measurement direction [°]	α	phase α -iron
PSD	Position sensitiv detector	K_N	Nitriding potential
CL	compound layer	σ_E	Residual stresses [MPa]
DZ	diffusion zone	p	Pressure [Pa]

2 Introduction

Nitriding is one of the oldest thermochemical heat treatment techniques for creation of surface to improve mechanical properties of the material. Specially residual stress state and surface hardness can have major effects on mechanical properties mainly under fatigue loading. Besides chemical and physical properties of the surface near region the knowledge of the origin of the stresses is of importance [2]. Compressive residual stresses are formed in the near surface region of the materials during the nitriding process due to the diffusion of nitrogen and the formation of nitride precipitations. The compressive stresses are depending on the nitriding parameters and also on the steel composition. Several theories related to the origin of residual stresses in gas-nitrided materials are discussed in the literature [2]. Some of them point out that predominant effects are associated with the DZ:

- ⇒ the change of the chemical composition in the DZ
- ⇒ the formation of precipitations in the DZ
- ⇒ the thermal effects, e.g. different thermal expansion coefficients between nitrides and the ferritic matrix during cooling or dilatations caused by lattice distortions
- ⇒ the volume changes during the growth of different phases in the CL

It is well known that residual stresses are induced after nitriding during cooling from process temperature to room temperature due to the different coefficients of expansion of the various nitrides in the ferrite matrix. In addition plastification of the crystal lattice due to the diffusion of nitrogen into the core of the material occurs, when residual stresses are developed [3]. For industrial applications, often chromium-alloyed steels are preferred for nitriding. Therefore the influence of the chromium content on the development of residual stresses during the nitriding process is of special interest.

3 Experiment

A special down-scaled nitriding equipment was developed for the in-situ measurements according to conventional nitriding facilities. With this equipment it is possible to nitride with defined parameters, e.g. K_N , temperature, nitriding time and cooling. The homogeneous temperature distribution over the sample and the possibility to control the nitriding number had been of high importance. Special attention has been paid to establish a homogeneous temperature distribution in the sample and the control the nitriding potential.

3.1 Experimental setup

The furnace with a suitable, gas tight and temperature resistant X-ray window is placed in a ψ -diffractometer with chromium K_α -radiation ($\lambda=0.22909$ nm). The diffractometer and the nitriding process are computer controlled. A gas mixture of nitrogen, hydrogen and ammonia, which is controlled by thermal mass flow controllers and a dissociation pipette is used for nitriding. The samples are directly

heated by a special high energy soldering cartridge. The temperature distribution is carefully determined by several thermocouples applied to different positions near the surface of the sample. The process controlling NiCrNi-thermocouple is located near the centre of incident X-ray spot. The shell of the furnace is cooled by water for a lower thermal load of the diffractometer. Because of the fact observing a dynamic process it is necessary to reduce the measuring time applying a position sensitiv detector (PSD) to measure 11 or 15 ψ -angles by a total time of about 20 min.

3.2 Samples

The steel grades DIN 42CrMo4 (SAE 4140) and DIN 31CrMoV9 (German nitriding steel) were chosen to study the effects of different chromium contents. The dimensions of the specimens are limited by the nitriding device. The upper side is fixed to the furnace top in the heat treatment chamber. The 2 mm wide X-ray spot was focused in the centre of the sample directly below the window. The chemical composition of the investigated steels are shown in the following, Table 1.

<i>Material</i>	<i>C</i>	<i>Si</i>	<i>Mn</i>	<i>P</i>	<i>S</i>	<i>Cr</i>	<i>Mo</i>	<i>V</i>
<i>SAE 4140</i>	0,41	0,27	0,74	0,014	0,019	1,06	0,17	---
<i>31CrMoV9</i>	0,28	0,27	0,58	0,02	0,025	2,26	0,19	0,077

Table 1: Chemical composition of the materials (weight-%) determined by means of glow discharge optical spectroscopy

3.3 Process Parameters

The properties of the nitride layer, specially the nitrides of the CL are determined by the nitriding parameters (temperature, time, nitriding atmosphere, K_N). According to the equation (1) the nitriding potential can be calculated with the partial pressures of ammonia and hydrogen in the nitriding atmosphere:

$$K_N = \frac{p_{\text{NH}_3}}{p_{\text{H}_2}^{1,5}} \quad (\text{equation 1}) \quad [4]$$

For a better comparison of the results observed on various samples of the chromium steel all samples were processed with approximately same nitriding temperatures and nitriding time, with regard to the influence of the chromium content on the formation of the CL and the DZ. In the beginning of the nitriding process the samples were heated for a short period in a nitrogen atmosphere as protective gas. The nitriding atmosphere was established manually after this heating step. At the end of nitriding a quick cooling to different temperatures (350°C and 220°C) followed. The temperatures were kept constant in order to measure the residual stresses. The process was completed with an atmosphere change to nitrogen and the measurement of the phases and the residual stresses at room temperature.

3.4 Metallographic and chemical analyses

The samples were cut for additional analysis in order to characterise the nitrided surface. The chemical composition of the near surface layers of the samples has been investigated by means of glow discharge optical spectroscopy, which also provides depth profiles. Additionally, the microstructure of the CL and the DZ were examined. Supplementary to these analyses hardness profile curves have been measured.

3.5 Residual Stress Evaluation

The evaluations of the residual stress determination were performed according to the $\sin^2\psi$ -method. The stress determinations were carried out at different temperatures: at nitriding temperature, at two holding temperatures during cooling and at room temperature. Therefore, the change of Young's modulus and Poisson ratio must be taken into account for the different temperatures during the process. A correction of these constants for the different temperatures was carried out according to Schlaak [5], with the expansion coefficients: α -Fe: $14,5 \cdot 10^{-6} \text{ K}^{-1}$; γ '-Fe₄N: $7,9 \cdot 10^{-6} \text{ K}^{-1}$; ϵ -Fe₂₋₃N: $22,2 \cdot 10^{-6} \text{ K}^{-1}$. The X-ray elastic constants (XEC) of iron were used which were corrected for the different diffraction lines with respect of their orientation factor according to Eshelby and Kröner [1].

4 Measurement Results

4.1 Metallographic and chemical analysis

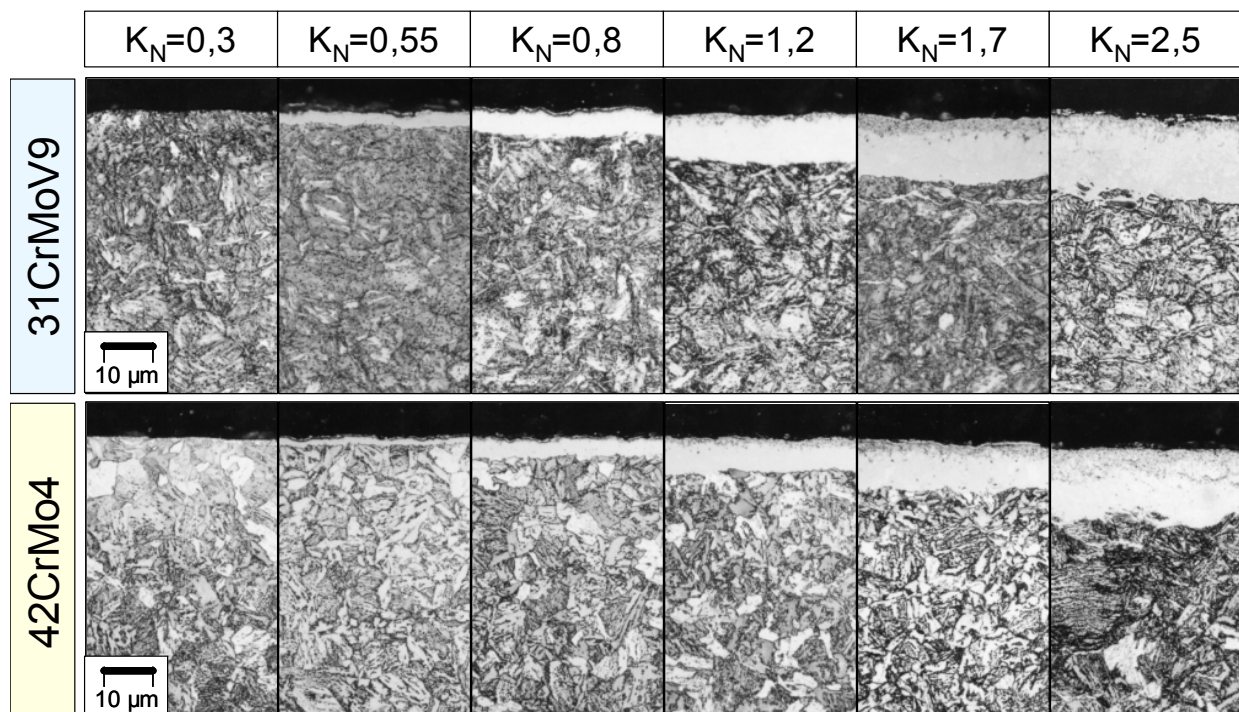


Figure 1: Metallographic analysis of the steel 31CrMoV9 and SAE4140 in comparison for the 6 several nitriding potentials K_N

Figure 1 shows a comparison of the metallographic structure of the materials SAE4140 and 31CrMoV9 for all nitriding potentials. As expected with increasing of the K_N from 0.3 to 2.5 the CL thickness also increases for both materials. For a K_N of 0.3, there is no CL formation observed. This depends on the partial pressures of NH_3 and H_2 according to the Lehrer-Diagram [4]. In comparison to the steel SAE4140 a higher thickness of the CL is measured for every K_N for the steel with the higher chromium content. Due to the higher content of chromium of the steel grade 31CrMoV9, the diffusion of nitrogen and a formation of first nitrides, which later leads to the formation of a closed CL, is preferred. For higher K_N upwards 1.2 a porous zone in the near surface region is observed. This porous zone depends on the content of the solved molecular nitrogen in the CL and is less smaller for the steel SAE4140.

By means of the glow discharge optical emission spectroscopy it is possible to compare the results of the metallographic analysis. Figure 2 shows the depth profiles of the near surface region of the element nitrogen for the investigated steel grades and the 6 several K_N in comparison.

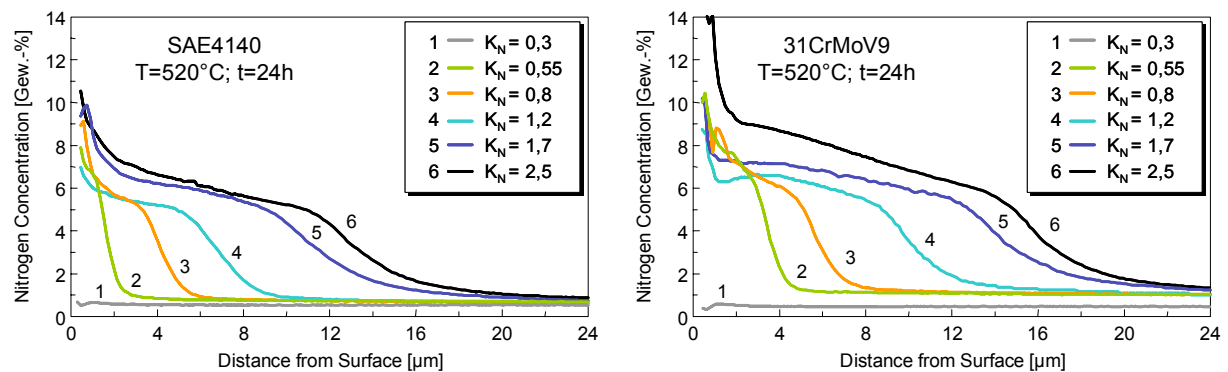


Figure 2: Chemical analysis - nitrogen depth profiles for the steel grades SAE4140 and 31CrMoV9; 6 several nitriding potentials in comparison

In dependence on the K_N and the steel grade the depth profiles show an nitrogen plateau, which is comparable with the CL thickness. With increasing the K_N the plateau and the content of nitrogen also increase. Corresponding to the results of the metallographic analysis, the steel 31CrMoV9 shows a higher nitrogen content and a larger plateau for each K_N in comparison to the steel SAE4140. The significant higher nitrogen content for a K_N upwards 1.2 of 31CrMoV9 in comparison to the steel SAE4140 refer to a higher content of the ϵ - $Fe_{2-3}N$ -phase.

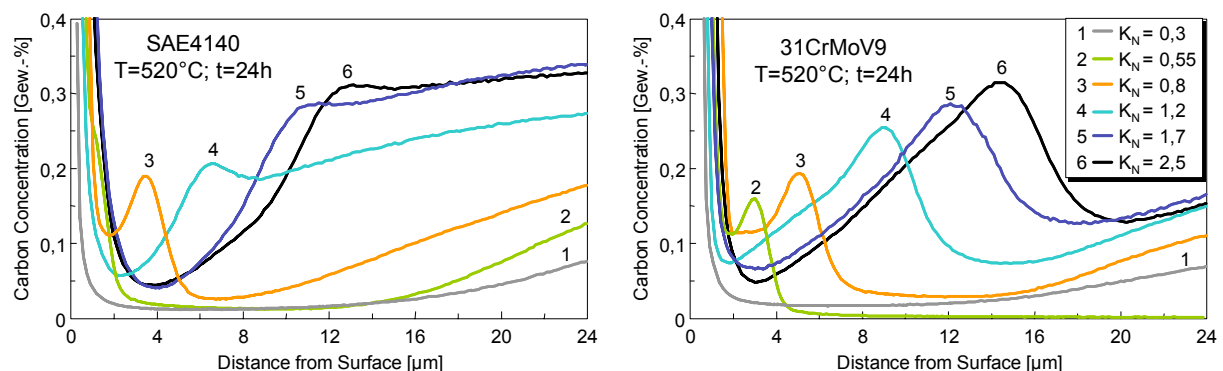


Figure 3: Chemical analysis - carbon depth profiles for the steel grades SAE4140 and 31CrMoV9; 6 several nitriding potentials in comparison

Figure 3 shows the depth profiles of the near surface region of the element carbon for the investigated steel grades and the 6 several K_N in comparison. The depth profiles show an carbon minimum below the surface and a carbon maximum below the CL in dependence on the K_N and the steel grade. Directly under the CL there is also a decarburizing area. A nitriding process causes a diffusion of carbon contrary the nitrogen diffusion due to the gradient of the concentration. The carbon diffusion out of the material was impeded by the nitrogen diffusion into the material. This leads to the carbon minimum below the surface. Due to the diffusion coefficients of the nitrides the carbon diffusion is slowing down, which leads to the carbon maximum below the CL. With increasing the K_N the carbon diffusion was impeded and because of that the maximum of carbon was moved to a deeper range of the base material. With increasing the thickness of the CL a decrease of the decarburizing area was

observed. This depends on the increasing of the nitrogen diffusion into the material. In comparison to the steel SAE4140 the steel grade 31CrMoV9 shows a stronger carbon minimum below the CL for higher nitriding potentials. This depends on the formation of the ϵ -Fe₂₋₃N-Phase and their higher solubility of carbon.

4.2 Residual stress measurements

Because of the dynamic nature of the formation of residual stresses during the nitriding process it was necessary to determine the residual stress state in a very short time. Therefore the residual stresses were measured only at the { 200} lattice plane of Fe₄N and the { 211} lattice plane of α -Fe, which were strong enough in intensity to guarantee a short measuring time for the recording of qualitative sufficient data for a reliable evaluation. As an example for the X-ray in-situ residual stress measurements the results of every one measurement with the same parameters for the two investigated materials and in comparison for the steel SAE1045 are discussed in the following.

4.2.1 Residual stress measurements in steel grade 42CrMo4 (SAE 4140)

The results of residual stress measurements on the { 200} -plane of Fe₄N and the α -Fe-{ 211} -interference line during nitriding are shown in Figure 4.1. The evaluation of the residual stresses observed at the Fe₄N-{ 200} -interference line shows compressive residual stresses from the very beginning. These residual stresses show an approximately constant level of -400 MPa during the nitriding process with a scatter range of ± 100 MPa. The compressive residual stresses in the CL increase during cooling. In contrast to the measured residual stresses in the CL, the residual stresses in the DZ are changing during the nitriding process from high compressive residual stresses of approximately -1100 MPa to lower compressive residual stresses of approximately -500 MPa. After the end of the nitriding process during cooling the residual stress values in the DZ are further reduced.

4.2.2 Residual stress measurements in steel grade DIN 31CrMoV9

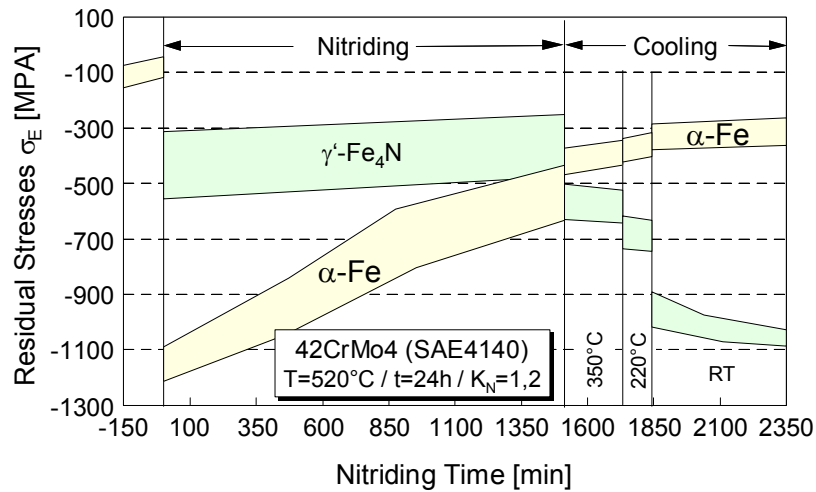
The steel 31CrMoV9 is a nitriding steel with a chromium content of approximately 2.5%. The results of residual stress measurements on the { 200} -plane of Fe₄N and the α -Fe-{ 211} -interference line during nitriding are shown in Figure 4.2. The behaviour regarding the formation of residual stresses observed for the phases Fe₄N and α -iron are showing a similar tendency as shown before for the steel grade SAE4140. The decrease of compressive residual stresses in α -iron during nitriding is considerably the same compared to the material with the lower chromium content. In contrast to the results of the steel SAE4140, the residual stresses are higher and changed from approximately -1300 MPa to -400 MPa. The compressive residual stresses in the CL show in comparison to the steel SAE4140 an approximately same constant level of -400 MPa during the nitriding process. After the end of the nitriding process during cooling the residual stress values in the DZ are further reduced, whereas in the CL a increase is observed.

4.2.3 Residual stress measurements in steel grade SAE1045

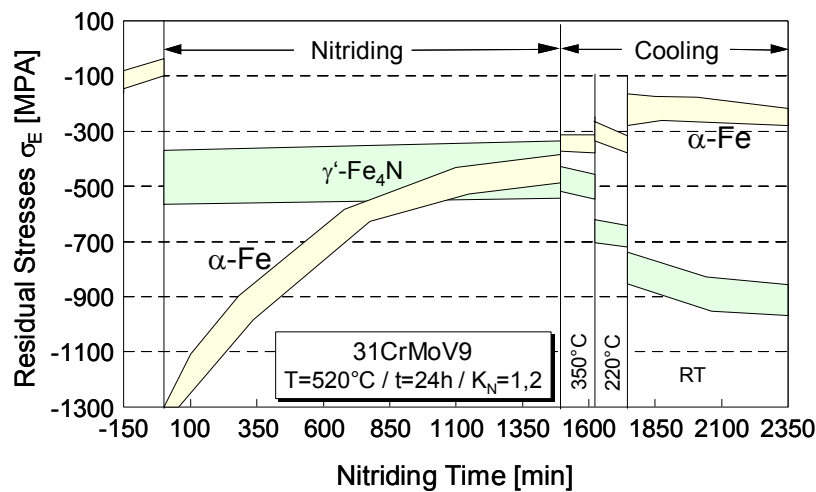
With the results measured at the unalloyed steel SAE1045 nitrided with the same parameters (figure 4.3) it is possible to assess and compare the influence of the chromium content of the formation of residual stresses. The development of the residual stresses in the CL shows a similar behaviour like the formation of residual

stresses in the preceding figures 4.1 and 4.2. In contrast to these, the residual stresses scattered around smaller compressive stresses. During the cooling process an increase of the compressive residual stresses in the CL is also observed. The results of the α -iron show a different behaviour compared to the results of the chromium-alloyed steels. The development of residual stresses in the α -iron shows an approximately constant behaviour during the nitriding.

4.1)
SAE4140



4.2)
31CrMoV9



4.3)
SAE1045

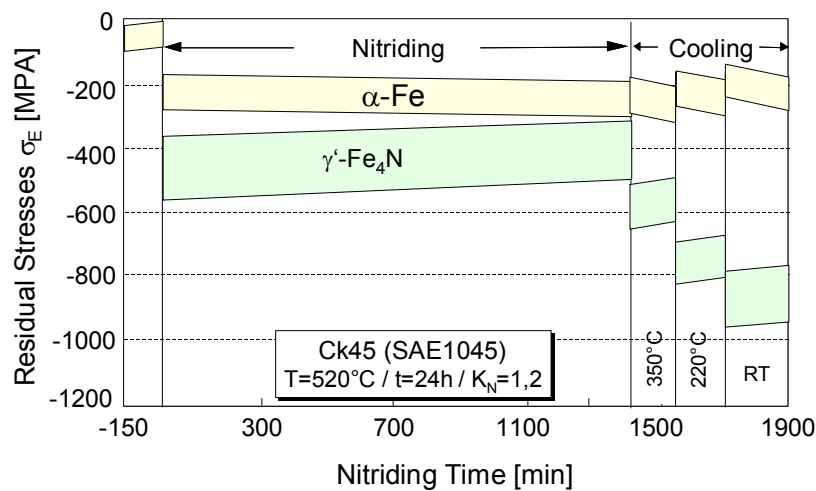


Figure 4: In-situ measurements of residual stresses at the γ' - $\{200\}$ - and at the Fe- $\{211\}$ -interference line during a nitriding treatment at 520°C, $K_N=0,8$

5 Discussion

At the beginning of the nitriding process, compressive residual stresses are generated in the DZ and simultaneously determined in the arising CL. These stresses were attributed to the diffusion of nitrogen into the material and the precipitation of the first iron nitrides, which later lead to the formation of the CL. The amount of these residual stresses depends on the K_N as well as on the C- and Cr-content of the steel matrix. The Cr-alloyed steels show higher compressive residual stresses in the DZ than the non-alloyed carbon steel. At the beginning of the nitriding process, besides the formation of first iron-nitrides Cr-nitrides are generated in the DZ of the Cr-alloyed steels. This formation of Cr-nitrides leads to higher yield points at elevated temperature, which determine the upper limit of potential residual stresses. The thermal yield points of non-nitrided materials amount to approximately 300 MPa for SAE1045, 540 MPa for SAE4140 and 650 MPa for 31CrMoV9. Due to the increasing of strength by nitriding the potential residual stresses are higher. In addition to that the formation of Cr-nitrides in Cr-alloyed steels leads to further hardening effect due to the lattice extension and a increasing of compressive residual stresses. When nitriding Cr-alloyed steels, the added nitrogen leads to the formation of few atomic planes fat, small, plate and semi-coherent nitride precipitates. Because of the slight solubility products of these nitrides the alloying elements are untied almost complete. Around the precipitates tetragonal distortions arise. Due to the homogeneous distribution of the nitride precipitates an isotropic total distortion is developing, which keep the cubic symmetry. Because of this distortion the metal matrix absorbs more nitrogen than the equilibrium solubility of pure iron allows. The additional integrated nitrogen is designated as "excess nitrogen", which is both dissolved interstitial and at the interfaces between the metal matrix and the precipitates [6].

Due to the diffusion of nitrogen into the α -iron lattice at the beginning of the nitriding, the lattice is distorted. This lattice distortion causes the formation of the residual stresses. The compressive residual stresses in the DZ and in the CL originate from the bulge of the nitrided surface in opposite to the untreated core of the sample. This distortion increases with the diffusion of nitrogen. With the nitrogen saturation no more distortion of the lattice can be detected at the interference lines.

The relations of the residual stresses in the CL of Cr-alloyed steels are approximately the same compared to non-alloyed steels. In contrast to non-alloyed steels the compressive residual stresses of the DZ of Cr-alloyed steels are decreasing during the nitriding process and also during cooling from compression to tension. This is tally with residual stress measurements at a temperature of 550°C carried out by Tietz and Härtel. The influence of the nitriding time during a gas nitriding process on the formation of residual stresses of the steel grade 30CrMoV9 were investigated. Figure 6 shows, that an increase of the nitriding time causes decreasing compressive residual stresses. These measurements confirm the results of the in-situ stress measurements presented in this investigation.

It is supposed that during a nitriding process original fine distributed nitrides are growing selective. The resulting coarsening of the nitride precipitates causes a decrease of the distortion state. As a result of this a modification of the precipitation type is possible to arise. The influence of Cr for nitriding has been reported in [7], [8]. At the beginning of nitriding the phase Cr_2N (smaller volume) is formed in the DZ. During the nitriding process the phase Cr_2N changes to the phase CrN, which has a higher volume.

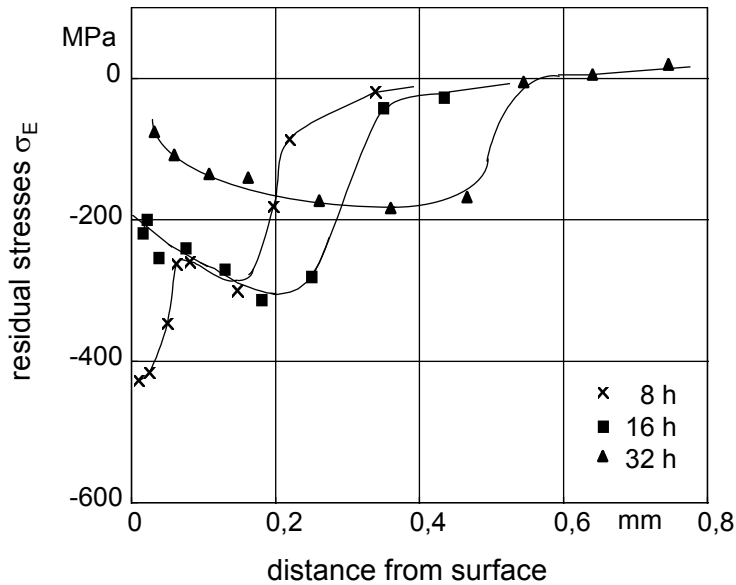


Figure 6: Influence of nitriding time during a short gas nitriding by $T= 550^{\circ}\text{C}+\text{O}_2$ at the formation of residual stresses of the steel grade 30CrMoV9

Figure 7 shows the relative volumes of the precipitates CrN and Cr_2N , which were formed during a nitriding treatment of Cr-alloyed steels.

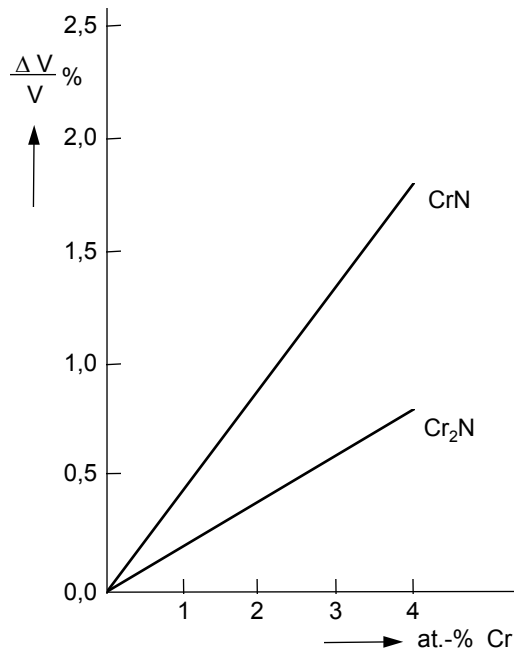


Figure 5: Relative volume changes due to precipitation of CrN / Cr_2N as compared to the iron-chromium solid solution, as a function of alloy composition [7]

It is possible to establish Cr-nitrides by X-ray phase analysis. All samples show besides the intensities of iron-nitride-phases and the α -iron-phase also intensities of Cr-nitrides. It is not possible to distinguish between CrN and Cr_2N , because the 2θ peak positions of both Cr-nitrides are approximately the same according to the ASTM or JCPDS standard. The steel with the higher Cr content (31CrMoV9) shows higher compressive residual stresses during nitriding in comparison to the steel SAE4140. The thermal yield point of the steel grade 31CrMoV9 is about 100 MPa higher than of the SAE4140-sample. The average residual stresses of the steel grade 31CrMoV9,

which were determined in-situ by X-ray methods during the nitriding, are about - 100 MPa higher than the residual stresses of the steel grade SAE4140. It is supposed that the carbon of the Cr-alloyed steels is set variable strong and that there is a different Cr-carbide distribution respectively vanadium carbide or iron carbide distribution. Different reasons are possible:

- ⇒ the kinetics of the precipitation of CrN / Cr₂N
- ⇒ different initial states with regard to the solution state of chromium

Especially a different Cr-carbide content and the resulting different contents of soluted Cr, which are influenced by the pre-heat treatment state, have an effect of the precipitation behaviour. Besides the size and the distribution of the Cr-carbides have also an influence on the residual stresses formation of Cr-alloyed steels.

During cooling the residual stresses of the SAE1045-samples show minor changes in the DZ due to the decrease of the soluted nitrogen. As a consequence iron nitrides are formed during cooling in the non-alloyed steel matrix, which leads to a decreasing amount of interstitial nitrogen. Regarding the Cr-alloyed steels the behaviour in the DZ can be assumed due to the different thermal expansion coefficients only. The Cr-nitrides CrN and Cr₂N in the Cr-alloyed steels are formed during the nitriding process in contrast to the iron nitrides of the non-alloyed steels which are formed during cooling. This is well-known, because "the cooling rate has no influence on the Cr-precipitation development during cooling in the DZ" [8].

Acknowledgments

This research work was founded by the Deutsche Forschungsgemeinschaft (DFG). The investigations were carried out in IWT Bremen. The authors would like to express their gratitude.

References

- [1] Hoffmann, F.; Mayr, P. ; Kreft, U.: "Formation of residual stresses in the CL during gas nitriding measured by a in-situ-technique"; Conf. Proceedings; 8thInt. Conf. on Surface Modification Technologie, 26.-28. Sept. 1994; Nice.
- [2] Kool, W. H.; Mittemeijer, E. J.; Schalkoord, D.: „ Characterization of surface layers on nitrided iron steels“; Micromechanica Acta; Heft 9; 1981
- [3] Somers, M.A.J; Mittemeijer E.J.: "Development and Relaxation of Stress in Surface Layers; Composition and Residual Stress Profiles in γ' -Fe₄N_{1-x} Layers on α -Fe Substrates", Met.Trans. 21A p.189, 1990.
- [4] Lehrer, E.: "Über das Eisen-Wasserstoff-Ammoniak-Gleichgewicht", Z.f.Elektrochemie 36 p.383, 1930 Met.Trans. 21A p.189, 1990.
- [5] Schlaak, U.: "Röntgenographische Ermittlung der Eigenspannungsumlagerung bei erhöhter Temperatur"; Dissertation Universität Bremen; Fortschrittsberichte VDI; Reihe 5; Nr. 148; VDI-Verlag Düsseldorf; 1988.
- [6] Mortimer, B.; Grieveson, P.; Jack, K.H.: „ Precipitation of Nitrides in Ferritic Iron Alloys Containing Cr“; Scand. Journal of Metallurgy; Vol. 1; 1972; S. 203-209
- [7] Mittemeijer, E.J.; Vogels, A.B.P.; van der Schaaf, P.J.: "Morphology of and lattice distortions in nitrided iron, iron chromium alloys and steels"; Laboratory of Metallurgy, Delft University of Technology, Netherlands; 1980
- [8] Kooi, B.J.; Somers, M.A.J.; Mittemeijer E.J.: „ Residualstresses in oxide layers on nitride layers“; AWT-Tagung „ Nitriren und Nitrocarburieren 1996; S. 263ff