Large (Ti, V) Carbonitride in Nonquenched and Tempered Steel 38MnVS6

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Large (Ti, V) carbonitrides with size even up to tens of microns in autoparts steel 38MnVS6 are studied in this work. A great number of micron-sized (Ti, V) carbonitrides are found in continuous casting billet, and the atomic ratios of V/Ti are mainly distributed in range 0.130–0.200 with an average value of 0.171. The large (Ti, V) carbonitrides have irregular morphologies, and some even have an obviously extending shape along the dendrite boundary. 3D morphologies of the large (Ti, V) carbonitride after being etched by AA solution present obvious long and flat shapes. The large (Ti, V) carbonitride has high thermal stability even at 1200 °C, even though the atomic ratio of V/Ti has a decreasing tendency. There are still many large (Ti, V) carbonitrides in the rolled bar and partially broken in some which are clearly visible. According to the Thermo-Calc calculation result, the large (Ti, V) carbonitride precipitates in liquid steel during solidification. The chemical compositional characteristic is the result of subsequent mutual diffusion of elements Ti, V, C, and N. Simply reducing the content of Ti, even 13 ppm cannot eliminate the large (Ti, V) carbonitride for the nitrogen-containing, nonquenched, and tempered steel, but the quantity and size of large carbonitride are significantly reduced.

1. Introduction

As a microalloying element, Ti is frequently applied in steel products, forming nitrides to pin austenite grain boundaries [1, 2], or precipitation strengthening by carbides [3], or even playing a heterogeneous nucleation role in macrostructure or microstructure control [4, 5] due to the strong binding force with O element, N element, C element, and S element. The precipitate in Ti-microalloying steel is usually nanosized Ti(Cx,Ny), and the chemical composition of precipitate will be more complex when another microalloying element such as V is also added. I. I. Gorbachev et al. made a detailed analysis of the laws of carbonitrides formation for the Fe-V-Ti-C-N system [6]. However, carbonitrides of larger size are often seen in microalloyed steel products [7–9]. The size can reach several microns, and the chemical composition is various and different from the equilibrium state. For example, Y. Xie found large (Ti, V) carbonitride and large V carbonitride in Ti-V-containing H13 steel billet. These large carbonitrides are usually generated in liquid steel during solidification, and the ones with some content of Ti have high thermal stability. The existence of large carbonitrides not only reduces the effectiveness of microalloying elements but is also harmful to the mechanics and fatigue performance of final products due to their high thermal stability and hardness. 38MnVS6, a medium carbon nonquenched and tempered steel, is often used to make automobile parts, such as crankshafts, steering knuckles, and pistons. Element Ti is usually added to refine the initial austenite grain to prevent stress cracking of billet during production due to high crack sensitivity. In addition, in order to improve the precipitation strengthening effect of microalloying element V, high content of element N is usually contained [10]. In this study, the characteristics of large carbonitride in 38MnVS6 are studied, providing a theoretical basis for subsequent control.

2. Producing Process and Sampling Method

38MnVS6 steel is produced under the process BOF-LF-RH-continuous casting (section size 280 mm × 320 mm)-hot rolling (bar size φ90 mm). A casting speed of 0.85 m/min and a water ratio of 0.30 L/kg in secondary cooling during the
continuous casting process are adopted. Before rolling, the billet is heated again in an industrial heating furnace. The heating temperature selected is not more than 1200°C and the time in the high-temperature period (1130–1200°C) is not more than 3 h to control the burning loss and decarburization.

Heat composition of 38MnVS6 is tested using the tundish sample and the tested result is shown in Table 1. Elements C, Si, Mn, S, V, and Ti are tested by the spectrometer. Element N is tested by a gas analyzer. It can be seen that 0.019% of Ti, 0.111% of V, and 0.0196% of N are contained.

As shown in Figure 1, three cubic samples with a side length of 20 mm are cut in edge, middle, and center position on the cross-section of billet. The samples are ground, polished, and etched by a saturated picric acid solution to analyze the characteristics of macrostructure and large precipitates under an optical microscope (OM). The morphology and composition of large phases are further tested by automatic scanning electron microscopy (SEM, equipment type EXPLORER 4) equipped with energy disperse spectroscopy (EDS), and the ones larger than 1 μm are recorded. Large precipitates in the rolled bar are also tested at 1/2R position on the longitudinal section.

### 3. Results and Analysis

#### 3.1. Characteristics of Large Carbonitride in Continuous Casting Billet

##### 3.1.1. Macrostructure of Billet

The macrostructure of continuous casting billet under OM is shown in Figure 2. Fine columnar crystals can be seen in the edge sample, and the average secondary dendrite arm spacing develops from about 60 μm in the chilled layer to inner 130 μm. The columnar crystals become coarser in the middle sample, and about 60 μm. Columnar crystals exist in the center sample, and the average secondary dendrite arm is about 234 μm.

##### 3.1.2. Size and Chemical Compositional Characteristics of Large Carbonitrides

Large secondary phases are seen obviously in the dendrite gap in billet under OM, including the grey ones and the light yellow ones, as shown in Figure 3. The light yellow phases have been marked by a red circle, and larger versions are also shown in the figure. The grey phases are mainly in the shape of blocks, while the light yellow ones are mostly irregular.

The grey phases and light yellow phases under OM are further tested and analyzed by SEM with EDS. The grey phases are MnS. The light yellow phases are (Ti, V) carbonitrides, and the typical morphologies under SEM are shown in Figure 4 (noted as Ti-V in figure). The large (Ti, V) carbonitride presents a variety of morphologies, such as the common quadrilateral shape (Figures 4(a) and 4(b)), but most have irregular shapes, such as the shape of the arrow (Figures 4(c) and 4(d)), the block shape with sharp corner (Figure 4(e)), and even obviously extending shape along the dendrite boundary (Figure 4(f)). In addition, part of (Ti, V) carbonitrides exists by combining with oxide or sulfide, as shown in Figures 4(g) and 4(h).

The chemical composition of part phases in Figure 4 is listed in Table 2. The tested result of elements iron, carbon, and nitrogen is for reference only because the content of Fe may be disturbed by the iron base and that of light elements C and N cannot be accurately measured by the EDS method. It can be seen that the content of Ti is obviously larger than that of V. The atomic ratios of V/Ti for more (Ti, V) carbonitrides are further analyzed and the distribution is shown in the form of scatter plot and box plot in Figure 5. It can be seen that the values are mainly distributed in the range 0.130–0.200, and the average value is 0.171. Little dates out of the range exist, such as the maximum value of 0.368 and the minimum value of 0.087.

2D statistical result of (Ti, V) carbonitride size in billet is shown in Figure 6. Although some difference exists between the 2D and the real morphology, the size distribution in Figure 6 still has a reference value. (Ti, V) carbonitride in the edge sample is mainly less than 10 μm, and the number is significantly less than that in middle and center samples. There is a certain number of (Ti, V) carbonitrides larger than 10 μm in the middle and center, especially some which are larger than 15 μm are detected in the middle.

##### 3.1.3. 3D Morphology of Large (Ti, V) Carbonitride

AA solution is used to corrode the surface of the billet samples to reveal the real morphologies of (Ti, V) carbonitride. The typical morphology results under SEM are shown in Figure 7. The upper part and bottom part of the picture is under SED mode and BSD mode, respectively. It is seen that their real morphologies tend to be irregularly long and flake shape, such as the triangle-like in Figure 7(a), the hook-like in Figure 7(b), the “I” shape in Figure 7(c), and the roll-like
in Figure 7(d). It is different with other studies in which only cube-like Ti-containing carbonitrides are found [11, 12].

3.2. Thermal Stability of Large (Ti, V) Carbonitride. As mentioned above, 1200°C is a common heating temperature for autoparts steel, and a higher temperature will aggravate the burning loss and decarburization of steel. Billet sample is placed in a box-type annealing furnace for 5 hours under temperature 1200°C to analyze the thermal stability of large (Ti, V) carbonitrides. To protect the sample from oxidation and decarburization under high temperature, the sample with a size of 10 mm × 10 mm × 10 mm is cut and placed in a quartz tube. After vacuuming air and then inputting inert gas Ar, the quartz tube is sealed by a fire gun. The sample in a sealed quartz tube is water cooled after heating and tested by SEM with EDS to analyze the thermal stability of large (Ti, V) carbonitrides.

As shown in Figure 8, no obvious changes in appearance happen even in the narrow region of large (Ti, V) carbonitrides (such as the ones shown in Figures 8(b)–8(d)), indicating that large (Ti, V) carbonitride has high thermal stability and cannot be dissolved by high-heat treatment. The atomic ratios of V/Ti are plotted in Figure 9 and compared with that in billet in Figure 5. The values after high-heat treatment are mainly distributed in the range 0.121–0.178, and the average value is 0.154. The statistic maximum and minimum value is 0.307 and 0.061, respectively. The value distribution changes little even though the decreasing tendency exists.

3.3. Characteristics of Large (Ti, V) Carbonitride in Hot-Rolled Bar. As shown in Figure 10, the large (Ti, V) carbonitride phase still exists in the hot-rolled bar, being consistent with the thermal stability result in Section 3.2. However, some difference in appearance compared with that in billet exists that (Ti, V) carbonitride in the bar is obviously partially broken.

4. Discussion

4.1. Prediction of the Solidification Process. Enrichment of elements in liquid steel will happen during solidification through the redistribution of solute with the development of columnar or equiaxed dendritic solidification structure. The primary precipitates will precipitate in liquid steel when the contents of alloying elements reach the precipitating condition. Here, the Scheil module in Thermo-Calc software is applied to predict the nonequilibrium solidification process based on the composition in Table 1, assuming that the
Figure 3: Typical micron-sized phases in dendrite gap in billet under OM (part of yellow phases are magnified). (a, b) Yellow phases with block shape and (c, d) rod-like shape.

Figure 4: Typical micron-sized (Ti, V) carbonitrides (marking "Ti-V") under SEM, including (a, b) common quadrilateral shape, (c–f) irregular shape, and (g, h) combination shape.
diffusion in the solid phases is so slow that it can be ignored, while the diffusion in the liquid phase is very fast. With this approximation, the conditions at the liquid/solid interface can be described as a local equilibrium. By making a stepping operation on the temperature variable with small decrementing steps, the new composition of the liquid can be determined. After each step, the amount of formed solid phase is removed and the overall composition is reset to the new liquid composition. In effect, the whole system is described as a nonequilibrium state regarding various parts of solidified phases at various solidification stages. Database TCFE7 is applied.

The calculated results are shown in Figure 11. The X-coordinate is the weight fraction of the solid and the Y-coordinate is the temperature. Four phases will appear in liquid steel during solidification, that is, the matrix ferrite phase, the matrix austenite phase, and the primary precipitates Ti-V phase and MnS. During solidification, Ti-V phase begins to precipitate when the solid fraction reaches 0.452. When the solid fraction reaches 0.861, MnS begins to precipitate.

The composition of the Ti-V phase is shown in Figure 12(a), and the large version in the box region in Figure 12(a) is further shown in Figure 12(b). The

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### Table 2: Atomic fraction of alloying elements in phases in Figure 4.

|          | Ti  | V   | C   | N   | Fe  |
|----------|-----|-----|-----|-----|-----|
| Figure 4(a) | 33.0| 3.3 | 15.0| 45.0| 3.7 |
| Figure 4(c) | 34.6| 7.8 | 13.9| 41.8| 1.9 |
| Figure 4(g), (Ti, V) carbonitride | 32.4| 5.7 | 14.9| 44.7| 2.3 |

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**Figure 5:** Atomic ratio of V/Ti in large (Ti, V) carbonitride in billet.

**Figure 6:** 2D size distribution of (Ti, V) carbonitride (≥1 μm) in billet.
Figure 7: Typical 3D morphologies of large (Ti, V) carbonitrides (marking “Ti-V”) in billet under SEM SED mode (upper part) and BSD mode (bottom part), including (a) triangle-like shape, (b) hook-like shape, (c) ”I” shape, and (d) roll-like shape.

Figure 8: Typical morphologies of large (Ti, V) carbonitrides (marking “Ti-V”) with (a) block shape and (b–d) narrow region after high-heat treatment (1200 °C/5h) under SEM.

Figure 9: Atomic ratio of V/Ti in large (Ti, V) carbonitride after high-heat treatment (1200°C/5h).
X-coordinate is the weight fraction of the solid phase, and the Y-coordinate is the mole fraction of the main alloying elements contained in the precipitated phase. Ti-N-rich carbonitride is kept as the main component in a wide range of X-coordinate. However, when the solid fraction reaches about 0.965 at the end of solidification, the ratio of Ti decreases rapidly and that of V increases indicating the precipitation of V carbonitride.

However, no single TiN or V carbonitride is found in the billet samples of 38MnVS6. (Ti, V) carbonitride in billet may be the subsequent mutual dissolution result of TiN and V carbonitride for the mutual solubility of phases having the same crystal structure [13]. Combining with the predicting result of the solidification process, the generating mechanism of large (Ti, V) carbonitride can be described as follows. As shown in Figure 13, Ti-N-rich carbonitride precipitates first in liquid steel during solidification when the nucleation condition has been achieved, and the composition changes little until the generation of V-rich precipitates at the end of solidification. V-rich carbonitride will precipitate on the Ti-N-rich carbonitride which has already existed in liquid steel to reduce the nucleation resistance. Diffusion of elements Ti, V, C, and N in the complex carbonitrides will happen for their mutual solubility, resulting in the formation of Ti-V carbonitride.
4.2. Thermal Stability Analysis of the Large Precipitates. The equilibrium phase under different temperature for 38MnVS6 is also calculated by Thermo-Calc. Database TCFE7 is applied. The total system is set as 1 g. The calculated result for temperature 1150°C—1400°C is shown in Figure 14(a).

Ti-phase is stable at 1200°C. The mole fraction of alloying elements in the Ti-phase is shown in Figure 14(b). Ti-phase is close to TiN with little content of V and C. The chemical composition of the Ti-phase at 1200°C is (Ti\(_{0.92}\)V\(_{0.08}\))(C\(_{0.05}\)N\(_{0.95}\)), that is, the chemical composition of carbonitride in 38MnVS6 will transform to the equilibrium state (Ti\(_{0.92}\)V\(_{0.08}\))(C\(_{0.05}\)N\(_{0.95}\)) if the steel is kept at 1200°C for a long time, and the atomic ratio of V/Ti will transform to 0.09. Plotting the calculated data into Figure 9, as shown in Figure 15, it can be seen that the transforming tendency for large (Ti, V) carbonitride in billet when being kept at 1200°C for 5 h is consistent with the calculated equilibrium state, and the atomic ratio of V/Ti will decrease toward 0.09 even though the transforming rate might be very slow for the low concentration difference between the equilibrium and actual state.

Decreasing the content of Ti is a usual method to control the large Ti-containing precipitates. The content of Ti in 38MnVS6 is attempted to decrease by selecting low-titanium alloy during the steel making process. The actual content of Ti tested in the improved billet is 13 ppm. As shown in Figure 16, when the content of Ti decreases to 13 ppm, large

**Figure 12:** (a) Mole fraction of alloying elements in Ti-V phase; (b) the large version of box region in (a).

**Figure 13:** Generating mechanism of large (Ti, V) carbonitride based on the calculation result.
(Ti, V) carbonitride can still be seen, but the quantity and size are significantly reduced. However, this will increase the production cost. Further optimizing the content of V and N without affecting the product performance is the next work.

5. Conclusion

(1) There are a large number of micron-sized (Ti, V) carbonitride in 38MnVS6 billet. The atomic ratios of V/Ti in large (Ti, V) carbonitrides are mainly distributed in the range 0.130–0.200, and the average value is 0.171.

(2) Based on the 2D statistical result, the number of (Ti, V) carbonitride in the edge position of billet is mainly less than 10 μm and is significantly less than that in the middle and center position. There is a certain number of (Ti, V) carbonitride larger than 10 μm in the middle and center, especially some that are larger than 15 μm are detected in the middle.

(3) Most of the large (Ti, V) carbonitrides present irregular morphologies, and some even has an obviously extending shape along the dendrite boundary. The 3D morphology after corrosion by AA solution indicates that (Ti, V) carbonitride actually has a long and flake shape.

(4) The large (Ti, V) carbonitride has high thermal stability even at 1200°C even though the atomic ratio of V/Ti has a decreasing tendency. There are still many large (Ti, V) carbonitride in the rolled bar, and some obvious difference in morphology found that (Ti, V) carbonitride in bar is partially broken.

(5) The nonequilibrium solidification process and equilibrium diagram of 38MnVS6 are analyzed by the Scheil model and equilibrium calculation, respectively, in Thermo-Calc software. The large (Ti,
(V) carbonitride precipitates in liquid steel during solidification. The chemical compositional characteristic is the result of subsequent mutual diffusion of element Ti, V, C, and N. Large (Ti, V) carbonitride will transform to the equilibrium state (Ti₀.₉₂V₀.₀₈)(C₀.₅₀N₀.₉₅) when being kept under 1200°C for a long time.

(6) Simply reducing the content of Ti even 13 ppm cannot eliminate the large (Ti, V) carbonitride totally for the nitrogen-containing nonquenched and tempered steel, but the quantity and size of large carbonitride is significantly reduced. However, it is not an economical method and further optimizing the content of V and N without affecting the product performance is the next work.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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