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Combined atom probe tomography and density functional theory investigation of the Al off-stoichiometry of κ-carbides in an austenitic Fe–Mn–Al–C low density steel

M.J. Yao [a], P. Dey [a, *], J.-B. Seol [b, **], P. Choi [a], M. Herbig [a], R.K.W. Marceau [c], T. Hickel [a], J. Neugebauer [a], D. Raabe [a]

[a] Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, 40237 Düsseldorf, Germany
[b] National Institute for Nanomaterials Technology, POSTECH, Pohang 790-784, South Korea
[c] Deakin University, Institute for Frontier Materials, Geelong, VIC 3216, Australia

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ABSTRACT

We report on the investigation of the off-stoichiometry and site-occupancy of κ-carbide precipitates within an austenitic (γ), Fe-29.8Mn-7.7Al-1.3C (wt.%) alloy using a combination of atom probe tomography and density functional theory. The chemical composition of the κ-carbides as measured by atom probe tomography indicates depletion of both interstitial C and substitutional Al, in comparison to the ideal stoichiometric $L'1_2$ bulk perovskite. In this work we demonstrate that both these effects are coupled. The off-stoichiometric concentration of Al can, to a certain extent, be explained by strain caused by the κ/γ mismatch, which facilitates occupation of Al sites in κ-carbide by Mn atoms ($\mathrm{Mn}^{\gamma}_{\mathrm{Al}}$ anti-site defects). The large anti-site concentrations observed by our experiments, however, can only be stabilized if there are C vacancies in the vicinity of the anti-site.

1. Introduction

There is a strong demand for the development of advanced high-strength steels for automotive applications, in order to reduce energy consumption and greenhouse gas emission. Austenitic Fe–Mn–Al–C steels show particularly outstanding mechanical properties [1–11] and are therefore highly promising candidates for such applications. Due to their good oxidation and corrosion resistance, these steels were originally developed in an attempt to substitute Cr-containing stainless steels [1], but recently they have regained interest due to their excellent strength-ductility balance and significantly reduced mass density due to alloying with Al [2–11].

A common characteristic of alloys showing excellent strength and ductility is a pronounced strain hardening capability, which continuously increases the strength and delays local necking during deformation. Transformation induced plasticity (TRIP) and twinning induced plasticity (TWIP) steels are typical examples for alloys showing high strain hardening capabilities [12,13], where martensitic transformation and formation of deformation twins are the respective dominant deformation and strain hardening mechanisms. The active deformation mechanisms are closely related to the stacking fault energy (SFE). Generally, as the SFE increases, the dominant deformation mechanism changes from TRIP to TWIP and from TWIP to dislocation gliding [14,15].

Gutierrez-Urrutia et al. attributed the excellent strain hardening capacity of solid solution austenitic Fe–Mn–Al–C alloys containing <5 wt.% Al to multiple stages of deformation during which sequential dislocation cell structures and, at higher loads, twin substructures are gradually formed [4]. For alloys of >5 wt.% Al, intragranular precipitation of nanometer-sized κ-carbides occurs at elevated temperatures (470 °C–710 °C) [16–19], which leads to a substantial increase in yield strength without a significant loss in ductility [3,5,8]. Planar dislocation substructures were observed in deformed κ-carbide containing austenitic Fe–Mn–Al–C alloys [5,6,10]. The occurrence of planar dislocation substructures in these alloys, which have high SFE values ranging from 80 to 110 mJ/m^2 [10], was ascribed to shearing of ordered κ-carbides by dislocations

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: p.dey@mpie.de (P. Dey), jb_seol@postech.ac.kr (J.-B. Seol).

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[6,8] and a mechanism referred to as "glide plane softening" [20]. According to this mechanism, the local order is destroyed by a leading dislocation shearing the ordered particle and thus facilitating the glide of consecutive trailing dislocations. For high strain levels, mechanisms of shear-band-induced plasticity (SIP) [2] and microband-induced plasticity (MBIP) [9,10] have been suggested, referring to homogeneous shear deformation and bands of very high dislocation density, respectively.

However, the interaction between dislocations and κ-carbide precipitates in age-hardened austenitic Fe–Mn–Al–C steels is still not well understood. Debates exist over the dominant co-deformation mechanism, i.e. the competition between dislocation looping [6] and precipitate shearing [8] during plastic deformation. It was reported that the critical size of ordered coherent precipitates for the transition from shearing to looping is associated with the antiphase boundary (APB) energy on the slip planes [21]. Therefore, an accurate determination of the stoichiometry and site-occupancy of κ-carbides is essential for understanding the strain hardening mechanisms in age-hardened austenitic Fe–Mn–Al–C alloys. Also, the exact sub-lattice occupancy in such a two-phase material containing ordered precipitates determines the elastic misfit across the hetero-interfaces. This will also contribute to the total system energy and to the strain hardening behavior.

The composition of κ-carbides is commonly given as $(Fe,Mn)_3AlC_x$, where the exact chemical composition of this phase is still unknown [17–19,22,23]. It is tacitly assumed to be a derivative from the Fe_3AlC_x-type ternary κ-carbide [24]. Due to the difficulty in determining C concentrations in small precipitates and also obtaining single-phase κ-carbide, the exact composition of the Fe_3AlC_x-type κ-carbide was uncertain for a long time [25,26]. In 1995, Palm et al. revealed a composition range for this phase between $Fe_{3.2}Al_{0.8}C_{0.71}$ and $Fe_{2.8}Al_{1.2}C_{0.42}$, i.e. $Fe_{3+y}Al_{1-y}C_x$ ($-0.2 < y < 0.2$, $0.42 < x < 0.71$), based on electron probe microanalysis (EPMA) [25]. The C content does not reach the stoichiometric 20 at.% and the Fe to Al ratio can vary between 2.3 and 4.0 instead of being equal to 3. Inspite of the fact that the deviation of the Fe to Al ratio is not appropriately considered in the common Fe_3AlC_x formula, it is still generally adopted. As for the $(Fe,Mn)_3AlC_x$ κ-carbide precipitates in Fe–Mn–Al–C alloys, since they are finely dispersed and only a few nanometers in size, their direct chemical characterization is challenging. Atom probe tomography (APT) is the ideal tool to resolve this composition uncertainty since it offers near-atomic spatial resolution and equal detection sensitivity to all elements [27–33]. To our knowledge, there are only two reports in the literature about APT analyses on κ-carbide-containing alloys. One is about κ-carbide precipitation in a ferritic matrix [34], with very different elemental partitioning behavior as compared to austenitic alloys. The second report deals with κ-carbide formation in austenitic Fe–Mn–Al–Si–Mo alloys [35], where Si is found to have a substantial effect on C partitioning. No APT data have been published on κ-carbide precipitates in quaternary austenitic Fe–Mn–Al–C alloys.

The crystal structure of κ-carbides is reported to be $L'1_2$ perovskite-type [17,22,36,37]. In such a derivative of the conventional face-centered cubic (fcc) crystal structure, the unit cell contains 5 atoms at 3 kinds of sites. In addition to the 4 atoms at one corner and three face-centered sites, as per fcc conventional unit cell, there is also one atom at the body-centered site. Conventionally, the elemental site-occupancy of the κ-carbide phase is such that Al occupies the corner site of the unit cell, Fe and Mn the face-centered positions, and C occupies the body-centered octahedral interstitial site, which is based on observations of electron diffraction patterns and calculations of structure factors [17,22,36]. In terms of atomic percentage, the stoichiometric $(Fe,Mn)_3AlC$ κ-carbide has 60% (Fe+Mn), 20% Al and remaining 20% C. However, the κ-carbides are commonly expected to be off-stoichiometric and thus the elemental site-occupancy remains unresolved. Since experimental characterization is challenging, a viable theoretical approach to elucidate the site-occupancy in κ-carbides is density functional theory (DFT).

In a separate work, the off-stoichiometry with respect to the depleted C concentration in κ-precipitates was interpreted with the aid of DFT simulations [38]. The off-stoichiometric C concentration was found to be driven by the minimization of the lattice misfit and hence the elastic strain between the coherent κ-precipitates and the γ-matrix. The current work is dedicated to the measurement of the chemical composition of κ-carbides at the atomic scale using APT followed by an interpretation of the experimental data on off-stoichiometry and site-occupancy in κ-carbide by means of DFT. The identified mechanisms are crucial for understanding the interaction between precipitates and dislocations during plastic deformation.

2. Methods

2.1. Alloy processing and APT measurements

The alloy of Fe-29.8Mn-7.7Al-1.3C (wt.%) (Fe-26.7Mn-14.1Al-5.3C (at.%)) as determined by wet chemical analysis was used in this study. It was prepared by vacuum-induction melting. The details of alloy casting and thermo-mechanical processing are reported elsewhere [5]. To obtain a homogenous microstructure, a solution heat treatment at 1100 °C for 2 h followed by water quenching was performed. Subsequently, the alloy was aged at 600 °C for 24 h to induce κ-precipitation. The grain size of the alloy ranged from ~50 to ~100 μm. The needle-like APT specimens, taken from grain interior regions, were prepared using a dual-beam focused-ion-beam (FIB) system (FEI Helios Nano-Lab 600*i*) by a standard FIB lift-out procedure, as described in Ref. [39]. Annular FIB milling was performed using a low acceleration voltage of 16 kV with final polishing at 2 kV to keep Ga^+ implantation into the samples at a negligible level. APT analyses were conducted using a LEAP 3000X HR system (Cameca Instruments) in voltage-pulsing mode at 200 kHz pulse repetition rate, 0.005 atom/pulse detection rate, 15% pulse fraction and 70 K. Six successful measurements were performed and evaluated, four of which contained more than 10 million ions. The APT data were evaluated using the IVAS software by Cameca Instruments (version 3.6.8), where the tip profile algorithm [40] was used for the reconstruction of APT maps.

2.2. Theoretical framework

The theoretical results were obtained using DFT [41,42] as implemented in the Vienna Ab Initio Simulation Package (VASP) [43]. Projector augmented wave (PAW) potentials were used to describe the electron–ion interaction [44] and the generalized-gradient approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE) [45] was employed. The single-electron wave functions were expanded using plane waves up to an energy cutoff of 500 eV. The Methfessel-Paxton method [46] was used for the Fermi surface smearing with a 6 × 6 × 6 Monkhorst-Pack grid [47] for 2 × 2 × 2 atomic supercells of both stoichiometric and off-stoichiometric κ-carbides. The energies converged to a precision of ≤ 1 meV/atom. Structural relaxations were performed until the forces on each atom were below 0.01 eV/Å. Cell shape and atomic positions were fully relaxed in all calculations, unless specified otherwise. The 2 × 2 × 2 supercell of stoichiometric $(Fe,Mn)_3AlC$ κ-carbide is composed of 8 unit cells in $L'1_2$ structure with 5 sites/unit cell and occupied by 40 atoms ($(Fe_{16}Mn_8)Al_8C_8$). Here, Fe/Mn are situated at face-centered sites of each unit cell, Al at corner sites