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Chemical composition and stress dependence of the elastic properties of κ-$(Fe,Mn)_3AlC$ thin films

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ABSTRACT

Although the formation of nanosized κ-precipitates in austenitic Fe-Mn-Al-C matrices cause coherency strains and affect both strength and ductility, the composition and stress dependence of the elastic properties has not been studied systematically for $(Fe,Mn)_3AlC$ ($Pm\bar{3}m$). An elastic modulus decrease of 49 and 64 GPa upon C- and Al-vacancy formation, respectively, was predicted and experimentally verified and is caused by concomitant weakening in average bond energy. The predicted increase of up to 33 GPa in elastic modulus due to the presence of 2 GPa compressive stress was corroborated experimentally and can be understood by pressure induced bond strengthening.

Austenitic Fe-Mn-Al-C steels with nanosized κ-carbide precipitates exhibit an outstanding combination of high specific strength and ductility [1–6]. The κ-precipitates play an important role in the strain hardening mechanism of these steels and are suggested to act as hydrogen traps [3,7–11]. The perovskite-type κ-carbides (space group $Pm\bar{3}m$) exist continuously from pure Fe to pure Mn based compounds and the chemical composition has been reported to deviate from stoichiometry [12–16]. Consistent with the published literature we refer to these non-stoichiometric carbides as κ-$(Fe,Mn)_3AlC$. Atom probe tomography studies combined with density functional theory calculations provide insights into the off-stoichiometry and defect configuration of the κ-precipitate with regard to the minimization of the lattice misfit between the austenitic matrix and the finely dispersed κ-$(Fe,Mn)_3AlC$ [15,16]. Minimization of the coherency strain at the interface is obtained by a lattice constant adaption of both κ-$(Fe,Mn)_3AlC$ and matrix [15], which is consistent with the observed coherent interfaces. The κ-precipitate possesses the larger lattice parameter and thus a compressive stress state. The κ-$(Fe,Mn)_3AlC$ phase was examined theoretically by *ab initio* or Calphad approaches [17–23]. Systematic experimental investigations of phase pure κ-$(Fe,Mn)_3AlC$-type are restricted to Fe_3AlC [13,24,25] or Mn_3AlC [14,26,27] based systems or cover the FeMn based κ-carbide but lack in elastic property characterization [12,24,28,29]. Hence, the correlation between chemical composition, structure, coherency induced stress, and elastic properties of the κ-$(Fe,Mn)_3AlC$ phase has not been systematically investigated so far.

In this letter, we describe the influence of chemical composition and stress evaluation on the elastic properties of the phase pure κ-$(Fe,Mn)_3AlC$ by *ab initio* calculations and experiments. Combinatorial Fe-Mn-Al-C thin films with continuous Al-C gradients and Fe/Mn ratios close to 1 and 3.5 were synthesized to explore the composition-structure-elastic properties relationship of κ-$(Fe,Mn)_3AlC$. As Fe/Mn ratios in austenitic alloys give rise to less pronounced modulations of elastic properties [30,31], Al-C gradients in the vicinity of a stoichiometric κ-$(Fe,Mn)_3AlC$ precipitate are probed in this work, previously unexplored for these systems. The experimental findings are consistent with *ab initio* predictions considering the influence of chemical composition, defect configuration, and stress evaluation on elastic properties of phase pure κ-carbide. The combination of *ab initio* calculations with the highly efficient combinatorial thin film composition-spread method is a powerful tool to rationalize composition-structure-property relationships [32].

The combinatorial Fe-Mn-Al-C thin films were deposited in a laboratory-scale sputtering system by direct current magnetron sputtering. The base pressure was below 3.2×10^{-5} Pa and the Ar deposition pressure was 0.6 Pa. An Al target (purity 99.9995%, power density 1.1 W/cm^2) and a C target (graphite, purity 99.999%, power density 9.9 W/cm^2) with an inclination angle of 45° with respect to the substrate normal were used in order to achieve the desired Al-C gradient in the thin films. Either a $Fe_{0.5}Mn_{0.5}$ target (purity 99.95%, power density 2.3 W/cm^2) or a $Fe_{0.75}Mn_{0.25}$ target (purity 99.95%, power density 2.4 W/cm^2) was facing the substrate to adjust the overall Fe and Mn content in the thin films. Polished single-crystalline MgO (001) substrates in a target-to-substrate distance of 10 cm were heated to 600 °C during deposition.

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The chemical composition of the thin films was determined by energy dispersive X-ray analysis (EDX) in an EDAX Genesis 2000 system. For quantification, standards measured by time-of-flight elastic recoil detection analysis (TOF-ERDA) were used. 36 MeV $^{127}I^{8+}$ primary ions were employed in a TOF-ERDA setup at the tandem accelerator at Uppsala University, Sweden. The recoil detection angle in these experiments was 45°. X-ray diffraction (XRD) was used to study the structure using a Bruker AXS D8 Discover XRD equipped with a General Area Detector Diffraction System (GADDS) for high-throughput measurements. The diffractometer was operated at a current of 30 mA and a voltage of 40 kV with Co Kα radiation at a fixed incident angle of 17° for the 2 θ-scans and varying χ and ϕ angles for texture analysis. The primary beam was collimated with a 0.5 mm pinhole. X-ray stress analysis (XSA) was done according to the theory developed by Genzel [33] for the 001-textured thin films or by $\sin^2\psi$ measurements for the non-textured thin films. The fitting was done according to our previous work [34] and the elastic compliance, Poisson's ratio, and elastic (Young's) moduli were taken from (experimentally verified) *ab initio* calculations in this work. Nanoindentation was carried out in a Hysitron TriboIndenter and the elastic (Young's) moduli of the thin films were determined by the method of Oliver and Pharr [35]. A Berkovich diamond tip was used with a maximum indentation depth of 10% of the film thickness (1.5 μm) and the tip area function was obtained on fused silica. The data for a minimum of 18 indents for each composition were averaged and the elastic modulus values were calculated from the reduced elastic modulus with the Poisson's ratio derived by *ab initio* calculations.

Elastic properties of κ-$(Fe,Mn)_3AlC$ were obtained using density functional theory [36] within the framework of Vienna *ab initio* simulation package (VASP) and projector augmented wave potentials [37–39]. The parametrization of these augmented wave potentials was carried out within the generalized-gradient approximation, as implemented by Perdew, Burke, and Ernzerhof [40]. The total energy in this work was treated within the Blöchl approach [41] and the integration in the Brillouin zone was carried out on 6x6x6 *k*-point Monkhorst-Pack mesh [42]. The stoichiometric configuration $(Fe,Mn)_3AlC$ was described with a supercell containing 40 atoms. Fe-Mn sublattice was randomized using special quasirandom structures (SQS) [43]. Locally self-consistent Green's function (LSGF) software [44,45] was employed for the SQS implementation in this study. Warren-Cowley short-range order parameter [46] within seven coordination shells was applied to account for randomness and served as input for the VASP code. Three different defect configurations (standard supercell size employed in literature [15]) were considered: (i) an Al vacancy concentration of 12.5%, (ii) a C vacancy concentration of 12.5%, and (iii) an antisite defect concentration of 12.5% Fe on the Al sublattice (Fe_{Al}). All κ configurations were spin polarized, exhibiting a ferromagnetic ordering. Full structural optimization was carried out for each configuration with the convergence criterion for the total energy of 0.01 meV and a 500 eV cut-off was used. Bulk moduli for all configurations were obtained from the Birch-Murnagham equation of state [47] and all elastic constants were calculated by structural distortions and fitting the energy-distortion data with second-order polynomial functions [48]. Elastic moduli and Poisson's ratios were obtained from the elastic constants (C_{11}, C_{12}, C_{44}) within the Hill approximation [49]. To determine the elastic (Young's) modulus as a function of temperature and stress state, the Debye-Grüneisen model [50] was used. By fitting the total energy – volume data to the Birch-Murnagham equation of state [47], equilibrium volume and bulk modulus were obtained. From this, the elastic modulus was estimated using the calculated Poisson ratio at 0 K. These total energy – volume data were then fitted to the Birch-Murnagham equation of state [47] at each temperature as well as a volume offset to account for a different stress state. The details on the Debye temperature estimation [51] and the Debye-Grüneisen model [50,52] can be found elsewhere. Data used to directly compare theoretical and experimental elasticity in this work were obtained at 300 K. Electronic structure analysis was carried out using LOBSTER [53,54] (in the framework of crystal orbital Hamilton populations [55]). Integrated crystal orbital Hamilton populations were employed to estimate the bond energy per spin channel.

Combinatorial Fe-Mn-Al-C thin films with two different Fe/Mn ratios of about 1 and 3.5 and continuous Al-C gradients were synthesized and evaluated by EDX/TOF-ERDA and XRD to explore the influence of chemical composition on the phase formation and structure evolution. Fig. 1 shows the ternary phase diagram (a) as well as XRD patterns of four selected chemical compositions (b). Phase pure κ with equal Fe and Mn contents of about 30–32 at.-% (Fe/Mn ≈ 1) exists for Al contents between 14 and 20 at.-% and C contents between 25 and 16 at.-%, accounting for Al/C ratios between 0.55 and 1.24. For the Fe-rich deposition (Fe/Mn ≈ 3.5), phase pure κ is present for Al contents between 13 and

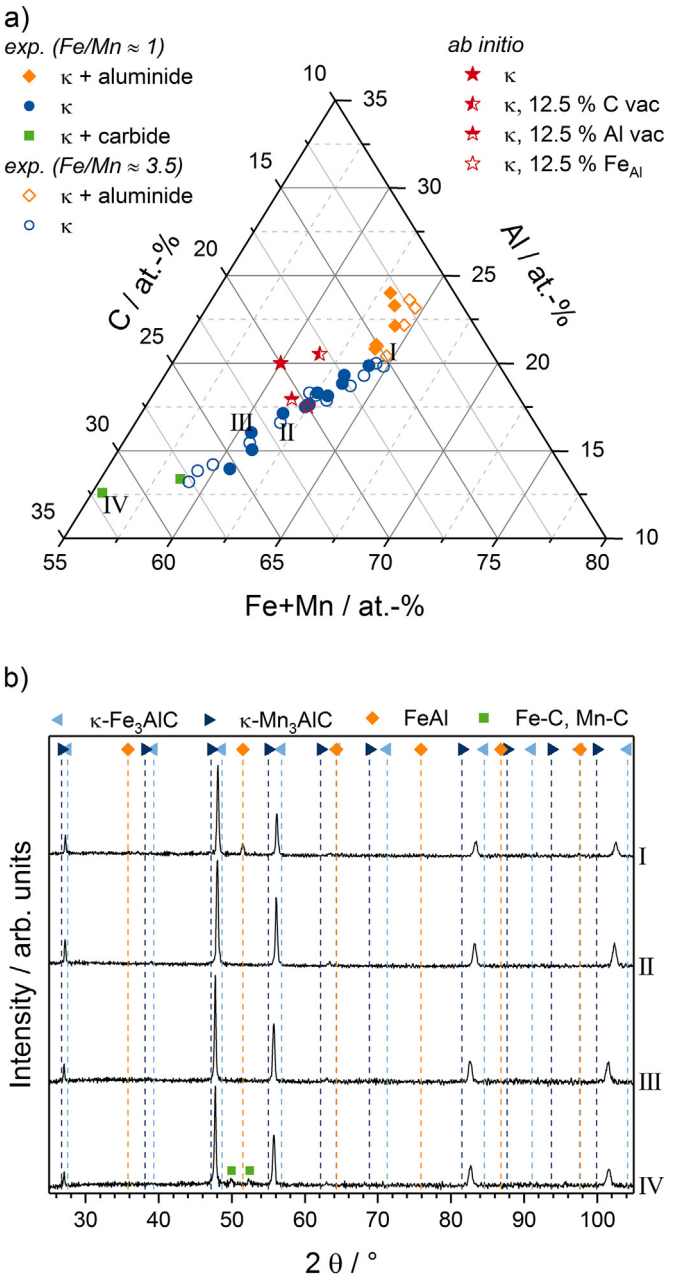

Fig. 1. a) Ternary phase diagram obtained experimentally by thin film combinatorics. For comparison, stars indicate the compositions of the calculated κ-$(Fe,Mn)_3AlC$ structures. b) XRD patterns of four selected chemical compositions indicated by I-IV in the phase diagram; 2 θ values for κ-Fe_3AlC (a = 3.76 Å [20]), κ-Mn_3AlC (a = 3.88 Å [14]), and FeAl (a = 2.91 Å [56]) are included for peak assignment.