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Three-dimensional atom probe microscopy study of interphase precipitation and nanoclusters in thermomechanically treated titanium–molybdenum steels

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Abstract

Atom probe microscopy was used to generate tomographic analyses of solute clustering and precipitation reactions in a Ti–Mo added microalloyed steel under simulated strip-rolling conditions. It was observed that the interphase row spacing of precipitates was reduced with the application of a pre-strain. The atom probe data also revealed the coexistence of nanoclusters and precipitate particles, even after isothermal holding for 3600 s. These microstructural features occurred both within 3-D interphase precipitate sheets, and in randomly selected fields of view. A bimodal distribution of larger (∼8–10 nm) precipitates coexisted with smaller nanoclusters (∼3 nm) within the interphase sheets/rows. Both the nanoclusters and the precipitates possessed a disc morphology, although nanoclusters with less than ∼30 atoms were more irregular in shape. The size of the nanoclusters and the precipitates was expressed as a Guinier radius, and this varied between 0.5 and 8 nm for both strain conditions, with the average size ∼1.8 nm. The composition of the nanoclusters varied over a wide range, yet was mostly rich in C. All of the nanoclusters and precipitates consisted of a mixture of Ti, Mo and C and the average precipitate composition was close to that of MC carbide stoichiometry, where M represents a mixture of Ti and Mo. In the majority of cases, the Ti/Mo ratio in the MC carbides was > 1. As the Guinier radius increased above 2.5 nm, the composition range became narrower, towards the MC carbide stoichiometry, with a small amount of Fe (∼3–12 at.%).

Keywords: Atom probe microscopy (APM); Low-alloy steel; Carbides; TEM; Nanoclusters

1. Introduction

Stringent environmental and safety requirements for the automotive industry across the globe have led to a major increase in research to develop advanced high-strength steels (AHSSs). This has led to the successful evolution of several AHSSs (dual phase, transformation-induced plasticity, twinning-induced plasticity steels, etc.) in recent years [1,2]. The development of AHSSs mostly involves the introduction of new strengthening mechanisms but, unfortunately, many of these alloys are fully or partially restricted to the laboratory due to the complex, and thus expensive, processing involved.

Recently, Funakawa et al. [3] reported the potential to improve strength through nanoscale precipitates distributed in a ferritic matrix, and processed by a conventional rolling set-up. They proposed a strength improvement of 300–350 MPa, which is 2–3 times higher than that expected from conventional precipitation hardening (90–150 MPa) in microalloyed steels [4]. It was suggested that this high strength was achieved via the formation of fine interphase precipitation in conventionally hot-rolled Ti–Mo added high-strength low-alloy steel. However, a detailed study of the precipitation reactions in this alloy system was not provided. Subsequently, we undertook an atom probe

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study of a similar steel, and reported that the precipitates were extremely fine and either aligned in interphase rows, or had nucleated upon dislocations [5]. Our observations were somewhat restricted as the precise processing conditions were not exactly known due to the industrial nature of the trials, and so it was not possible to correlate the applied processing with the observed microstructures.

The presence of interphase precipitates was first reported by Morrison in a Nb-microalloyed steel [6]. This was followed by several other studies, mainly on highly alloyed steels, and resulted in the proposition that the formation of interphase precipitation [7–9] occurs along the austenite–ferrite (γ/α) interface during ferrite growth, by the ledge mechanism [7]. As a result, when observed under transmission electron microscopy (TEM), these precipitates occur as regularly spaced rows of carbides, reflecting the fact that they occur as sheets in the plane of the migrating γ/α interface. However, TEM experiments also indicate that these characteristic rows of precipitates are detected only when foils are tilted to a certain angle, i.e. when the precipitate sheets are nearly parallel to the electron beam [7,10]. Moreover, there have been no reports of precipitate formation on the face of moving γ/α boundaries; this conclusion follows from the observation that there is no precipitate formation between the rows.

Earlier work by Davenport and Honeycombe [7] revealed that interphase precipitates form on the lowest-energy planar dislocation boundary during the growth of the ferrite through the ledge mechanism, i.e. $\{110\}_\alpha // \{111\}_\gamma$ [11,12]. Later Ricks and Howell [13] showed that interphase precipitates can also be regularly arranged at a non-planar high-energy interface. They proposed a "quasi-ledge" mechanism to explain the occurrence of precipitation in these non-planar curved sheets. Here, a bowing mechanism operates, via the pinning of the migrating γ/α transformation interface by the freshly nucleated precipitates, activating a sidewise ledge-growth mechanism. Recently, Okamoto et al. [10] proposed that the selection of the precipitation plane depends on the orientation relationship between the austenite and ferrite phases, and therefore there exist several crystallographic planes, other than the $\{110\}_\alpha$ planes suggested earlier, on which interphase precipitation might form.

It is important to note that, to date, conventional TEM is the only analytical instrument to have been used extensively for these precipitation studies. However, conventional TEM has certain limitations as to the quantitative analysis of the shape, size, distribution and chemical composition of nanoclusters and the fine-scale precipitate particles that form during different thermomechanical treatments of steels such as those described here. These limitations arise because: (i) there is a high dislocation density formed during the thermomechanical processes, which makes it extremely difficult to achieve clear contrast from very fine precipitates; (ii) whilst carbon extraction replica techniques can partially mitigate this issue, it is very difficult to extract and examine precipitates smaller than ~2–5 nm size; (iii) the ferromagnetic nature of the steel sample makes high-resolution TEM analysis particularly difficult; and (iv) as with other scattering-based techniques, TEM is not effective at the analysis of non-periodic structures such as solute clusters.

On the other hand, atom probe microscopy (APM) provides great opportunities to overcome the above shortcomings [14]. Nevertheless, the majority of the precipitation studies using APM have been on non-ferrous alloys and highly alloyed steels [15–18]. There is a relative paucity of APM studies of low-carbon AHSSs, which are commercially very significant. Some APM studies have been conducted on quenched and aged low-carbon steels [19]. However, industrial processes will necessarily involve controlled rolling, accelerated cooling and coiling. Thus, the microstructural development and precipitation formation in hot-rolling conditions are completely different from those in the quenched and aged condition. In particular, the interphase precipitation reaction is coupled with the process of austenite decomposition, and hence it is not possible to simulate this in quenched and aged samples. Moreover, the formation of polygonal ferrite is one of the most important aspects for commercial steels to achieve isotropic properties and it is notoriously difficult to form polygonal ferrite via quenching/ageing treatments [20]. Another aspect that is deserving of study is the increasing recognition that solute atom clustering reactions occurring early in the decomposition process can influence the evolution of microstructure and properties.

In this work, a Ti–Mo modified microalloyed steel has undergone a thermomechanical simulation relevant to industrial hot-rolling conditions in order to simulate interphase precipitation processes. The role of thermomechanical processing (TMCP) parameters on the evolution of microstructure, and particularly on solute nanoclusters and precipitation reactions, has been examined as a function of the retained strain in the austenite prior to transformation. Therefore, what follows is an in-depth APM and TEM study aimed at a quantitative understanding of the shape, size, distribution and composition of the nanoclusters and fine-scale precipitates that form in ferrite in this steel.

2. Experimental procedure

In this work, a steel of composition 0.04C–1.52Mn–0.21Si–0.08Ti–0.22Mo (wt.%) (0.2C–1.5Mn–0.4Si–0.09Ti–0.13Mo (at.%)) was used, based on earlier work by the JFE Steel Corporation Group [3]. The thermomechanical simulation of the hot strip-rolling conditions was performed using a Servotest 500 kN machine.

These types of Ti–Mo steels were mainly developed for hot strip mills. For industrial production, after run-out table cooling, the steels are coiled, which essentially leads to the isothermal transformation from austenite to ferrite and/or precipitation. It is very important to form the majority of the precipitates either during ferrite