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Microstructural characterization and thermodynamic analysis of precipitates in ultra-low-carbon bake hardened steel

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ABSTRACT

The effects of niobium (Nb) addition on the morphologies, size distributions, crystallography, and thermodynamics of precipitates in ultra-low-carbon bake hardened steels (ULC-BH) were investigated using energy-dispersive X-ray spectrometry (EDS), electron diffraction and high resolution transmission electron microscopy (TEM). The calculated nucleation rate of NbC precipitates indicate that the observed fine precipitates and saturation of yield strength with Nb 90 ppm steel are closely connected to thermodynamic factors. A TEM analysis was also carried out for other fine precipitates in two nitride modes: hexagonal AlN and fcc TiN. The Cu_2S–MnS complex precipitate was found to manifest a core–shell structure; the core part formed Cu_2S and the shell part formed MnS. MnS and Cu_2S have an orientation relationship between $(001)_{MnS}//(001)_{Cu_2S}$ and $[001]_{MnS}//[001]_{Cu_2S}$.

1. Introduction

Interstitial free (IF) steels can achieve good strength, formability and dent resistance by using the process of bake hardenability. IF steel has thus been widely used in the automobile industry [1–3]. It is well known that the bake hardenability phenomenon improves yield strength of steel sheet after press forming and paint baking due to the Cottrell atmosphere [2]. The primary mechanism of the Cottrell atmosphere that is responsible for additional strengthening is the immobilization of dislocations by the interaction of interstitial C and N, which are spread around dislocations [4].

IF steel sheets are made of Ruhrstahl-Heraues (RH) degassed with Ti or Nb for free interstitial solutes such as C and N in the ferrite matrix. Because there are many interstitial solute atoms, C and N are the major cause of stretcher-strain marks on steel sheets after the press forming process [2,5–7]. Since 1980, the use of partially stabilized IF steels, which were first developed by a batch annealing method with Ti or Nb to precipitate carbide and leave a proper amount of C in the steel, has widely expanded due to the rapid development of steel making technology [2,8].

Nb can improve high temperature strength by solid solution hardening of Nb. Furthermore, solute Nb is readily precipitated as NbC when the steel is used at high temperature of around 900 °C for a long time. Because NbC precipitates are FCC, they may form either within the austenite matrix, at the austenite and ferrite interface during the austenite to ferrite transformation, or in the ferrite matrix during cooling or subsequent aging. Thus, the high temperature strength can be affected by the solute Nb [9]. This is in addition to the formation of NbC precipitates during the hot rolling process; the precipitates refine the recrystallized grains by pinning the grain boundaries, resulting in increased yield strength and tensile strength. NbC precipitates play a major role in controlling the final microstructure and the product properties in ULC-BH steel [9–12]. An appropriate amount of alloy elements such as Ti or Nb is thus important to derive maximum benefit from the microstructure and the mechanical properties [13].

In the present study, the alloying element Nb was added to ULC-BH steel in minimal quantities, and resultant improvements in the steels' mechanical properties were confirmed by a microstructural analysis. The morphologies, size distributions, and crystal structures of the nano-size precipitates were investigated by transmission electron microscopy (TEM). Consequently, we provide the optimum amounts of Nb in steel with the result that draw a conclusion from the microstructure analysis coupled with thermodynamic calculations. It was determined that the microstructure of the precipitates provide a mechanism that under certain processing conditions can significantly improve the mechanical properties of ULC-BH steel.

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2. Experimental procedure

The chemical compositions of the steels used in the present work are listed in Table 1. For furnace homogenization, the specimens were heated to 1200 °C and the slabs were fed into a rolling mill and passed through seven times, producing 3.2 mm-thick hot sheets. The rolling temperature at completion of this step was about 900 °C. The surface temperature of the slabs during the rolling test was measured by pyrometer. After rolling, the hot bands were cooled using a water cooling system. The hot-rolled sheets were then cold-rolled to 0.7 mm thicknesses, after which they were annealed at approximately 800 °C.

The microstructures were studied using optical microscopy (OM) and TEM. In preparation for a conventional OM analysis of the grain size, mechanically polished specimens were etched using a 5% nital solution. TEM samples were made using the standard carbon extraction replica method for a conventional high resolution TEM analysis of the chemical compositions, distributions, and atomic structures of the various precipitates. We carried out the carbon extraction replica method by using mechanical polishing in an aqueous solution containing 0.5 μm diamond colloidal particles; this was then collected on a carbon film using a 3% nital solution chemical attack. The bulk precipitation density calculation was found to include errors because the thickness of the thin foil specimens was not uniform. On the other hand, the precipitation surface density calculation from the carbon extraction replica specimen was error-free, owing to the identical surface conditions of the specimens. The measured surface density and size were the average values derived from 500 randomly selected precipitations of the carbon extraction replica specimens. A JEOL-2100F TEM equipped with an energy-dispersive X-ray spectroscopy (EDS) detector operated at 200 kV was employed in the analysis.

3. Results and discussion

3.1. Mechanical properties

Fig. 1 shows the measured mechanical properties of the steel sheets in different conditions. The yield strengths were calculated to be 221 MPa, 238 MPa, 262 MPa, 269 MPa, and 269 MPa. The BH values were 62 MPa, 35 MPa, 24 MPa, 19 MPa, and 8 MPa in the samples for each condition. Thus, the effect of Nb addition on the yield strength of steel sheets was enhanced but the BH value decreased. Fig. 2 shows the average diameters and surface densities of the precipitates in the steels. The fine precipitates in each steel sheet were less than 20 nm in diameter; the calculated average sizes were 15.8 nm, 11.3 nm, 6.7 nm, 7.7 nm, and 6.8 nm. The surface density of the precipitates was saturated for the Nb 90 ppm steel at $4.7 \times 10^{10}/cm^2$. The increase of the yield strength could thus be attributed to the fine precipitates. Nb 90 ppm and Nb 120 ppm steels had higher levels of surface density and smaller average precipitate size than did the other steels; it is speculated that the precipitates in the steel sheets were distributed more uniformly and densely, and this resulted from the Nb addition.

It is well known that the bake hardening phenomenon occurs when dislocations are pinned by interstitial C and N atoms [2,4,14]. However, Dehghani [15] reported that nano grain size, compared with its coarse grain counterpart, led to an 88–100% increase in bake hardenability. Furthermore, Alihosseini [16] showed that fine grained low carbon steel had an increase in bake hardenability. Fig. 3 shows OM images of the steel sheets in different conditions. The measured grain size were about 24 μm, 20 μm, 18 μm, 18 μm, and 18 μm. This illustrates that the grain size of the steel sheets in this study cannot be attributed to the bake hardenability. As is well known, the BH value of Nb 120 ppm steel was measured more than lower Nb 90 ppm steel, and this result appears to be attributed to the precipitate of Nb 120 ppm steel having higher density than Nb 90 ppm steel. However, Fig. 2 shows that the precipitates saturated with Nb 90 ppm steel. These explain that the major observed precipitate were less than 50 nm in diameter, because the precipitation hardening mechanism depends on the size of the precipitate and the critical radius of the precipitate

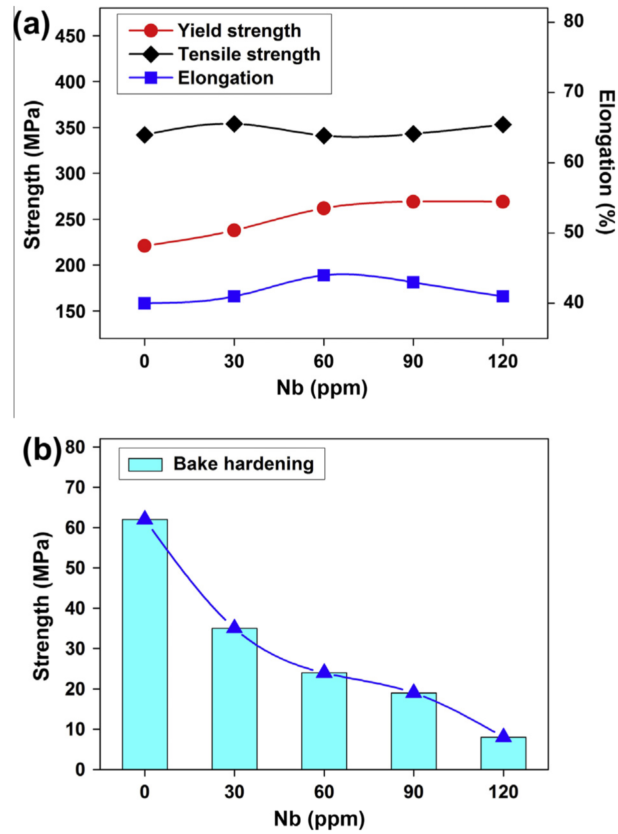

Fig. 1. Measured mechanical properties of steels.

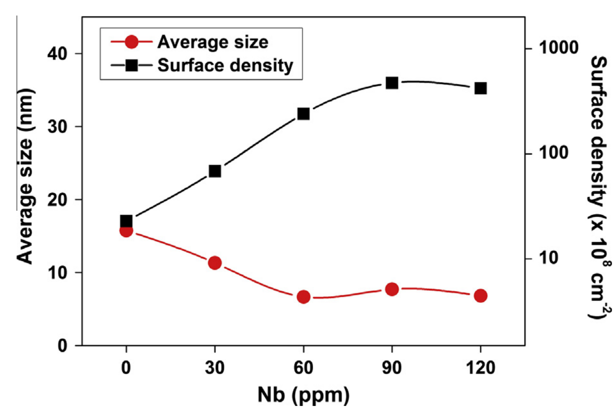

Fig. 2. Average size and surface density of precipitates.

Table 1
Chemical compositions of steels.

Element (wt.%)	C	Mn	Si	P	S	Al	Cu	N	Ti	Nb
Nb 0 ppm	0.0014	0.14	0.06	0.06	0.01	0.027	0.05	0.0015	0.001	0.001
Nb 30 ppm	0.0014	0.14	0.06	0.01	0.05	0.036	0.05	0.0015	0.001	0.003
Nb 60 ppm	0.0018	0.15	0.06	0.06	0.01	0.035	0.06	0.002	0.001	0.006
Nb 90 ppm	0.0018	0.15	0.06	0.06	0.01	0.035	0.06	0.002	0.001	0.009
Nb 120 ppm	0.0018	0.15	0.06	0.06	0.01	0.035	0.06	0.002	0.001	0.012