Experimental observation of κ -phase formation sequences by *in-situ* synchrotron diffraction

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Abstract

In-situ annealing experiments using synchrotron diffraction depict the separation of {100}-superlattice peaks ascribed to C-enrichment of pre-existing, C-lean $L'1_2$ -ordered structures into C-rich κ -carbides of alike crystal structure during heating of a high-Al lightweight steel. The peak separation is the first experimental *in-situ* investigation of the transformation sequence during Fe_3AlC -phase formation. A detailed analysis of the lattice parameter evolution and thermal expansion behavior was carried out to validate the assignment of phases by comparison with theoretical calculations and available experimental data.

Keywords: synchrotron diffraction, intermetallics, ordering, phase transformation

1 Introduction

The addition of noteworthy amounts of aluminum to steel yields a twofold advantage by reducing the overall density of steel whilst increasing its strength due to the formation of intermetallic phases. Latter strengthening contribution requires a profound knowledge of the phase transformation involving the precipitation of intermetallic phases. The Fe_3AlC - or κ -phase can be stabilized in high-Al alloys either within a face-centered cubic (fcc) austenite or body-centered cubic (bcc) ferrite matrix. The beneficial contribution of the κ -phase to the mechanical properties of fully austenitic high-manganese steels has led to research on the underlying phase transformations [1,2].

Spinodal decomposition was proposed to occur during phase transformation from austenite (γ) to the κ -phase [3,4]. The decisive distinction between disordered γ and the ordered configurations lies in a transition from fcc to simple cubic structures and thus an additional superlattice reflection. The κ -phase exhibits a $L'1_2$ -crystal structure, wherein Fe and Al are ordered on simple cubic sublattices and C occupies the center of the lattice structure, forming a perovskite-like structure. {100}-superreflection corresponding to a single crystal lattice structure were identified in Fe-Mn-Al-C steels upon water quenching [5,6]. A possible κ -formation sequence is shown schematically in Figure 1. Possible reaction sequences for first-order order-disorder transformations are discussed in detail by Soffa and Laughlin [7]. Therein, a disordered fcc state is cooled from high temperatures and undergoes in full long-range ordering by diffusion over the range of a few atomic distances. Following, this ordered structure separates into a disordered fcc and a $L'1_2$ -structured κ -phase, possibly by spinodal decomposition. The aforementioned reaction sequence was also suggested by Tan et al. [8] for Ni-base superalloys.

The first formed ordered phase and the equilibrium κ -phase both exhibit a $L'1_2$ crystal structure, whereby the difference lies in the Al- and C-concentration (c.f. Figure 1). Hence, the two types of configurations are denoted as C-lean and C-rich κ -phase, respectively.

The lack of *in-situ* studies on the κ -phase formation constitute uncertainties regarding the κ -phase transformation sequence and its underlying kinetics during κ -phase formation. In the current work, the first *in-situ* experimental observation of the κ -formation was conducted by synchrotron diffraction during heating of a high-Al alloyed lightweight steel.

2 Experimental section

The two-phase alloy X100AlMnNi 10-7-6 was vacuum induction melted into ingots. The alloy composition was determined by wet-chemical analysis and X-ray fluorescence. The chemical composition is provided in Table 1. Homogenization was conducted at 1200 °C for 5 h prior to open-die hot forging at 1200°C with a total strain of 0.7 and subsequent water quenching. The slabs of dimension 40 mm x 40 mm x 320 mm were solution annealing at 1200 °C for 2 h followed by water quenching.

Synchrotron X-ray diffraction was carried out in the high-resolution powder diffraction beamline P02.1 at DESY, Hamburg. A fixed wavelength of approx. 0.207 Å was used to acquire diffraction pattern on a PerkinElmer XRD1621 fast area detector. The 2Θ -range expands from $\sim 2^\circ$ - 16° . *In-situ* heating was conducted in a ceramic heating oven using sealed quartz capillaries. Heating rates of 15 °C/min were employed until an isothermal holding temperature of 800 °C was reached. During heating, diffraction patterns are acquired in steps of 50 °C. Image acquisition during holding is divided into steps of 30 s. Data analysis is carried out using Fit2D [9] for conversion of 2D patterns into 1D intensity profiles. The subsequent Rietveld analysis is performed using the open source software ‘Materials Analysis Using Diffraction’ [10]. The 2Θ -range was reduced to $\sim 10^\circ$, limiting data analysis to completely acquired Debye Scherrer rings.

3 Results and discussion

The diffraction profile of the duplex alloy after solution annealing is displayed in Figure 2a. $\{111\}_{fcc}$ - and $\{110\}_{bcc}$ -peaks confirm the presence of austenite and ferrite. In addition, ordered phases of the $L'1_2$ - and B2-type are present as visualized in Figure 2b by an enlarged view of the superlattice reflections corresponding to the $\{100\}_{L'1_2}$ - and $\{110\}_{L'1_2}$ -peak as well as the $\{100\}_{B2}$ -peak.

Figure 2c displays the evolution of the $\{100\}_{L'1_2}$ -superlattice reflection during heating from 200 °C to 800 °C. The peak intensity increases during heating up to 600 °C, indicating an increase in volume fraction of $L'1_2$ -ordered phases. Simultaneously, the peak position shifts continuously towards lower angles due to thermal expansion of the lattice structure. Heating above 600 °C results in a pronounced peak separation of the initial peak by a secondary reflection at lower diffraction angles (c.f. Figure 2c).

The considerable shift in peak position of the secondary reflection accentuates the occurrence of a phase transformation. The phase transformation is accompanied by a decrease in volume fraction of the initial phase. At 700 °C, the majority share of the superlattice reflection has transformed into the newly formed configuration. The transformation is concluded upon reaching 750 °C and thus occurs in approximately 5 minutes.

Figure 3a depicts the time-resolved evolution of the lattice parameter corresponding to the diverse superlattice reflections. During heating, the room temperature lattice parameter yields 3.672 Å and increases up to 3.735 Å. The ordering transformation commences at 650 °C and results in an increase of lattice parameter to an overall average of 3.821 Å ± 0.039 Å (errors as standard error).

The schematic reaction sequence in Figure 1 suggests that fcc- and κ-phase may reach their respective equilibrium state thermodynamically. In contrast, the matrix-particle coherency between the fcc- and κ-phase restrains the phases to maintain an alike lattice parameter. However, the equilibrium lattice parameters are different, with κ-phase having a clearly larger lattice parameter. The lattice parameter of the κ-phase increases with, in particular, the C content. Therefore, the coherently constrained κ-phase has a lower C content than the equilibrium κ-phase. Consequently, the observed peak separation of the superlattice reflection is ascribed to the transformation from the C-lean to the C-rich κ-phase. Both configurations evoke superlattice reflections, while an enrichment of the C-lean κ-phase is anticipated to induce a prompt increase in lattice parameter. The assignment of the peak separation to C-enrichment of the C-lean κ-phase is corroborated by the fast kinetics associated with the high C mobility at elevated temperatures. Under latter consideration, the completion of ordering and the subsequent phase separation to a C-rich κ-phase is considered plausible under certain cooling conditions, thus suppressing the measurement of the C-lean κ-phase.

The κ-phase frequently exhibits an under-stoichiometric concentration of Al and C [11]. In general, the enrichment of fcc and its related ordered structure with C is expected to cause an increase in lattice constant [12,13]. The C-enrichment of the κ-phase with respect to its parent fcc-phase is well documented by atom probe tomography measurements [12,14]. The C-enrichment induces an increase in lattice parameter by approximately 0.09 Å at 650 °C. The thermal expansion of the C-lean L'1₂-phase was investigated in detail in Figure 3b. Its room temperature lattice parameter of about 3.672 Å increases approximately linear with temperature and the thermal expansion is approximated empirically to:

$$a_{L'1_2}^{C-lean}(T) = (3.66505 \pm 0.00285) \text{ Å} + (8.06418 * 10^{-5} \pm 0.66981 * 10^{-5}) \text{ Å/K} * T \quad \text{Equation 1}$$

Experimental measurements [12,13,15,16] and theoretical calculations [11,17] of the room temperature lattice constant associated with the C-rich κ-phase yield a range from 3.72 Å - 3.78 Å. Under assumption of an identical thermal expansion, the room temperature lattice parameter of the C-rich κ-phase $a_{L'1_2}^{C-rich}(RT)$ would yield approximately 3.756 Å by recalculating $a_{L'1_2}^{C-rich}(800^\circ\text{C})$ assuming the thermal expansion coefficient of the C-lean κ-phase in Equation 1.

The lack of experimental observations of the C-lean κ -phase impedes a validation of the measured lattice parameter. Nevertheless, the C-lean κ -phase resembles in first approximation the C-free $\text{Fe}_3\text{Al-L1}_2$ phase. Maugis [18] used ab-initio calculations to determine the room temperature lattice parameter of the $\text{Fe}_3\text{Al-L1}_2$ and $\text{Fe}_3\text{AlC-L}'1_2$ as 3.65 Å and 3.75 Å, respectively. Similar calculations of theoretical lattice parameter of $\text{L1}_2\text{-Fe}_3\text{Al}$ and $\text{L}'1_2\text{-Fe}_3\text{AlC}$ yielded differences of 0.04 Å-0.10 Å [17,19]. The accordance of theoretical calculations and experimental observations in lattice parameter with respect to absolute values and differences confirms the transformation sequence from disordered fcc phase to an ordered, C-lean κ -phase followed by a phase separation into disordered fcc and C-rich κ -phase.

4 Conclusions

In-situ synchrotron diffraction facilitates the identification of the κ -phase formation sequence, wherein the peak separation of superlattice reflections corresponding to a $\text{L}'1_2$ -crystal structure was linked to the development of a C-rich κ -phase from an ordered C-lean κ -precursor. The allocation of phases was validated by comparison of lattice parameter to theoretical calculations and experimental data. The observed transformation sequence suggests a prior ordering of the disordered fcc-phase into a long-range ordered, C-lean κ -precursor, which subsequently undergoes phase separation into a disordered fcc- and C-rich κ -phase.

5 Acknowledgements

The financial support of the Deutsche Forschungsgemeinschaft (DFG), Grant no. SO1431 and the support by the DESY synchrotron beamline P02.1 is gratefully acknowledged.

6 References

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Table 1: Chemical composition of the multi-phase alloy.

Fe-10Al-7Mn-6Ni-1C	C	Mn	Si	P	S	N	Al	Ni
wt.-%	0.95	6.8	0.025	0.012	0.011	0.012	10.1	6.1

Figure 1 Schematic illustration of Gibbs energy curves in dependence of the Al- and C-concentration and the crystal structures of participating phases.

Figure 2: Synchrotron diffraction profile of the duplex alloy in the as-quenched condition (a) with an enlarged view (b) of superreflections corresponding to L₁₂- and B₂-structures. (c) Evolution of {100}_{L₁₂}--superlattice reflection during heating from 200 °C to isothermal holding temperature of 800 °C.

Figure 3 Evolution of the lattice parameter during heating of the C-lean and C-rich $L'1_2$ structure (a) and thermal expansion of the C-lean $L'1_2$ -phase.