On the direct nucleation and growth of ferrite and cementite without austenite

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The direct nucleation and growth of ferrite and cementite has been investigated in an Fe–C metallic glass using X-ray diffraction, transmission electron microscopy and atom probe tomography. The nucleation and growth proceeds via primary crystallization of ferrite, without the formation of austenite. There is no carbon gradient at ferrite/amorphous interfaces, indicating that the transformation rate is controlled by the low mobility of these interfaces compared to the mobility of C atoms. A thermodynamic description is proposed to explain the delayed nucleation of cementite.
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Optimization of the microstructures of steels, and hence of their properties, often depends strongly on the control of phase transformations during thermomechanical processing [1]. The decomposition of austenite is of particular interest as it is the parent phase for most of the microstructures of importance, e.g. martensite, bainite or pearlite. When the transformation rate is relatively low, the austenite (face-centered cubic) transforms at low temperature into ferrite (body-centered cubic, bcc) and cementite (orthorhombic) [2]. This transformation proceeds via discontinuous precipitation where austenite grain boundaries act as nucleation sites, both for pro-eutectoid ferrite or pro-eutectoid cementite, and also for pearlite when these two phases grow simultaneously [3,4]. Thus, these resulting microstructures are strongly controlled by the mechanisms of nucleation. In addition, it is relatively well established that the rate-controlling mechanism is determined by the carbon diffusion in austenite or along boundaries [3,4]. Then, an interesting question is how ferrite and cementite would nucleate and grow in the absence of prior defects in austenite (namely grain boundaries), or from a parent phase other than austenite. Experimental investigations have shown that it is impossible to directly nucleate these phases from the melt. Indeed, a very fast cooling rate leads to the nucleation of the metastable ε phase [5,6] or to the formation of a metallic glass [5–8]. The crystallization of such a metallic glass upon annealing strongly depends on the carbon content. If the carbon content is below 20 at.%, then it proceeds at low temperature via primary crystallization in two steps. First, ferrite nucleates, followed by the formation of carbides [7,8], as in the ternary Fe–C–B system [5]. If the carbon concentration exceeds 25 at.%, then the amorphous phase transforms completely into carbides [9], as in Mn–C and Cr–C systems [10]. In the case of primary crystallization, the kinetics of nucleation and growth into the amorphous structure is often controlled by the partitioning of elements [11,12]. This involves atomic diffusion in the amorphous matrix and eventually the formation of concentration gradients at crystal/amorphous interfaces during the primary crystallization process [13]. Thus, the transformation rate could be influenced by large differences in the diffusivity of interstitial species (e.g. carbon in iron) in an amorphous and crystalline phase [14]. The aim of this work was first to understand how ferrite and cementite nucleate from a parent phase other than austenite, namely a metallic glass. Second, by investigating concentration gradients through the amorphous/crystalline interfaces we studied the influence of carbon diffusion in the possible cooperative growth of these two phases.

To achieve these goals, Fe–C amorphous films ~500 nm thick were obtained by reactive magnetron sputtering using CH_4 as reactive gas and a Fe target (purity 99.5%) (see details in Ref. [15]). Films containing about 15 at.% C were

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deposited on Si substrates for X-ray diffraction (XRD) analysis, on standard Al foil for transmission electron microscopy (TEM) characterization (the substrate was dissolved in NaOH solution) and finally on interstitial-free (IF) steel to investigate the influence of a pre-existing interface (amorphous/ferrite) on the nucleation and growth mechanisms. Films were annealed under vacuum (10^{-6} mbar) up to 500 °C. Crystalline phases were identified by XRD using a Rigaku diffractometer (Cu-target X-ray source and scintillation detector). Cross-section TEM foils were prepared using a focused ion beam (FIB; NVISION-40 Zeiss). Samples were observed in a JEOL ARM200F microscope operated at 200 kV. Energy-filtered (EF) TEM images were recorded using a Gatan Imaging Filter (GIF Quantum). In situ annealing experiments were carried out to follow growth kinetics using a Gatan Tantalum heating holder in an aberration-corrected Titan environmental transmission electron microscope operated at 300 kV. Composition gradients across crystalline/amorphous interfaces were measured by atom probe tomography (APT). Samples were prepared using FIB and then analyzed in an energy-compensated atom probe (EcoTAP CAMECA) using electric pulses (repetition rate 30 kHz and 20% pulse fraction) at 80 K. Carbon quantification was done following the procedure proposed by Sha et al. [16].

Both XRD measurements (Fig. 1b) and selected-area electron diffraction (SAED) performed in the transmission electron microscope (not shown here) confirmed that the as-prepared material was fully amorphous. APT analyses were carried out to check both the composition of the metallic glass (Table 1) and the distribution of carbon atoms within the structure. As shown on the 3-D reconstruction (Fig. 1a), no significant composition variations were observed and the computed frequency distribution of carbon atoms corresponded relatively well to a random distribution. During isothermal annealing for 1 h at low temperature (250 °C) the ferrite phase nucleated first (Fig. 1b), indicating a primary crystallization process consistent with data reported on the crystallization of similar metallic glasses prepared by splat cooling [7,8]. At higher temperatures (300 °C and above), peaks corresponding to both ferrite and cementite are detected. In situ TEM also confirmed that the ferrite nucleates before cementite (see Fig. 1c), which is qualitatively very consistent with the XRD data shown in Figure 1b. At completion of the transformation the material exhibits a nanoscaled structure (Fig. 2a). Equiaxed and slightly faceted ferrite grains that have nucleated by primary crystallization are homogeneously distributed and exhibit an average diameter of 50–100 nm. They are embedded in much larger grains (200–400 nm) identified as cementite (Fe_3C). EFTEM data showing the carbon distribution (Fig. 2c) clearly indicates, as expected, a strong partitioning of carbon between the two phases. In the carbides, the large density of stacking faults, clearly visible on the TEM bright-field image (Fig. 2a), gives rise to characteristic streaks on the diffraction pattern (Fig. 2b). Such faulted carbides have been previously reported in high-carbon crystallized Fe–C metallic glasses (e.g. [10]) as well as in tempered martensite [17]. It was concluded that this transformation occurred without
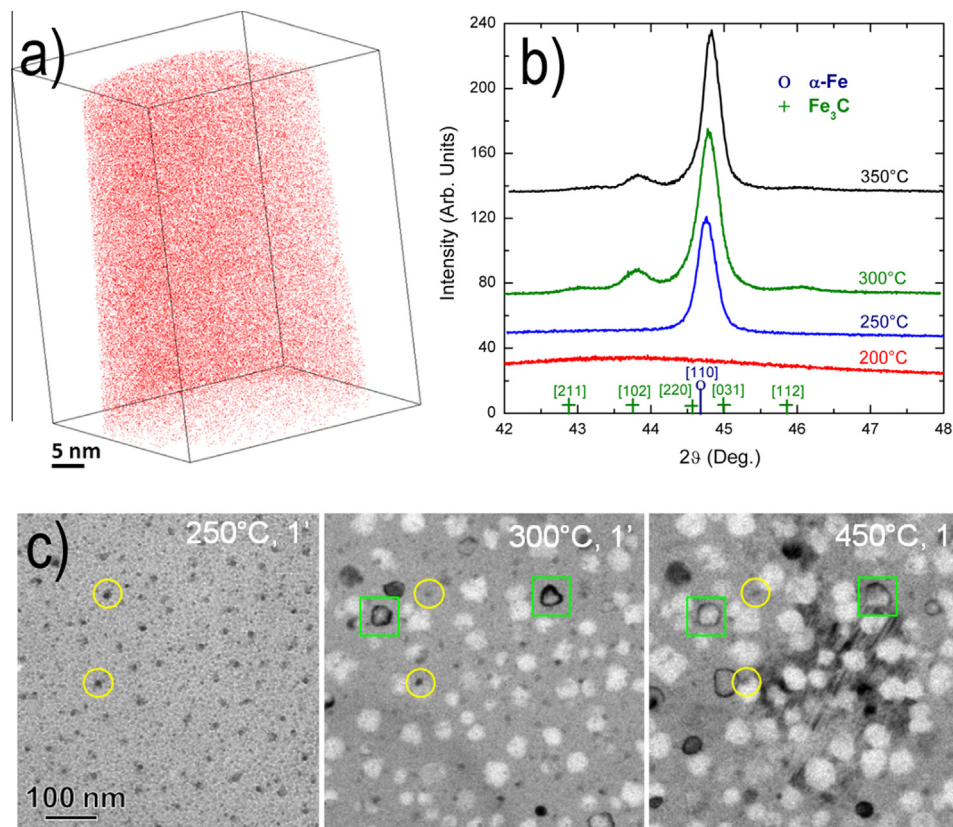

Fig. 1. (a) 3-D reconstruction of a volume analyzed in the as-prepared Fe–C film showing the distribution of C atoms; (b) XRD spectra recorded after isothermal annealing (3600 s) at various temperatures; (c) in situ TEM bright-field images taken after holding for 3600 s at 250, 350 and 450 °C, showing the successive crystallization of ferrite and cementite (circles and squares are used as a guide to follow the growth).