JOURNAL OF MATERIALS SCIENCE 24 (1989) 105–109

The effect of titanium and nitrogen contents on the austenite grain coarsening temperature

SHYI-CHIN WANG
R & D Department, China Steel Corporation, Kaohsiung, Taiwan

Three series of titanium steels with different nitrogen contents were used to evaluate the effect of titanium and nitrogen contents on the grain coarsening behaviour of austenite during reheating. Quantitative metallography and transmission electron microscopy were employed to measure the austenite grain size and TiN particle size after being reheated and quenched from austenitization temperatures. The results show that for steels with the same nitrogen content the highest grain coarsening temperature occurs around the Ti/N stoichiometric ratio, i.e. 3.42 and an increase in grain coarsening temperatures with increasing nitrogen content also occurs at Ti/N around 3.42. Higher titanium content beyond the stoichiometric ratio decreases the grain coarsening temperature as a result of TiN particle growth.

1. Introduction

It is well known that fine-grained materials have many beneficial effects on mechanical properties such as strength and toughness. The grain coarsening behaviour of steels during reheating for thermal processing is an important factor in achieving fine-grained products. The austenite grain coarsening behaviour during reheating has been studied experimentally and theoretically by many workers [1–8]. From Zener's model, $D = 4r/3f$, it can be seen that a smaller austenite grain diameter D can be obtained by the particle pinning effect with smaller particle size r (radius) and larger particle volume fraction f [1]. Microalloying elements such as niobium, vanadium and titanium have been used extensively to form carbide and nitride in steels to prevent austenite grain growth during reheating by the pinning effect [3–8]. It has been found that titanium is the most effective element in achieving this effect by forming a very stable particle TiN [4, 8], whose solubility is the lowest among the carbides and nitrides of the microalloying elements. However, systematic investigation of the effect of titanium and nitrogen contents on the austenite grain coarsening behaviour has scarcely been reported, especially in steels with Ti/N ratio over the stoichiometric value, i.e. 3.42.

The present aim is to study the effect of titanium and nitrogen contents on the grain coarsening behaviour of austenite during reheating.

2. Experimental procedures

Three series of steels with different nitrogen contents were made for a base composition of 0.11C–0.25Si–1.3Mn. In each series four steels were made with different titanium contents. The chemical compositions of these steels are listed in Table I. All the steels were prepared from 250 kg vacuum melted heats and casted as 160 mm square ingots.

Specimens of 25 × 25 × 30 mm^3 were cut directly from the ingots. They were austenitized by heating in a box furnace to various temperatures ranging from 950 to 1260° C for 1.5 h followed by quenching in iced brine.

For metallographic examination, specimens were mechanically polished and etched in a saturated aqueous picric solution at 70° C to reveal the prior-austenite grain boundaries. Grain sizes were determined by a comparison method with grain size charts. The volume fraction of coarse grains as a function of temperatures was measured by point counting method under a microscope for 20 frames at a magnification of 200 in random.

A carbon extraction replica was prepared from quenched specimens for the measurement of the TiN particle size distribution using a transmission electron

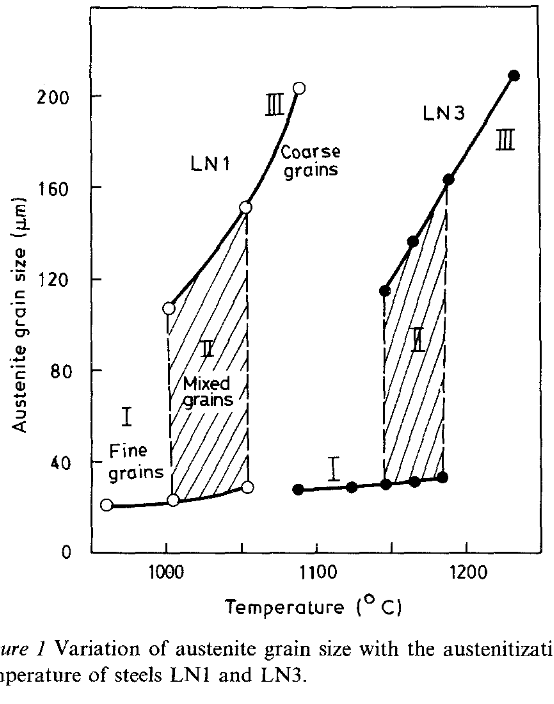

Figure 1 Variation of austenite grain size with the austenitization temperature of steels LN1 and LN3.

0022–2461/89 $03.00 + .12 © *1989 Chapman and Hall Ltd.*

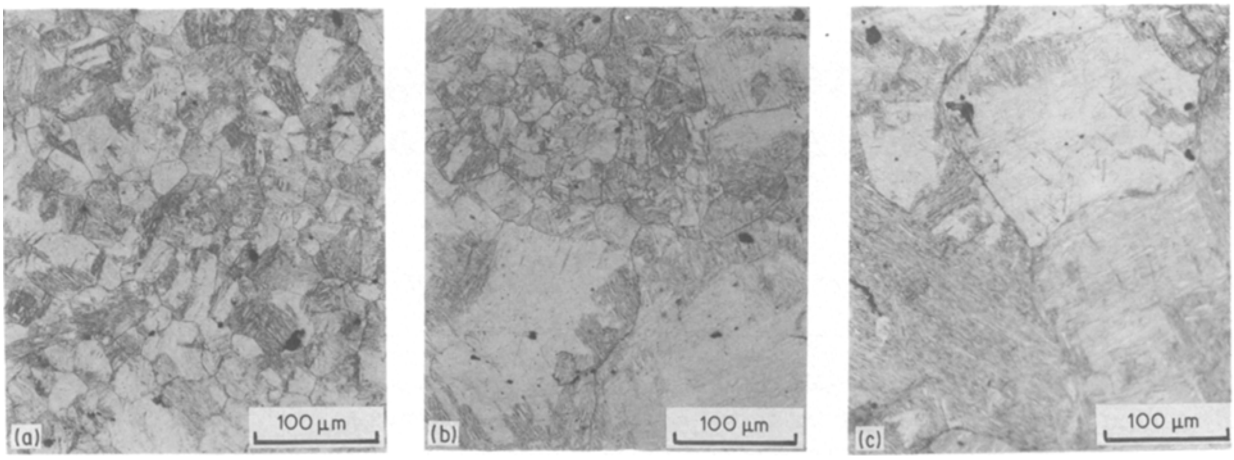

Figure 2 Microstructure of steel LN3 austenitized and quenched from (a), 1123° C, (b) 1165° C, and (c) 1232° C.

microscopy. An average of 200 particles was measured for each specimen.

3. Results and discussion

Following austenitization at high temperatures all steels exhibit three stages of discontinuous grain growth behaviour as reported previously [3]. The typical observations for steels LN1 and LN3 are shown in Fig. 1. Stage 2, which is cross-hatched in Fig. 1, is the grain coarsening temperature region. Stages 1 and 3 are uniform fine and coarse grain regions, respectively.

The microstructures corresponding to each of the three stages of coarsening of steel LN3 are shown in Fig. 2. It can be seen that below the grain coarsening temperature, which was about 1120° C for LN3, austenite grains were uniform and fine (Fig. 2a). The grain size was around 25 µm in diameter and did not increase significantly with temperature up to the grain coarsening temperature. At grain coarsening temperature region some grains began to grow extensively at the expense of the surrounding fine grains. This produces a mixed grain structure (Fig. 2b). At higher temperatures above the coarsening temperature the grains became uniform again but very large as shown in Fig. 2c.

The volume fraction of coarse grains as a function of temperature for these steels is shown in Fig. 3. As can be seen, each steel shows a sigmoid curve in the corresponding grain coarsening temperature region. For titanium-free steels the grain coarsening temperatures were about 1000° C. This is controlled by the pinning effect of AlN and its dissolution [3]. A small amount of titanium addition can increase the grain coarsening temperature significantly as a result of TiN formation and the corresponding pinning effect [4, 8]. The grain coarsening temperature up to 1220° C is possible in some steels like HN2 and HN3. It was also found that when Ti/N ratio is higher, like steels LN4, MN4 and HN4, the grain coarsening temperatures decrease as shown in Fig. 3. Moreover, the sigmoidal curve changed to a more flatten shape. It suggests that the temperature regions of the mixed grain structure formation are extended.

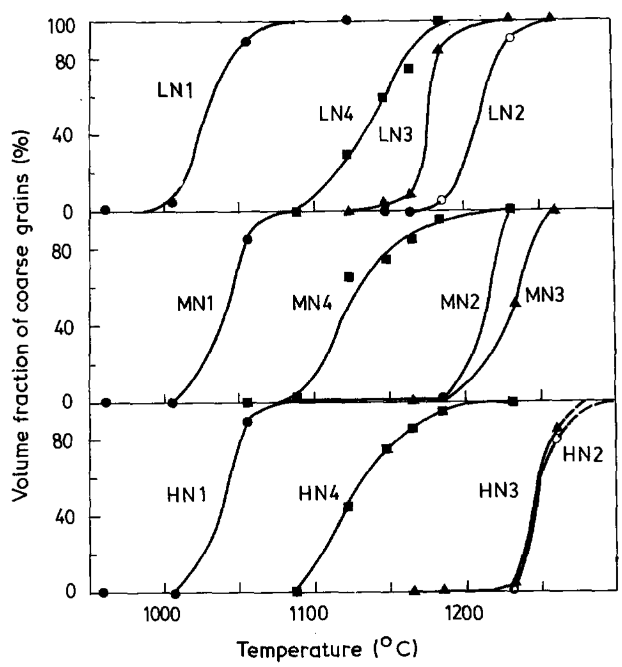

Figure 3 Variation of volume fraction of coarse grains with austenitization temperature.

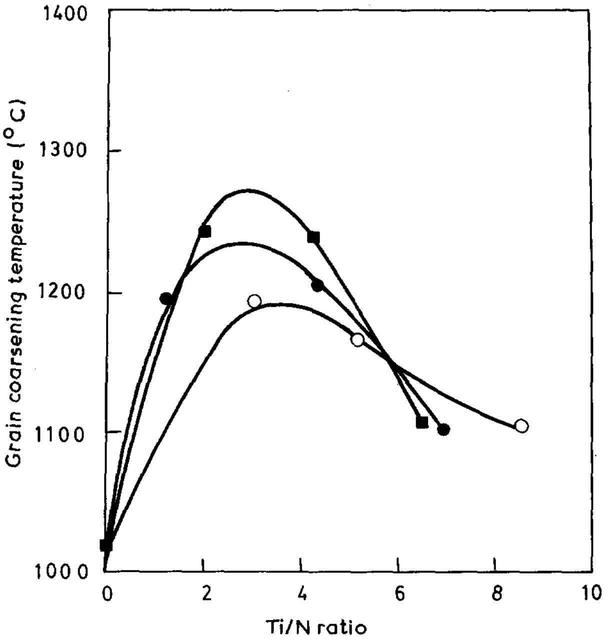

Figure 4 Variation of grain coarsening temperature defined by 10% coarse grain formation with the Ti/N ratio. (○ LN series, ● MN series, ■ series)

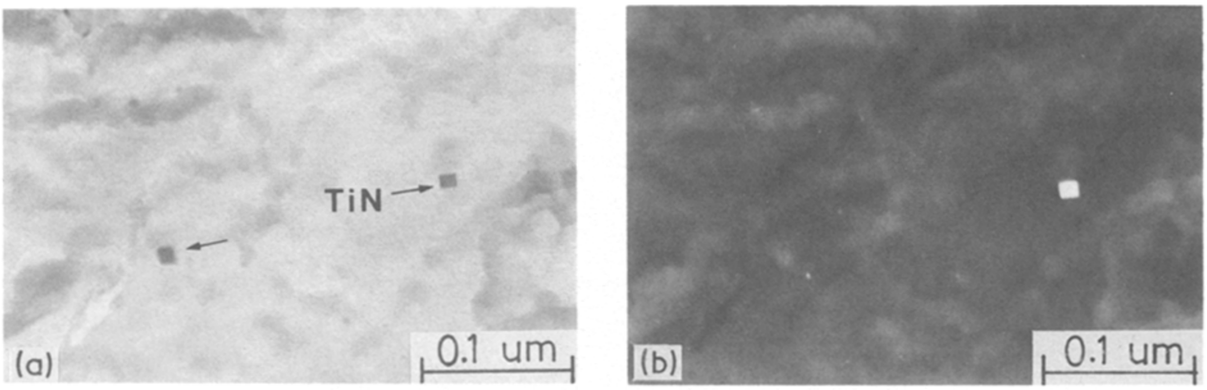

Figure 5 TEM micrograph of steel MN3 austenitized and quenched from 1005° C. (a) bright field image, (b) dark field image.

The grain coarsening temperature of these steels defined by 10% coarse grain formation as a function of Ti/N ratio and nitrogen content is shown in Fig. 4. It can be seen that there is a maximum grain coarsening temperature around the Ti/N stoichiometric ratio, i.e., 3.42 for all of these three series of steels with different nitrogen contents. The grain coarsening temperature of steels with higher titanium content over this range decrease abruptly. At the Ti/N ratio around 3.42, apparently, that higher grain coarsening temperature can be achieved with higher nitrogen content within the range of this study.

The TEM micrograph in Fig. 5 shows the TiN particles of steels MN3. The shape of TiN is typically rectangular and can readily be identified. The size distribution of TiN particles for the specimens austenitized and quenched from 1005° C is shown in Fig. 6. It can be seen that the size distribution is similar for steels with the Ti/N ratio lower and around 3.42. Its mean size was about 10–15 nm in diagonal length. The size distribution was slightly sharper for steels LN2 and LN3. When the Ti/N ratio is higher such as above 6.5 for steels LN4, MN4 and HN4, the particle size coarsening occurs significantly and the size distribution becomes broadening. It was also found that the TiN particles distribution is uneven. As shown in Fig. 7a the number of TiN particles in the region containing large TiN particles is less than that of the region containing small TiN particles Fig. 7b. The uneven TiN particles distribution and the broadening of size distribution of steels LN4, MN4 and HN4 resulted in the uneven pinning effect of TiN on grain boundaries from area to area. This could be the reason for the extension of the temperature region of mixed grains formation in steels LN4, MN4 and HN4.

According to the solubility product equation of TiN [4]

$$\log\,[\mathrm{Ti}]\,[\mathrm{N}] = -8000/T + 0.32$$

it is possible to calculate the volume fraction of TiN particle from the steels composition and austenitization temperature. At 1000° C the equilibrium particle volume fraction of TiN was calculated as function of Ti/N ratio at 30, 50 and 70 p.p.m. nitrogen content. The results are shown in Fig. 8. It can be found that in the case of Ti/N ratio less than its stoichiometric ratio the amount of TiN formation is proportional to the Ti/N ratio and nitrogen contents. However if an increase in titanium content is beyond the stoichiometric ratio, the amount of TiN levels off and increases negligibly. The plateaux of TiN formation rise with increasing nitrogen content.

According to Zener's theory [1] and the above experimental results, it can be concluded that in the case of Ti/N ratio lower than 3.42, an increase in Ti/N ratio and nitrogen contents can increase grain coarsening temperatures for the reason of more TiN formation. Higher titanium content above the stoichiometric ratio causes the coarsening of TiN particles significantly, but the amount of TiN increment is negligibly small. The coarsening of TiN deteriorates the grain growth restriction effect and results in the decrease of grain coarsening temperature.

4. Summary and conclusions

For steels with the same nitrogen content the highest

TABLE I The chemical compositions of steel specimens

Steel	C	Mn	Si	P	S	Al	Ti	N (p.p.m.)	Ti/N
LN1	0.11	1.36	0.27	0.014	0.0078	0.024	–	27	0
LN2	0.12	1.29	0.25	0.015	0.0076	0.026	0.008	26	3.0
LN3	0.11	1.35	0.26	0.014	0.0078	0.026	0.014	27	5.2
LN4	0.12	1.30	0.25	0.014	0.0078	0.031	0.022	26	8.5
MN1	0.12	1.31	0.25	0.015	0.0075	0.027	–	46	0
MN2	0.12	1.28	0.23	0.013	0.0077	0.021	0.006	49	1.2
MN3	0.12	1.28	0.25	0.014	0.0075	0.030	0.020	46	4.3
MN4	0.12	1.32	0.24	0.014	0.0077	0.026	0.034	49	6.9
HN1	0.11	1.23	0.24	0.013	0.0080	0.022	–	58	0
HN2	0.12	1.28	0.24	0.014	0.0076	0.022	0.013	65	2.0
HN3	0.11	1.23	0.24	0.013	0.0080	0.022	0.025	58	4.3
HN4	0.12	1.28	0.24	0.014	0.0076	0.022	0.042	65	6.5

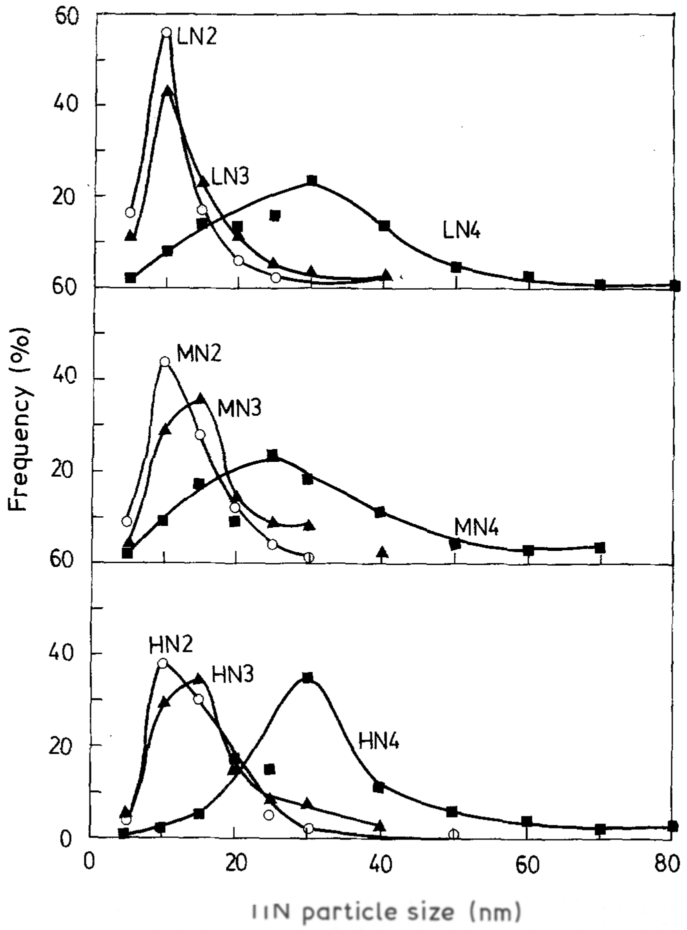

Figure 6 The TiN particle size distribution of specimens austenitized and quenched from 1005° C.

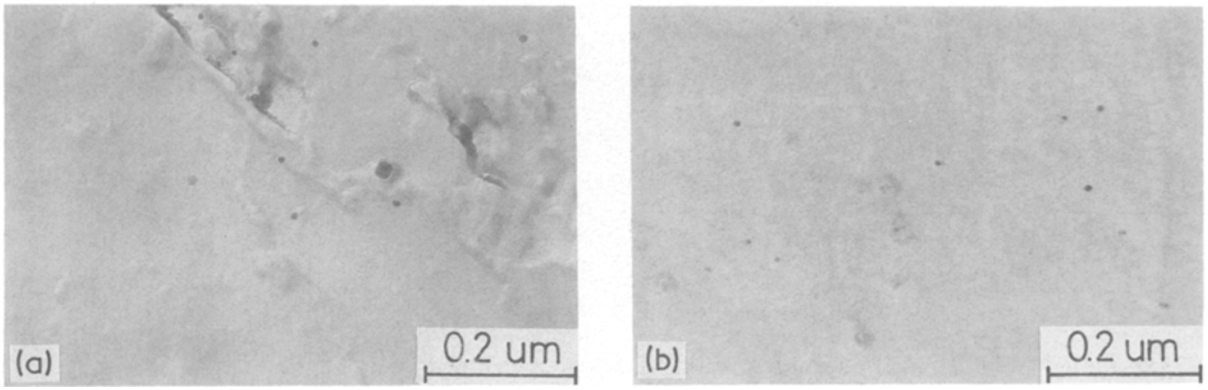

Figure 7 The TiN particles distribution of steel MN4 at regions (a) large particle, (b) small particle.

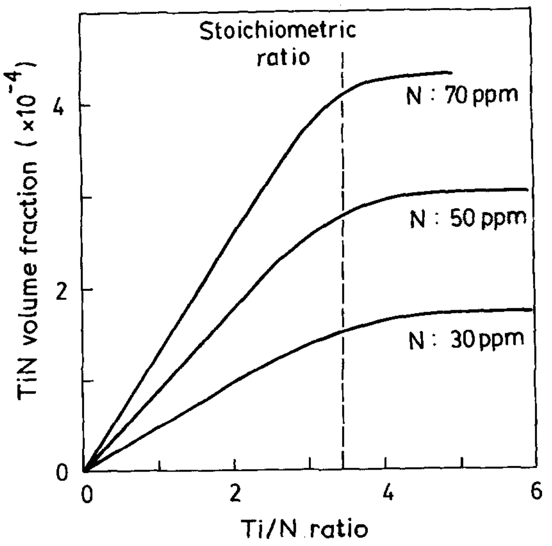

Figure 8 Variation of equilibrium TiN volume fraction at 1000° C with the Ti/N ratio and nitrogen content of 30, 50 and 70 p.p.m.

grain coarsening temperature occurs around the Ti/N stoichiometric ratio, i.e. 3.42. An increase in grain coarsening temperatures with increasing nitrogen content also occurs at Ti/N around 3.42 as a result of more TiN formation. The TiN particle size increases significantly and the grain coarsening temperature decreases accordingly at higher titanium content beyond the stoichiometric ratio.

Acknowledgement

The author is grateful to the China Steel Corporation for permission to publish this paper.

References

1. C. ZENER, private communication to C. S. Smith, *Trans. Amer. Inst. Min. Eng.* **175** (1949) 15.
2. T. GLADMAN, *Proc. R. Soc. A* **294** (1966) 298.
3. T. GLADMAN and F. B. PICKERING, *J. Iron Steel Inst.* **205** (1966) 298.

4. S. MATSUDA and N. OKUMURA, *J. Iron Steel Inst. Japan.* **62** (1976) 1209.
5. H. KOBAYASHI and Y. KASAMATU, *ibid.* **67** (1981) 1990.
6. I. WEISS, G. L. FITZSIMONS and A. J. DeARDO, In Proceedings of the Thermomechanical Processing of Microalloyed Austenite, Pittsburg, 1982, edited by A. J. DeArdo (Pittsburg) p. 33.
7. R. K. AMIN and F. B. PICKERING, *ibid.* p. 1.
8. L. J. CUDDY and J. C. RALEY, *Met. Trans.* **14A** (1983) 1989.

Received 1 December 1987
and accepted 29 April 1988