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TAILORING THE MICROSTRUCTURE FOR MICROALLOYED CARBURIZING STEELS BY AN ICME APPROACH

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Abstract

Integrative Computational Materials Engineering (ICME) is a new method for efficient development of new materials and new processes by computer-based simulation on different length scales over different process steps. We developed ICME tools and applied them successfully for several new concepts for Nb microalloyed gear steels.

A common ICME platform that combines empirical and rigorous models for casting, rolling, forging, machining, heat treatment and welding has been developed and evaluated for several test cases. The platform requirements and the simulation tools used are described.

Our ICME approach has been successfully demonstrated for the development of new case hardening steels with a reduced Al content to meet the requirements of improved cleanness and lifetime. By microalloying with Nb a stable, fine grain size can be ensured, even for an energy efficient high temperature case hardening heat treatment.

Introduction

An important factor for the optimization of fatigue properties of carburized steels is the oxide steel cleanness [1-3]. Typically, a microalloying concept based on Al is used for deoxidation to reduce the oxygen content in the melt. During this process, hard, round Al-oxides might be formed that eventually limit the life of gear components. Additionally, Al affects the fine-grain stability positively. For the improvement of steel cleanness, various metallurgical methods were successfully implemented in industrial processes [4]. A material-based approach for the improvement of the steel cleanness can be achieved by reducing the Al content. This concept was successfully evaluated for bearing steels [5]. However, such low Al contents cannot ensure fine-grain stability in case hardening steels.

In this work a new alloying concept for steel 25MoCr4, alloyed with Nb and with reduced Al content, is introduced. The aim of the work is to improve the oxide steel cleanness by reducing the Al content, and in parallel increase the fine-grain stability at a high carburizing temperature of about 1050 °C, by substitution of Al by Nb. The development of an Al-free alloying concept is based on thermodynamic calculations. For validation, a laboratory melt has been made and investigated regarding steel cleanness and fine-grain stability at high carburizing temperatures for different process routes.

Procedures

Materials

The reference material is an industrial microalloyed steel, 25MoCr4, with conventional Al, Nb, Ti and N contents, which provides the fine-grain stability during high temperature carburization at 1050 °C for 1 hour 30 minutes [6]. The material was hot rolled to bars of diameter 75 mm and annealed to give a ferrite-pearlite microstructure.

By thermodynamic calculations, target values for the chemical composition were determined for the modified steel, 25MoCr4 with a reduced Al content. The level of S was kept low for an additional improvement of the steel cleanness and the P level was also reduced from 104 to 22 ppm. The new material was melted in a laboratory vacuum furnace with an ingot weight of 80 kg. The casting was made in a square ingot of 140 x 140 mm cross section. The ingot was forged in several passes with repeated intermediate annealing at approx. 1320 °C using the Semi-Product Simulation Center (SPSC) at IEHK. The forged ingot, with a cross-section of 75 x 75 mm, was cooled in air. After cutting of the semi-finished block into two halves, the pieces were forged again to a cross section of 65 x 65 mm from the same homogenization temperature. At the end, the forged material was cooled down to 500 °C in 10 minutes. After the material reached this temperature, the blocks were soaked for 45 minutes in a furnace to attain a bainite structure. The chemical compositions of both investigated materials are shown in Table I.

Table I. Chemical Composition of Investigated Steel Grades 25MoCr4 in wt.%

	C	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**	**Al**	**N**	**Nb**	**Ti**	**$O_{tot.}$ ppm**
Ref	0.24	0.22	0.89	0.0104	0.0172	0.92	0.43	0.0227	0.0161	0.0337	0.0089	17
Al-free	0.23	0.21	0.83	0.0022	0.0016	0.92	0.44	0.0022	0.0137	0.0823	0.0005	17

Determination of the New Material Concept

Thermo-Calc is a commercial software package with integrated CALPHAD-model. Using the thermodynamic database TCFE6, simulation of the amount of precipitation was performed for the microalloyed steel 25MoCr4 and its modified version under equilibrium conditions. The thermodynamic calculation was performed for the given material compositions without consideration of oxide formation. For the determination of microalloying additions, the total volume fractions of Al-nitrides and (Nb,Ti)-carbonitrides were calculated and compared for different conditions. The aim of the calculation was to ensure the same volume fraction of particles in the Al-free case hardening steel as in the classical gear steel, for case hardening temperatures between 950 and 1050 °C.

Experimental Procedure

Three samples were investigated for steel cleanness using DIN EN 50602 in the as-received state for the reference material or in the hot forged state for the Al-free material. After a short austenitization time at 900 °C, followed by quenching in water, the samples were analyzed using the K-value method. An additional comparison of the investigated materials was made for non-metallic inclusions and coarse particles using the SEM (Scanning Electron Microscope). The individual inclusions were analyzed for their chemical composition by EDX (Energy Dispersive X-ray spectroscopy).

For experimental investigations of fine-grain stability, samples were cut from the materials and treated in a conventional furnace under different conditions simulating various industrial process routes with subsequent blank hardening. The dimensions of the treated samples were 25 x 25 x 20 mm. Some of the samples were annealed, to allow dissolution of particles before the heat treatment, at 1300 °C for 30 minutes with the aim to investigate the influence of the solution annealing on the fine-grain stability. The heat treatment of the samples was performed using four different process routes. The first group of samples was annealed to give a ferrite-pearlite structure (FP) using an austenitization treatment at 930 °C for 75 minutes and then holding at 680 °C for 3 hours. A recrystallization annealing (RX) at 700 °C for 3 hours was chosen as the second process route. The samples without the dissolution annealing were additionally tempered at 500 °C for 2 hours or investigated without any heat treatment prior to blank hardening. Figure 1 shows the various process route heat treatments used.

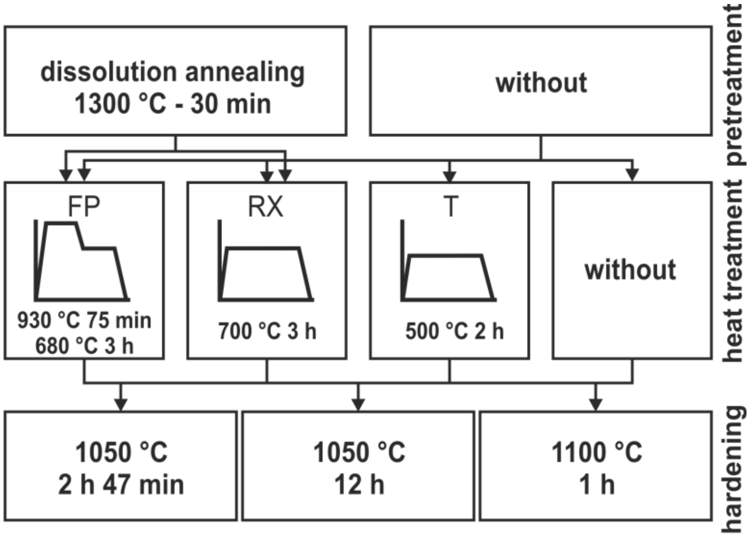


Figure 1. Experimental process routes for investigation of fine-grain stability dependence on heat treatment.

Additional samples were cooled slowly after the hardening step to produce a ferrite-pearlite structure after the heat treatment and investigated with the aim of estimating the thickness of the decarburized layer. This layer was excluded from further investigations. The blank hardening of the samples was carried out at a typical high carburization temperature of 1050 °C for 2 hours 47 minutes or for 12 hours. At an ultra-high carburization temperature of 1100 °C the holding time was only 1 hour.

All investigated samples were sectioned in half in the longitudinal direction before the investigation. The blank hardened samples were etched to reveal prior austenite grains using picric acid. For the elimination of the influence of decarburization, the austenite grain analysis was performed a minimum distance of 3 mm from the edge. The whole sample surface was analyzed for abnormal grain growth. For determination of grain size distribution, several pictures with a total number of over 1000 grains were analyzed. The prior austenite grain size distribution is shown as a cumulative frequency versus the grain size value G according to DIN EN ISO 643. The ideal normal grain size distribution should be a straight line on this scale. Here, a straight line indicates continuous normal grain growth. According to the internal standard of ZF (Zahnradfabrik Friedrichshafen), the material is fine-grain stable if 90% of the investigated area has the grain size G5 or finer and no grain is coarser then G3 [7]. If the cumulative frequency is tending to the region of coarser grains, this is an indication of abnormal or discontinuous grain growth.

For further comparison, a characteristic value G^{90} is introduced. It indicates a maximum grain size for 90% of the investigated area. This means that less than 10% of the investigated microstructure possessed a grain size coarser than G^{90} (Figure 2). For a fine-grain structure without abnormal grain formation, the G^{90} value must be a grain size class G5 or higher and the grain size distribution must be almost a straight line in this type of description.

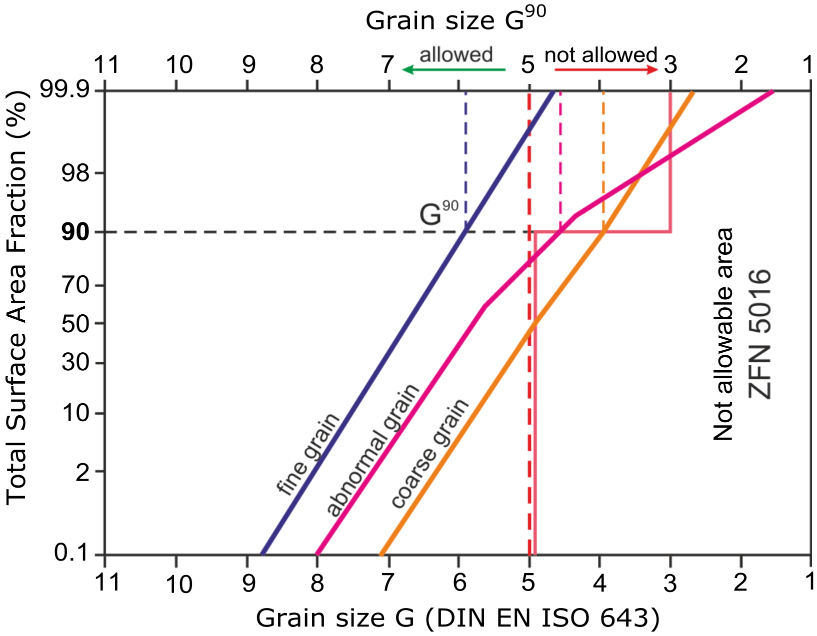


Figure 2. Determination of G^{90} value and presentation of acceptable grain size area.

Thermodynamic and Kinetic Simulations

Determination of the Necessary Nb-addition

An optimal Nb addition was calculated to ensure fine-grain stability during high temperature carburization. Based on the classical description of the Zener-force [8], the grain growth inhibition by a stable microalloying phase depends on the size, the amount and the distribution of the precipitation. The particle size can be changed by heat treatment, but at this stage of material design the particle size is neglected. Here, it is required that the volume fraction of grain growth inhibiting particles at the carburizing temperature of 1050 °C in the Al-free material is equal to the amount in the reference material, under equilibrium conditions. The calculation of the maximum possible precipitation amount and its dependence on temperature was carried out using the thermodynamic software Thermo-Calc.

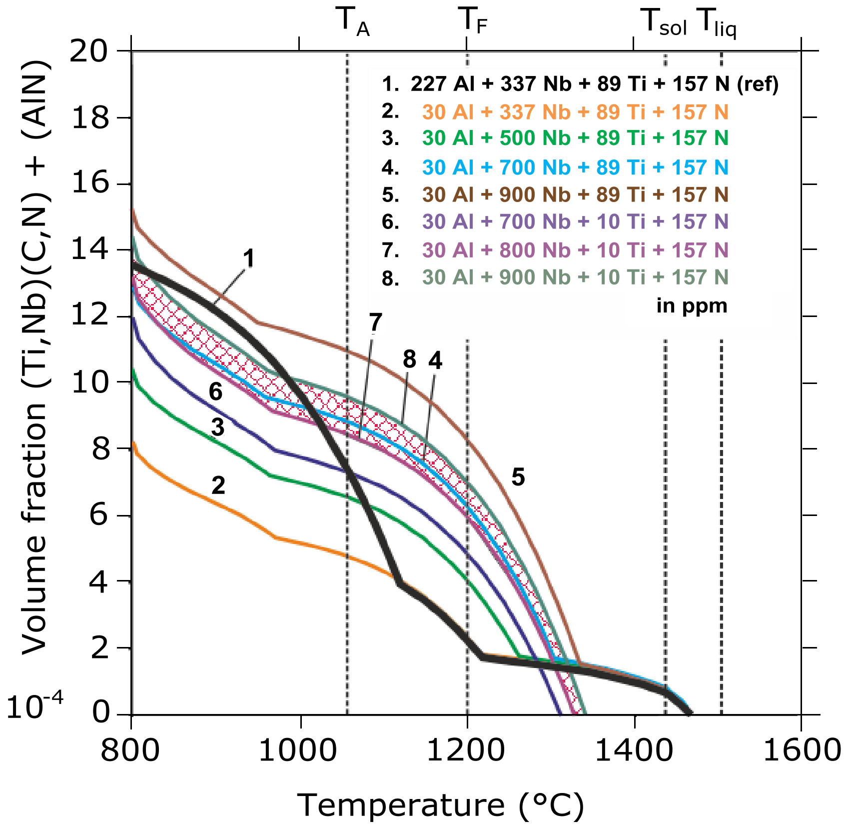


Figure 3. Determination of target alloy system for Al-free carburizing steel by varying Nb and Ti contents.

For a first approximation, the calculation for the reduced Al content steel was performed at 30 ppm Al and compared with the reference material (Figure 3). The volume fraction of particles at the carburization temperature of 1050 °C (T_A) is noticeably lower in comparison to the reference material. In the following calculations, the Nb-content was increased step by step in order to achieve an equal volume fraction as compared to the reference material.

Additional calculations were performed for a reduced Ti content of around 10 ppm. The analysis of the calculation results shows that at 89 ppm Ti the microalloying phases can be stable in the liquid-solid region and this can lead to the formation of coarse primary particles. Such coarse particles reduce cleanness and are not effective for fine-grain stability. The high formation temperature of particles is caused by the high stability of Ti-nitrides. By reduction of the Ti content, an additional element of material optimization was realized, whereby the formation temperature of particles in the equilibrium state can decrease to approximately 1320 °C. Further reduction of the Ti content has no influence on the formation temperature of particles because of the higher Nb content. The target amounts of 800-900 ppm Nb, <30 ppm Al and approximately 10 ppm Ti have been determined. The target area for the Al-free case hardening steel with the desired fine-grain stability is shown as the hatched area in Figure 3. In line with this calculated microalloying amount, a laboratory melt was produced. The actual alloy contents in the test material are listed in Table I.

A large amount of undissolved precipitates is expected in the Al-free material at typical forming temperatures of around 1200 °C (T_F). This can lead to a decrease in fine-grain stability due to coarsening of the Nb particles. The hot formability as well as recrystallization can be affected by a higher particle volume fraction and precipitation driving force. At temperatures below 1050 °C the particle volume fraction is lower in comparison to the microalloyed reference material, which might cause reduced fine-grain stability at typical carburization temperatures.

Experimental Results

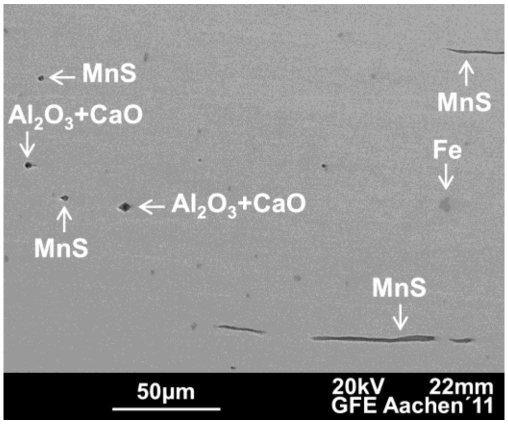
Steel Cleanness

The results of oxide steel cleanness measurements show that the modified Al-free grade has a smaller amount of harmful coarse inclusions. This is associated with improved cleanness, based on K1 and K4 values according to DIN 50602, in comparison to the reference material (Table II). These results are expected because of the reduction of the Al content**.**

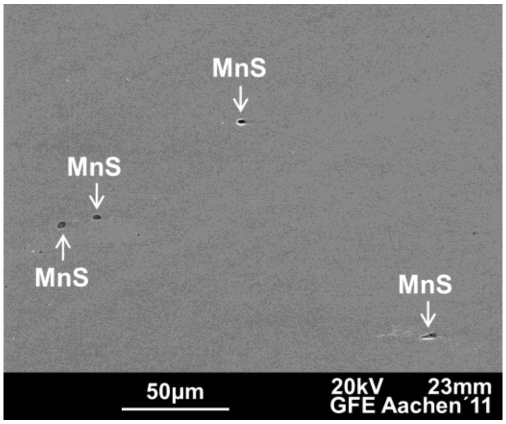
Table II. Oxide Steel Cleanness for Reference and Al-free Material according to DIN 50602

	K1	**K4**
Ref	3.0	2.1
Al-free	0.5	0.0

The analyses of individual inclusions with SEM show a significantly lower volume fraction of inclusions as well as a smaller size in the modified material (Figure 4). The Mn sulfides are mostly either globular or elongated. The size or the length of the elongated inclusions is smaller than in the reference material. The reason for this is the significantly lower S content in the Al-free material.



(a) ref



(b) Al-free

Figure 4. SEM analysis of reference (a) and Al-free material (b).

In the reference material, coarse square Ti and Nb particles with sizes larger than 1 µm have been found [9], which were probably formed in the liquid-solid region because of the high stability of Ti-nitrides. These particles are not effective for the suppression of grain boundary movement. The results of the investigation show that the formation of Al-oxides cannot be avoided completely in the low Al steel. However, the probability of formation is much lower in comparison to the reference material.

Results of Fine-grain Stability for Different Process Routes

An overview of the G^{90} results for all of the investigated material conditions and process routes is shown in Table III. The comparison of the investigated materials after blank hardening for 2 hours 47 minutes at 1050 °C demonstrates that fine-grain stability is evident for all the investigated process routes in both materials. The spread of the G^{90} values for the reference material is small. This could be evidence of optimal precipitation conditions in the as-delivered condition. The Al-free material generally has a slightly coarser grain size and a significant dependence of the G^{90} value on the process route could be observed. This means that some potential for optimization exists for the Al-free material regarding the precipitation state. The process route with the FP-annealing step has the best overall fine-grain stability in the two materials.

The results for other heat treatment processes show the grain size to be coarser than for the 1050 °C for 2.78 hours treatment. However, only the Al-free material can provide sufficient fine-grain stability for holding 12 hours at 1050 °C. The reference material tends to a coarse or abnormal grain growth regime. In the Al-free material only a dissolution heat treatment with RX-annealing can improve the precipitation state to give adequate fine-grain stability. For the Al-free material the temperature for dissolution heat treatment can be insufficient and that can lead to particle coarsening and poor fine-grain stability.

For a hardening temperature at 1100 °C with a holding time of 1 hour, the G^{90}-values for the reference material are lower than the allowed level. In contrast, the Al-free material has still sufficient fine-grain stability for all of the process routes. Furthermore, it should be noted that the process route with an FP annealing step shows significantly finer grains for the Al-free material.

Table III. Grain size of Prior Austenite According to G^{90} Value after Different Process Routes with Blank Hardening at 1050 or 1100 °C (G^{90} <5 – indicates coarse or abnormal grains).

Hardening Treatment	**Steel**	**Dissolution**		**No Pretreatment**			
		FP	**RX**	**FP**	**RX**	**T**	**-**
1050 °C 2.78 hours	Ref	6.1	6.2	6.9	6.8	6.6	7.1
	Al-free	6.5	5.1	6.2	5.1	5.5	5.7
1050 °C 12 hours	Ref	**1.4**	5.0	**3.9**	**4.1**	**4.4**	**4.6**
	Al-free	**2.7**	**3.5**	6.4	5.8	5.0	5.2
1100 °C 1 hour	Ref	**0.5**	**3.0**	**2.2**	**2.8**	**4.4**	**4.0**
	Al-free	6.7	5.1	6.5	5.4	5.5	5.5

Discussion

A new microalloying concept for case hardening steel 25MoCr4 has been determined using thermodynamic modeling. The new material has a considerably reduced Al content with a distinctly improved steel cleanness level and can ensure fine-grain stability at high carburizing temperatures up to 1100 °C.

The reduction of the Al content shows a significant positive effect on the oxide steel cleanness as measured by K1 and K4 analysis. Nevertheless, some Al-oxides, Mn-sulfides and coarse (Ti,Nb)-carbonitrides have been detected using SEM with EDX, yet the Al-free material has a significantly smaller amount of Al-oxides and Mn-sulfides as a result of the reduction of the Al and S contents.

The analysis of calculated equilibrium temperatures, using thermodynamic simulation, shows a high stability of Ti-nitrides in the liquid-solid area. This leads to the formation of coarse Ti-particles with a size larger than 1 µm. This can worsen the steel cleanness and reduce the efficiency of Ti-nitrides in preventing grain coarsening. Reduction of the Ti content from 89 to 10 ppm causes the precipitation temperature to be lowered leading to the formation of smaller particles in the solid phase.

The G^{90} value is an extension of an internal ZF standard, ZFN 5016, to quantify the fine-grain stability. The results for the reference material did not show any influence of the process route on the fine-grain stability for a hardening cycle of 2 hours and 47 minutes at 1050 °C. This can be achieved by an optimal particle state before the hardening heat treatment. In contrast, the austenite grain size in the Al-free material can be controlled and influenced by the process route. The FP-annealing produces a fine austenite grain in the Al-free material. The formation kinetics of Nb-carbonitrides are at a maximum at temperatures between 900 – 1000 °C [10-13]. In this temperature range new small particles can be formed sufficiently quickly. Cooling after austenitization above 700 °C decreases Nb diffusion and the particle coarsening effect considerably. This is likely to be the reason for the improved fine-grain stability after the FP-annealing cycle. Al-nitrides can form at temperatures below 700 °C [14,15] and in the case of RX-annealing after a dissolution heat treatment produces a better distribution of small Al-nitrides and consequently sufficient fine-grain stability for long hardening times in the reference material.

The modified Al-free material possessed sufficient fine-grain stability after blank hardening at 1050 °C for 12 hours and in fact fine-grain stability could be achieved for all the process routes which excluded dissolution heat treatment. The Al-free material has G^{90}-values lower than 5 after a solution heat treatment which indicates abnormal grain growth. This can be explained by an incomplete dissolution of precipitates and coarsening of particles. A clearly improved fine-grain stability can be found for the Al-free material after blank hardening at 1100 °C for 1 hour, compared to the reference material, for all process routes.

In the new alloying concept, the Nb content is high enough for Nb carbonitrides to be stable at 1320 °C under equilibrium conditions. Furthermore, the high Nb level can lead to a significant stability increase of Nb carbonitrides in the melt. As a result, Nb particles can be formed with sizes up to 1 µm . These coarse particles can reduce the fine-grain stability of the material. The dissolution of Nb particles and redistribution of Nb requires a further heat treatment of the material. By using kinetic simulations the optimal process parameters for heat treatment and forging will be determined in further work**.**

Conclusions

In this paper, a new Al-reduced microalloying concept for case hardening steel 25MoCr4 was introduced, which has improved steel cleanness and fine-grain stability at high carburization temperatures.

Al and Ti contents were reduced to avoid the formation of coarse precipitates and oxide inclusions.

The reduction in Al and Ti was compensated by an increase in the Nb level which is beneficial for fine-grain stability.

The required amount of Nb was calculated from thermodynamic simulations. The new material shows a sufficiently high grain coarsening resistance for a range of process routes.

The most stable austenite grain size can be found in the modified Al-free material after blank carburizing and annealing at 1050 °C for 12 hours or by annealing at 1100 °C for one hour after a process chain which includes FP-annealing.

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