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Mechanisms of subgrain coarsening and its effect on the mechanical properties of carbon-supersaturated nanocrystalline hypereutectoid steel

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Abstract—Carbon-supersaturated nanocrystalline hypereutectoid steels with a tensile strength of 6.35 GPa were produced from severely cold-drawn pearlite. The nanocrystalline material undergoes softening upon annealing at temperatures between 200 and 450 °C. The ductility in terms of elongation to failure exhibits a non-monotonic dependence on temperature. Here, the microstructural mechanisms responsible for changes in the mechanical properties were studied using transmission electron microscopy (TEM), TEM-based automated scanning nanobeam diffraction and atom probe tomography (APT). TEM and APT investigations of the nanocrystalline hypereutectoid steel show subgrain coarsening upon annealing, which leads to strength reduction following a Hall–Petch law. APT analyzes of the Mn distribution near subgrain boundaries and in the cementite give strong evidence of capillary-driven subgrain coarsening occurring through subgrain boundary migration. The pronounced deterioration of ductility after annealing at temperatures above 350 °C is attributed to the formation of cementite at subgrain boundaries. The overall segregation of carbon atoms at ferrite subgrain boundaries gives the nanocrystalline material excellent thermal stability upon annealing.

Keywords: Cold-drawn pearlitic steel; Nanocrystalline steels; Strength softening; Annealing; Subgrain coarsening

1. Introduction

Cold-drawn pearlitic steel wires are important engineering materials for a variety of applications such as automobile tire cords, suspension bridge and power cables, piano strings, and springs due to their ultrahigh strength. In 1995 it was reported that severe cold-drawing of pearlite yields a tensile strength of 5 GPa [1]. In the following years the tensile strength of cold-drawn pearlitic steel wires has been increased to 6.35 GPa [2] and very recently even up to 7 GPa [3]. The extraordinary strength has made the materials attractive not only for engineering applications but also for studying basic relationships between structure and mechanical properties of nanoscaled alloys. During the past 50 years great efforts have been made to understand the microstructural evolution and its effect on strength upon cold drawing [3–9]. The most frequently reported finding is deformation-induced cementite decomposition [10–19] and its "unexpected" consequence on strain hardening, i.e. the decomposition of the hard phase—cementite—surprisingly does not adversely affect the material's strength. On the contrary, the tensile strength continuously increases upon cold drawing [3,4,20], even when the cementite has been significantly dissolved [3,18,19]. It is worth noting that the mechanism of deformation-induced cementite decomposition is still under dispute. Different from the assumption that the decomposition takes place upon cold drawing, due to the interaction between dislocations and carbon [3,18,19], Takahashi et al. [21] suggested that it mainly occurs upon low-temperature aging after cold drawing. With the development of characterization techniques such as Mössbauer spectroscopy [10], field ion microscopy (FIM) [11,15,22–25] and atom probe tomography (APT) [12–16,18,19] a deeper understanding of the mechanisms of cementite decomposition and their effects on microstructure and strength has been achieved. Among these characterization techniques APT is able to provide nano- and atomic-scale information on the carbon distribution in both cementite and ferrite with high compositional accuracy and statistical significance [2,19]. Recently, Li et al. [3] observed that above a true drawing strain of 4.19 the original lamellar ferrite/cementite structure in a hypereutectoid steel wire is gradually replaced by a 2-D nanoscaled ferrite subgrain structure upon further drawing. The dissolved carbon atoms were found to be

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segregated at ferrite subgrain boundaries (SGBs), suppressing dynamic recovery and thus stabilizing the dislocation structure. Hence, the heavily deformed wires are no longer hypereutectoid pearlitic steels but carbon-supersaturated nanocrystalline hypereutectoid steels. At a true drawing strain of 6.52 the subgrain size has been reduced to below 10 nm, which provides a tensile strength of up to 7 GPa [3].

In many engineering applications such as suspension bridges and power cables cold-drawn hypereutectoid steel wires are subjected to hot-dip galvanization or blueing (a heat treatment to simulate the hot-dip galvanized process, up to 550 °C for 15 min after cold drawing) to improve their anti-corrosion property [26,27]. Such processes may reduce the tensile strength because the temperature during galvanizing can approach 500 °C [26,27]. Thus, it is essential to study the thermal stability of heavily cold-drawn pearlite as well as the microstructural mechanisms associated with strength reduction during annealing. The strength reduction of cold-drawn pearlite during annealing has been reported in Refs. [21,26–28,30]. Some results obtained by microstructural investigations using TEM and APT can be found in Refs. [13,26,28–30]. It is known that for the same heat-treatment condition the annealed microstructure of a material strongly depends on its microstructure prior to annealing. For cold-drawn pearlitic steels this prior microstructure, depending on the drawing strain ϵ_d, can be either a heterophase-dominated lamellar structure at low strains or a nanosized carbon-supersaturated ferrite subgrain-dominated dislocation structure at extremely high strains [3]. The materials investigated in the abovementioned studies were mainly subjected to relatively low drawing strain, where the lamellar structure still prevails. The observations were often performed under relatively short and not sufficiently systematic annealing conditions. In this sense, the strength–microstructure relationships during annealing of cold-drawn pearlite have not yet been systematically studied, especially for wires with extremely high drawing strains.

Here we study the microstructure–property relationships of annealed carbon-supersaturated nanocrystalline hypereutectoid (0.98 wt.% C) steels produced from severely cold-drawn pearlite by a true strain ϵ_d of 6.0. This initial microstructure prior to annealing is significantly different from the materials studied in previous papers in which heterophase boundaries are still dominant [13,21,26–30]. The present work focuses mainly on the evolution of the nanoscaled subgrain structure in ferrite during annealing. More specifically, first, systematic investigations have been performed on the evolution of the nanosized ferrite subgrain structure during annealing. Second, quantitative analyzes of the subgrain structures in terms of area fractions of low-angle and high-angle grain boundaries have been performed as a function of the annealing temperature T_a using scanning nanobeam diffraction and the software ASTAR [31]. Third, subgrain coarsening is for the first time experimentally studied at the atomic scale and understood through triple-junction-controlled migration of subgrain boundaries. Finally, the effect of T_a on the ductility of annealed wires is also studied. The relationship between tensile strength and ferrite subgrain size can be described by a Hall–Petch law. On the basis of these investigations the effects of microstructural evolution on the mechanical properties of the carbon-supersaturated nanocrystalline steel upon annealing are discussed.

2. Experimental

2.1. Material and processing

The original pearlitic steel wires subjected to heavy cold drawing were of hypereutectoid composition (Fe–0.98C–0.31Mn–0.20Si–0.20Cr–0.01Cu–0.006P–0.007S in wt.% or Fe–4.40C–0.30Mn–0.39Si–0.21Cr–0.003Cu–0.01P–0.01S in at.%), and were provided by Suzuki Metal Industry Co. Ltd. Before cold drawing the wires were austenitized at 950 °C for 80 s followed by pearlitic transformation in a lead bath at 580 °C for 20 s and subsequent quenching in water. After this treatment specimens were subjected to cold drawing up to a true drawing strain of $\epsilon_d = 6.0$. The cold-drawn wire is characterized by a nanoscale ferrite subgrain structure associated with strong yet incomplete chemical decomposition of the cementite. The nanosized subgrains exhibit a two-dimensional columnar morphology which is elongated along the drawing direction. The subgrain size in the transverse cross-section (perpendicular to the wire axis) of the wire is 10 nm [3]. The carbon-supersaturated nanocrystalline steel samples were annealed for 30 min between 150 and 450 °C in 50 °C intervals. Short time annealing for 2 min was also performed at several selected temperatures.

2.2. Mechanical testing

The tensile strength of the annealed samples was measured at room temperature with a Dia Stron LEX 810 device at an initial strain rate of $\dot{\epsilon}_0 = 1.16 \times 10^{-3}\ \mathrm{s}^{-1}$. The true tensile strain is determined by $\epsilon = \ln\frac{l_0+\Delta l}{l_0}$, where l_0 and Δl are the initial gauge length and the length change of the wires, respectively. The wire tensile elongation was measured by subtracting the machine elongation from the total length change. The true tensile stress is determined by $\sigma = \frac{F}{S_0} \cdot \exp(\epsilon)$, where F is the force and S_0 the initial cross-section of the wires.

2.3. Characterization techniques

A JEOL JEM-2200FS operated at 200 kV was applied to investigate the as-annealed samples in both TEM and scanning TEM (STEM) modes. Crystallographic orientation and phase mapping were performed by nanobeam diffraction in scanning mode using a transmission electron microscope equipped with a NanoMEGAS ASTAR system [31]. The scanning was conducted at 0.5 nm spot and 1.25 nm step size.

APT investigations were performed using a local electrode atom probe (LEAP 3000X HR™, Cameca Instruments) in voltage mode at 70 K, a pulse fraction of 15%, a pulse repetition rate of 200 kHz, and a detection rate of 0.005 atoms per pulse. Readers are referred to our previous works [2,19] regarding the detailed analyzes of APT data including chemical identification and 3-D reconstruction.

Samples for both TEM and APT were prepared using a dual-beam focused-ion-beam (FIB) (FEI Helios NanoLab 600TM). TEM investigations were performed on the cross-sections of wires. APT samples were prepared with their tips perpendicular to the wire axis according to the procedure described in Ref. [32] in order to reduce the local magnification effect [17,33] and to probe as many ferrite subgrains as possible.