

# Development of High-Strength Steels for Bolts

Manabu KUBOTA\*<sup>1</sup>  
Shingo YAMASAKI\*<sup>3</sup>

Toshimi TARUI\*<sup>2</sup>  
Tatsuro OCHI\*<sup>1</sup>

## Abstract

*A technology to render hydrogen harmless by using nanometer-size precipitates and another technology to control microstructures, both developed as measures to improve the delayed fracture property of high-strength steels, are explained. High-strength steels for bolts (12-16T) have excellent qualities in delayed fracture property developed on the basis of these technologies are also introduced. The developed steels exhibit a high critical diffusible hydrogen amount thanks to a high hydrogen trapping capacity and have excellent delayed fracture property as a result of microstructural control and consequent inhibition of grain boundary fracture.*

## 1. Introduction

Weight reduction and performance enhancement of automobiles and the construction of large-scale, high-rise buildings require higher quality joints and manpower reduction in connection work, and these in turn, require higher strength steel bolts<sup>1,2)</sup>. The strength of high-strength bolts is realized generally through quenching and tempering, and the microstructures of such products consist of tempered martensite. When the tensile strength of tempered martensite steel exceeds 1,200 MPa, even a very small amount of hydrogen embrittles the boundaries of prior  $\gamma$  grains, and the steel material may fail during use. This phenomenon, which is known as delayed fracture, has hindered the strengthening of steel bolts, and their highest strength has long been limited to somewhere around 10T (tensile strength of 1,000 to 1,200 MPa). For improving the delayed fracture property of high-strength steel, it is effective to 1) render hydrogen harmless and 2) make microstructure resistant to hydrogen.

From this point of view, the present paper reports 1) a technology to render hydrogen harmless by use of nanometer-size precipitates and 2) another to control microstructure. This paper also introduces new steels that are excellent in a delayed fracture property for high-strength bolts of 12T (tensile strength of 1,200 to 1,400 MPa), 14T (tensile strength of 1,400 to 1,600 MPa) and 16T (tensile strength of 1,600 to 1,800 MPa) grades, developed on the basis of the above technologies to respond to the demands for higher-strength bolts.

## 2. Technology to Render Hydrogen Harmless Using Nanometer-size Precipitates

Delayed fracture is caused by hydrogen that is absorbed into steel from outside through such processes as corrosion and plating; therefore the delayed fracture property of a steel material can be improved by rendering the hydrogen that is absorbed harmless. It is well known that carbide-forming alloying elements such as Mo and V, dissolved in the steel matrix during the heating for quenching, precipitate coherently in the form of nanometer-size carbide particles during tempering to realize a significant precipitation hardening effect. Recently, carbides of Mo, V, Ti and Nb were found to be capable of trapping hydrogen in steel<sup>3-7)</sup>. For the purpose of clarifying their hydrogen-trapping capacity, the authors examined the behavior of hydrogen in steel, using a modified SCM 440 steel containing V as a specimen steel and controlling its tensile strength to approximately 1,500 MPa through quenching and tempering.

**Fig. 1** shows the relationship between the time of exposure to the atmosphere at room temperature and the hydrogen evolution curves for the specimen steel containing V; the curves were obtained through thermal desorption analysis after hydrogen charging and Cd plating of the specimen steel<sup>4)</sup>. One can see here that immediately after hydrogen charging, hydrogen exists in a state to form a peak near 373 K (hereinafter referred to as the first peak), which appears with ordinary tempered martensite, and in addition, in another state to form a

\*<sup>1</sup> Muroran R&D Lab.  
\*<sup>2</sup> Steel Research Laboratories

\*<sup>3</sup> Kimitsu R&D Lab.

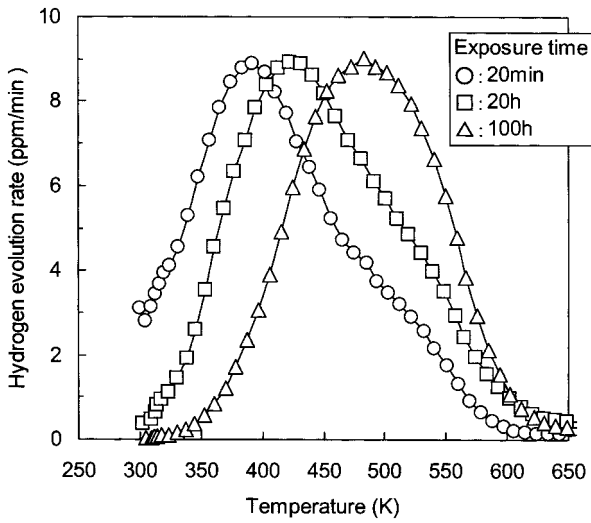


Fig. 1 Dependence of hydrogen evolution rate curves on atmospheric exposure time after hydrogen charging and Cd plating for V added steel

peak near 473 K (hereinafter referred to as the second peak). The hydrogen evolution peak shifts from 373 to 473 K with the time of exposure to the atmosphere at room temperature, indicating that hydrogen is trapped as it diffuses at sites having higher trapping energy. In addition, it has been known that, with a steel containing V, the hydrogen absorption increases when the steel is tempered at approximately 873 K, the temperature range in which carbonitride of V precipitates in fine particles several nanometers in size<sup>5)</sup>.

Fig. 2 shows photomicrographs of nanometer-size V carbide particles that have precipitated during tempering. The hydrogen that forms the second peak in steels containing V, Mo and/or Ti are presumed to be those that were trapped near the coherent interfaces of carbonitrides of these elements. Fig. 3<sup>4)</sup> shows the hydrogen evolution curves of two specimens of a V-containing steel; the specimens underwent hydrogen charging followed by Cd plating and an atmospheric exposure at room temperature for five days, the Cd coating was removed, and then one of the specimens was subjected to the hydrogen evolution measurement immediately after the coating removal (0d) and the other after an additional exposure at room temperature for 15 days (15d). The amount of the hydrogen that forms the second peak decreased as a result of the exposure at room

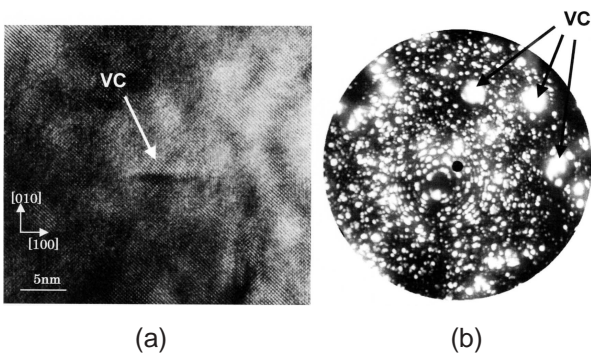


Fig. 2 Micrographs of VC which precipitates during tempering (a) TEM, (b) FIM

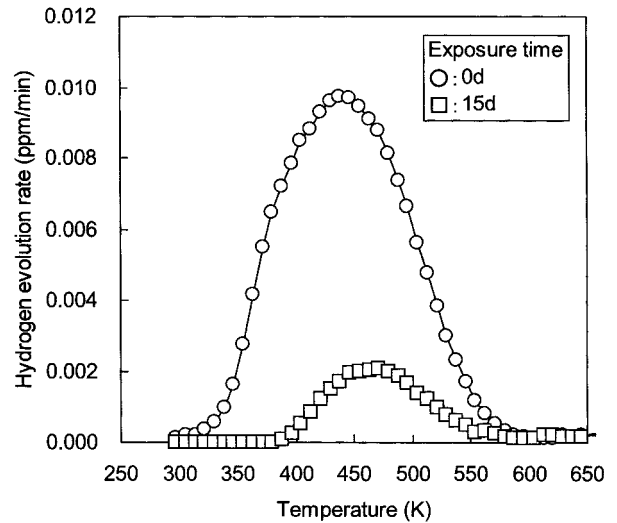


Fig. 3 Dependence of hydrogen evolution rate curves on atmospheric exposure time after hydrogen charging for V added steel

perature, indicating that it had diffused at room temperature and evolved to outside the steel. Kushida et al.<sup>9)</sup> examined the hydrogen diffusion coefficient in V-containing steels by the electrochemical hydrogen permeation method, and reported that the coefficient was lower than that of steels that did not contain V by a decimal place or more. From the above results, the hydrogen of the second peak that was trapped by carbides of V and other alloying elements is presumed to be diffusible hydrogen, although its diffusion coefficient is lower than that of the hydrogen that forms the first peak.

Then, for the purpose of clarifying the relationship between the hydrogen of the second peak and delayed fracture property, the authors carried out delayed fracture tests. The critical diffusible hydrogen amount method proposed by Yamasaki et al.<sup>4)</sup> was used for the tests, whereby the upper limit amount of diffusible hydrogen not to cause delayed fracture (critical diffusible hydrogen amount  $[H_c]$ ) was compared with the amount of hydrogen that is absorbed into steel from the environment (absorbed hydrogen amount  $[H_E]$ ). Fig. 4<sup>9)</sup> shows the influence of the state of hydrogen in steel on the shape of delayed fracture surface for a specimen steel containing V. In the case where the specimens underwent the delayed fracture tests immediately after cathodic hydrogen charging, namely where most of the hydrogen was what formed the first peak, the fracture was typi-

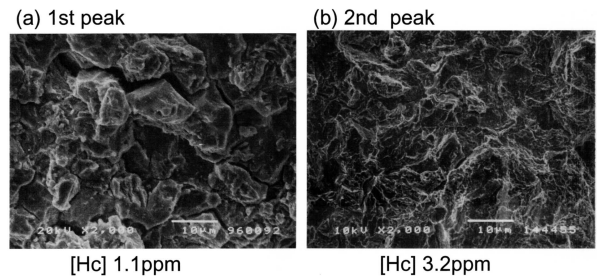


Fig. 4 Typical fracture surface of V added steel for which the peak temperature in the hydrogen evolution rate curve are (a) 373K (the first peak), and (b) 473K (the second peak).

cal intergranular fracture along the prior  $\gamma$  grain boundary and  $[H_C]$  was low.

In contrast, in the case where the specimens underwent the delayed fracture test after the hydrogen charging and an atmospheric exposure at room temperature for 96 h to let hydrogen shift to the state of the second peak, the fracture was a quasi-cleavage fracture and  $[H_C]$  was high. This was interpreted to indicate that the hydrogen of the second peak trapped by V carbide is diffusible hydrogen, but its diffusion coefficient is low and does not exert any significant influence on delayed fracture. The rate of absorption of hydrogen under normal environmental conditions is far lower than that under cathodic hydrogen charging, and therefore most of hydrogen that was absorbed into a steel containing carbides of elements such as V, Mo and/or Ti formed the second peak. Based on the above, the authors made hydrogen in a 1,500MPa class V-containing steel shift to the state to form the second peak, measured the value of  $[H_C]$ , and found it as high as several ppm. Comparing this with the value of  $[H_C]$  of a 1,500 MPa class SCM 440 steel, which is on the order of 0.1 ppm, the excellent delayed fracture property of a V-containing steel is quite clear. On the other hand, the amount of hydrogen absorption from the environment  $[H_E]$  into a V-containing steel has been confirmed to be higher than that into ordinary tempered martensite because of the hydrogen trapping effect<sup>4)</sup>.

Fig. 5<sup>9)</sup> shows the results of measurement of the change of  $[H_E]$  during an exposure test of real bolts in Okinawa Prefecture. The maximum value of  $[H_E]$  was approximately 0.8 ppm; although it is higher than that of an ordinary steel for bolts, it is still lower than  $[H_C]$ . Therefore, as far as the possibility of the occurrence of delayed fracture is evaluated based on the amount of hydrogen, the possibility is extremely small. In fact, during nine years of exposure tests of several thousand bolts, there has not been any case of delayed fracture at all. Judging from the above results, a hydrogen trapping steel containing nanometer-size V carbide particles has a function to change the hydrogen of the first peak, harmful in terms of delayed fracture, into the harmless hydrogen of the second peak during periods in which corrosion proceeds (in rainy weather, etc.), and evolve the harmless hydrogen of the second peak into the atmosphere during periods in which corrosion stops (in fine weather, etc.). Thus, such steel has in

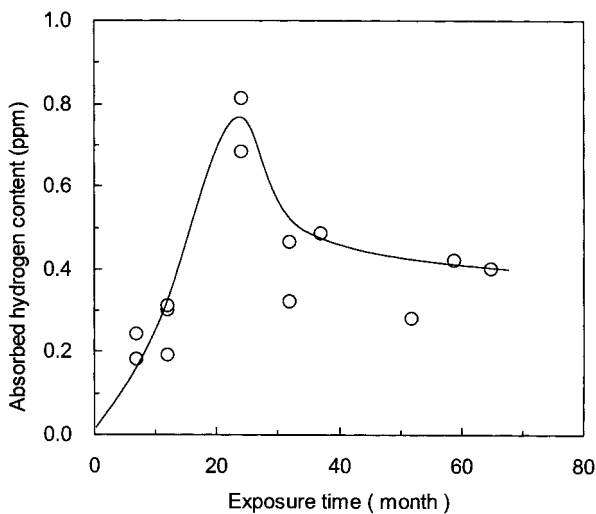


Fig. 5 Variation of absorbed hydrogen content during atmospheric exposure

addition to the function of precipitation hardening, an intelligent function to render hydrogen harmless.

### 3. Microstructural Control Technology Using Nanometer-size Precipitates

It has been empirically known that the delayed fracture property improves as the temperature of tempering becomes higher. For that reason, in order to enable both the high temperatures associated with tempering, and high strengths, Mo and V were added to use precipitation hardening with nanosize carbide particles that precipitate during tempering<sup>10,11)</sup>. However, the mechanism of the improvement of the delayed fracture property through tempering at higher temperatures is not clear, and it has been scarcely studied. This is because, when the influence of tempering temperature is investigated using specimens of the same steel and changing the temperature, strength changes and the influence of strength cannot be separated, and when it is investigated using specimens having different chemical composition to equalize strength at different tempering temperatures, on the other hand, the influence of chemical composition cannot be separated. What is more, owing to the influence of the hydrogen trapping by precipitates of alloying elements, it is difficult to evaluate the influence purely of tempering temperature.

In view of the above, using a steel containing Mo and V in combination, which exerts a greater precipitation hardening effect than was conventionally possible, the authors attempted to compare delayed fracture property obtained at different tempering temperatures with the same chemical composition at the same strength<sup>12)</sup>. Fig. 6 shows the variation in tensile strength of the steel containing Mo and V obtained at different tempering temperatures. A steel of this chemical composition shows a strength peak of the secondary hardening at approximately 873 K, and thus the same tensile strength is obtained at tempering temperatures below and above the peak temperature. This means that it is possible to investigate the influence of tempering temperature on delayed fracture property using the same steel grade and at the same strength. The delayed fracture test was conducted using notched test pieces under a constant load during cathodic hydrogen charging at a current density of 1 mA/cm<sup>2</sup> in a H<sub>2</sub>SO<sub>4</sub> solution of pH 3.0. The ratio of the upper limit load stress not to

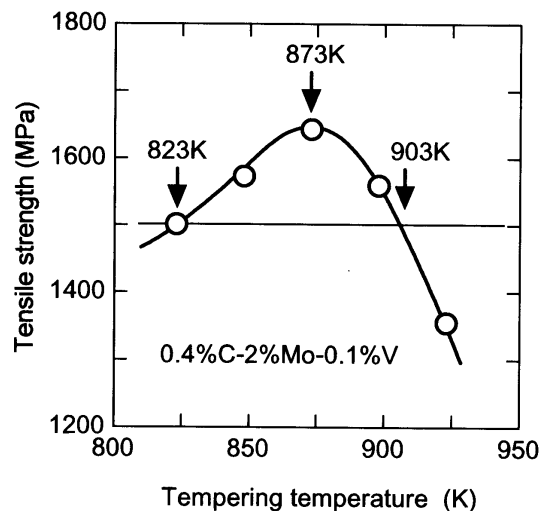


Fig. 6 Variation in tensile strength with tempering temperature of Mo-V added steel

cause fracture in 200 h to the fracture stress in normal atmosphere was defined as delayed fracture strength ratio, and this ratio was used as an index of delayed fracture property. Since hydrogen that form the first peak are supplied continuously by the cathodic hydrogen charging under this test condition as explained in the preceding section, the influence of hydrogen trapping on delayed fracture property is presumed to be comparatively small.

Fig. 7 shows the results of the delayed fracture test. The graph also shows the test results of SCM 440 for comparison purposes. Whereas the delayed fracture index of SCM 440 decreased monotonously with the increase in tensile strength, the change of the index of the steel containing Mo and V could not be accounted for in terms of tensile strength; the index improved rather with higher tempering temperature. This demonstrates that tempering temperature influences the delayed fracture property of the specimen steel more than tensile strength does.

Fig. 8 shows photomicrographs of the delayed fracture surfaces of the specimens tempered at 823 and 903 K. Whereas the starting point of the fracture of the specimen tempered at 823 K is a distinct intergranular fracture, that of the specimen tempered at 903 K is a quasi-cleavage crack, namely an intragranular fracture. The above indicates that, even in an environment of only a small influence of hydrogen trapping, intergranular fracture is better suppressed as tempering temperature rises. The improvement of delayed fracture property with higher tempering temperature is attributable, presumably, to the increase in the strength of grain boundaries. Since it seemed

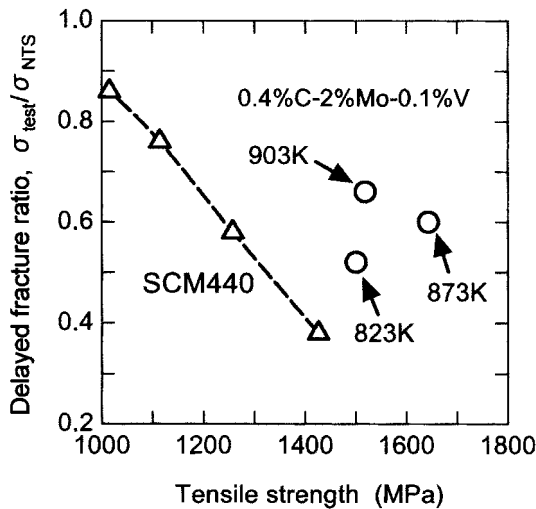


Fig. 7 Effect of tempering temperature on delayed fracture properties of Mo-V added steel

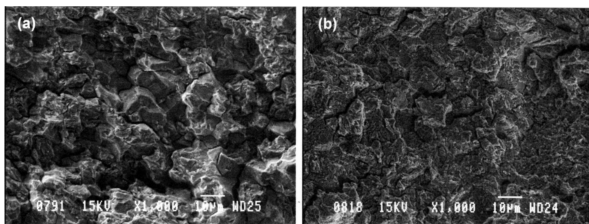


Fig. 8 Effect of tempering temperature on delayed fracture surfaces of Mo-V added steel (a) 823K tempered, (b) 903K tempered

likely that the strengthening of grain boundaries with higher tempering temperature resulted from microstructural change with higher tempering temperature, the authors observed the microstructures of the specimens using a field emission type scanning electron microscope (FE-SEM). Fig. 9 shows the results. While the microstructures of both the specimens tempered at 823 and 903 K consisted of a matrix of tempered martensite with dispersed cementite, the dispersion of cementite was different between the two: whereas fine acicular cementite dispersed both at the boundaries between prior  $\gamma$  grains and inside them in the specimen tempered at 823 K, cementite existed in comparatively large spherical particles at prior  $\gamma$  grain boundaries in the specimen tempered at 903 K. In order to examine the difference in the dispersion of cementite in more detail, the authors observed prior  $\gamma$  grain boundaries with a transmission electron microscope (TEM) by the thin film method. Fig. 10 shows the results. Fine cementite particles are seen in a high density at grain boundaries of the specimen tempered at 823 K. The particles seem to be similar to the thin-film cementite that Nakazato et al<sup>13)</sup> observed at grain boundaries of SCM 3 specimens tempered at 300 K. On the other hand, although the coarse cementite particles that had been found at the FE-SEM observation existed at boundaries between prior  $\gamma$  grains of the specimen tempered at 903 K, the particles were distributed comparatively sparsely, and the area ratio of grain boundaries covered by cementite was smaller than that in the specimen tempered at 823 K.

Judging from the above, it is likely that the area ratio of boundaries between prior  $\gamma$  grains covered by cementite decreases as tempering temperature becomes higher, increasing the binding strength of the boundaries and thus inhibiting the occurrence of intergranular fracture. Therefore, the above test results indicate that optimizing the addition amounts of Mo and V, taking advantage of the large precipitation hardening effects of the nanometer-size particles of the carbides of these elements and raising the temperature of tempering are effective in both strengthening of material and enhancement of delayed fracture property, which were conventionally incompatible with each other.

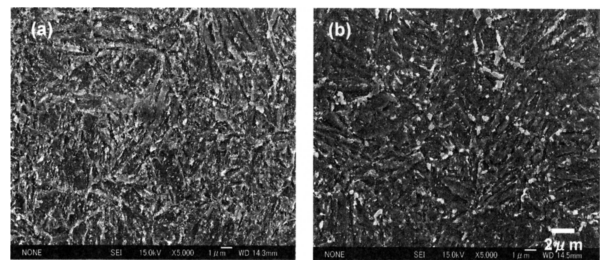


Fig. 9 Effect of tempering temperature on dispersion of cementite (a) 823K tempered, (b) 903K tempered

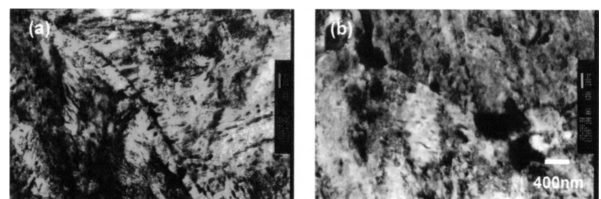


Fig. 10 TEM micrographs of pre-austenite grain boundaries (a) 823K tempered, (b) 903K tempered

Table 1 Examples of chemical composition of high strength steel for bolts

Steel	Level	(mass %)							
		C	Si	Mn	P	S	Cr	Mo	V
MB12	12T	0.37	Decrease	0.50	Decrease	Decrease	1.20	0.25	0.30
MB14	14T	0.40	Decrease	0.50	Decrease	Decrease	1.20	0.70	0.35
MB16	16T	0.40	Decrease	0.50	Decrease	Decrease	–	2.00	0.15

#### 4. High-strength Steels for Bolts

Nippon Steel has developed steels for high-strength bolts of 12 to 16T grades. In addition to the conventional measures to enhance delayed fracture property, namely (1) reduction of the amounts of impurity elements such as P and S, which segregate at grain boundaries, and (2) reduction of the grain boundary segregation of the impurity elements by refining prior  $\gamma$  grains, new technologies of (3) rendering hydrogen harmless by hydrogen trapping with nanometer-size precipitate particles, and (4) improving microstructure by precipitation strengthening (by high-temperature tempering) were effectively utilized in the development.

Table 1 shows examples of the chemical compositions of the developed steels. The developed steels characterize themselves by comparatively high contents of Mo and V. This is because these elements are effective in improving the delayed fracture property in more than one aspects: V is effective in effects such as refining  $\gamma$  grains, strengthening steel by precipitation hardening (by high-temperature tempering) and hydrogen trapping with its carbide, and Mo in the latter two. Another reason is that the solubility of the carbides of Mo and V in  $\gamma$  is larger than that of the carbides of other elements that have similar effects such as Nb and Ti, and the carbides of Mo and V are solutionized easily at the practical quenching temperatures (1,123 to 1,223 K) of bolts. In order to realize the above effects, the addition amounts of Mo and V and the balance between their addition amounts are controlled in consideration of required strength and quenching temperature. MB12 (12T) has been actually used for application to automobile engine bolts, and MB14 (14T) in the form of F14T Super High-tension Bolts (SHTB)<sup>14)</sup> for civil and building construction.

#### 5. Conclusion

Developed hydrogen trapping steels, which effectively utilize V carbide, exhibit high values of the critical diffusible hydrogen amount  $[H_c]$  and have excellent the delayed fracture property. Since the absorbed hydrogen amount  $[H_e]$  is less than the critical diffusible hydrogen amount  $[H_c]$ , the steels are expected to exhibit excellent the delayed fracture property in the environments of actual use.

Comparison of the delayed fracture property of a steel containing both Mo and V under the condition of the same strength made it clear that the delayed fracture property improved as the temperature of tempering was raised. Intergranular fracture is suppressed more at higher tempering temperatures.

Through application of countermeasures against delayed fracture based on the above findings, steels excellent in delayed fracture property for high-strength bolts of 12, 14 and 16T grades have been developed.

#### References

- 1) Tanaka, A.: Tetsu-to-Hagané. 88 (10), 578 (2002)
- 2) Okada, Y.: Special Steel. 51 (12), 7 (2003)
- 3) Totsuka, N., Nakai, Y.: Tetsu-to-Hagané. 69, A113 (1983)
- 4) Yamasaki, S., Takahashi, T.: Tetsu-to-Hagané. 83 (7), 454 (1997)
- 5) Tsuchida, T., Hara, T., Tsuzaki, K.: Tetsu-to-Hagané. 88 (11), 771 (2002)
- 6) Stevens, M.F., Bernstein, I.M.: Metall. Trans. A. 20A, 909 (1989)
- 7) Ohmura, T. et al.: Tetsu-to-Hagané. 90 (2), 106 (2004)
- 8) Kushida, T. et al. Tetsu-to-Hagané. 82 (4), 297 (1996)
- 9) Tarui, T. et al.: CAMP-ISIJ. 15, 1045 (2002)
- 10) Kubota, M., Kanisawa, H.: CAMP-ISIJ. 9, 511 (1996)
- 11) Yamasaki, S., Kubota, M., Tarui, T.: Shinnittetsu Giho. (370), 51 (1999)
- 12) Kubota, M., Ochi, T.: CAMP-ISIJ. 16, 1540 (2003)
- 13) Nakazato, F., Terasaki, F.: Tetsu-to-Hagané. 61, 841 (1975)
- 14) Uno, N.: Architecture & Society. 81 (4), 51 (2000)