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# Study on the modification of $Cr_{12}$MoV die steel by titanium

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In this paper, $Cr_{12}$MoV die steel was modified by Ti. Microstructural analysis of samples with different Ti contents was performed and mechanical properties were measured. The results show that after the Ti modification, the microstructure of $Cr_{12}$MoV die steel shows obvious changes. The carbide network is broken, and many little lumpy and granular phases are produced as well. The tensile strength and hardness of $Cr_{12}$MoV die steel have a slightly increase, but the impact toughness is improved remarkably. When the Ti content is 0.5 wt.%, the impact toughness is 2.8 times that of unmodified $Cr_{12}$MoV die steel.
**Keywords**: $Cr_{12}$MoV steel, Ti modification, microstructure, mechanical properties.

Описана штамповая сталь $Cr_{12}$MoV, модифицированная с использованием Ti. Проведен микроструктурный анализ и механические свойства образцов с различным содержанием Ti. Результаты показывают, что после модификации Ti микроструктура штамповой стали $Cr_{12}$MoV изменяется. Карбидная сетка разрушена и возникает много мелких кусковых и зернистых фаз. Прочность на растяжение и твердость стали $Cr_{12}$MoV увеличиваются немного, но ударная вязкость значительно улучшается. При содержании Ti 0,5 мас.%, ударная вязкость в 2,8 раза превышает ударную вязкость немодифицированной штамповой стали $Cr_{12}$MoV.

**Дослідження модифікації штампової сталі $Cr_{12}$MoV титаном**. *Fu Sijing, Jiang Binghua, Wang Jing, Cheng Hong*.

Описано штампову сталь $Cr_{12}$MoV, модифіковану з використанням Ti. Проведено мікроструктурний аналіз і виміряно механічні властивості зразків з різним вмістом Ti. Результати свідчать, що після модифікації Ti мікроструктура штампової сталі $Cr_{12}$MoV демонструє зміни. Карбідна мережа зруйнована і виникає багато маленьких кускових і зернистих фаз. Міцність на розтягнення і твердість сталі $Cr_{12}$MoV збільшуються трохи, але ударна в'язкість значно поліпшується. Коли вміст Ti становить 0,5 мас.%, ударна в'язкість у 2,8 рази перевищує ударну в'язкість немодифікованої штампової сталі $Cr_{12}$MoV.

## *1. Introduction*

Since the $Cr_{12}$MoV die steel has the advantages of good hardenability, high hardness, good wear resistance and small heat treatment deformation, it is often used to manufacture cold working dies with heavy load, large batch production and complex shape [1–3]. However, as it is a high carbon and high chrome steel, the coarse ledeburite eutectic segregation will be formed in the $Cr_{12}$MoV die steel inevitably especially in high dimension steel ingots and at low cooling rates; these factors cause the $Cr_{12}$MoV die steel to be prone to brittleness in use. Therefore, it is of great attention for different researchers to improve the toughness of $Cr_{12}$MoV die steel and extend the service

Table 1. The composition of different $Cr_{12}MoV$ die steel

| Sample No. | Element and content, wt.% | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Cr | Mo | V | Si | Mn | S | P | Ti | Fe |
| Z1 | 1.632 | 11.462 | 1.121 | 0.228 | 0.338 | 0.354 | 0.023 | 0.026 | 0 | Balance |
| Z2 | 1.632 | 11.462 | 1.121 | 0.228 | 0.338 | 0.354 | 0.023 | 0.026 | 0.1 | Balance |
| Z3 | 1.632 | 11.462 | 1.121 | 0.228 | 0.338 | 0.354 | 0.023 | 0.026 | 0.2 | Balance |
| Z4 | 1.632 | 11.462 | 1.121 | 0.228 | 0.338 | 0.354 | 0.023 | 0.026 | 0.3 | Balance |
| Z5 | 1.632 | 11.462 | 1.121 | 0.228 | 0.338 | 0.354 | 0.023 | 0.026 | 0.4 | Balance |
| Z6 | 1.632 | 11.462 | 1.121 | 0.228 | 0.338 | 0.354 | 0.023 | 0.026 | 0.5 | Balance |

life of the die. The results show that the toughness of the $Cr_{12}MoV$ die steel can be effectively increased by improving the morphology and distribution of carbides.

Common processes of changing carbide morphology and distribution include forging and heat treatment such as spheroidizing annealing, quenching and tempering, solid solution double refinement, cooling quenching, isothermal quenching etc. [4–6]. However, the forging process on the $Cr_{12}MoV$ die steel will confront some difficulties. On one hand, the irregular and network eutectic carbides in $Cr_{12}MoV$ die steel are distributed along the grain boundaries, where the $Cr_{12}MoV$ die steel melting point decreases, so the forging heating temperature can not be too high. On the other hand, the forging heating temperature can not be too low because of the large deformation resistance of the $Cr_{12}MoV$ die steel. Therefore, the forging temperature range is relatively narrow. In addition, the modification treatment has been used to improve the morphology and distribution of carbides in high carbon and high alloy steel. For example, in [7] authors analyzed the effect of Al–Zn modification on the microstructure and mechanical properties of cast Cr12 die steel. In [8, 9], microstructure and properties of high speed steel modified by RE–Mg–Ti were studied. This paper investigates the properties of modified steel $Cr_{12}MoV$.

## 2. Experimental

The composition of different $Cr_{12}MoV$ die steels was given in Table 1. $Cr_{12}MoV$ die steel scrap, steel scrap, pig iron, ferrochromium, ferromolybedenum, ferrovanadium and ferrotitanium, as raw materials, were melted to produce different $Cr_{12}MoV$ die steels by using a medium frequency vacuum induction furnace, and the vacuum degree was 20 Pa.

The microstructure of different $Cr_{12}MoV$ die steels was analyzed by using an OLYMPUS metallurgical microscope and a SS3400N scanning electron microscope (SEM) equipped with an energy dispersive spectrum (EDS) analysis attachment. The impact toughness, the tensile strength and hardness of different $Cr_{12}MoV$ die steels were tested by a JB30A pendulum impact testing machine, a CMT-6104 electronic universal testing machine and a 200 HRS-150 Rockwell hardness meter, respectively.

## 3. Results and disscussion

As-cast microstructure of Z1–Z6 samples is shown in Fig. 1–6; the microstructure consists of austenite matrix and carbide. It can be seen in Fig. 1 that a coarse carbide network distributes along austenite grain boundaries, and it can be concluded that the coarse carbide network is a carbide compound (Cr, Mo, V, Fe)C. Since the $Cr_{12}MoV$ die steel is a high carbon and high alloy steel, in the stage of solidification, eutectic reaction takes place and the coarse ledeburite will be formed inevitably. As-cast SEM micrographs of samples Z3–Z6 are shown in Fig. 7–10. In comparison with the corresponding $Cr_{12}MoV$ die steel without modification (sample Z1), the microstructure of the $Cr_{12}MoV$ die steel modified with Ti shows obvious differences. The carbide network is broken, and many little lumpy and granular phases occur as well. The amount of these lumpy and granular phases becomes more and more with the increasing of Ti content in the Cr12MoV die steel. Fig. 11 and Fig. 12 show the SEM micrographs and the results of a micro-zone component analysis of samples Z3 and Z6, respectively. The Table 2 and Table 3 give the micro-zone component analysis results of the little lumpy and granular phases. It can be concluded that the phases marked by A and B in Fig. 11 are a carbide compound (Ti, Cr, Mo, V, Fe)C, and the phases marked by A, B, C and D in Fig. 12 are also the carbide compound (Ti, Cr, Mo, V, Fe)C. Fig.

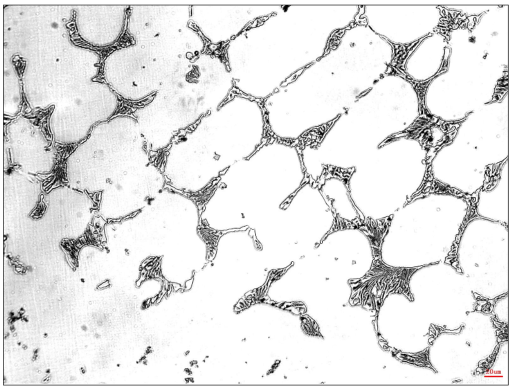

Fig. 1. The microstructure of sample with 0 % Ti

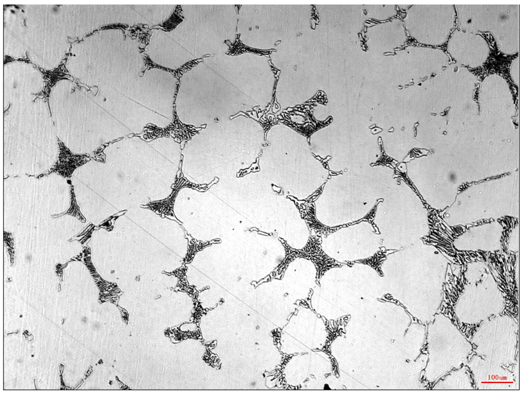

Fig. 2. The microstructure of sample with 0.1 % Ti.

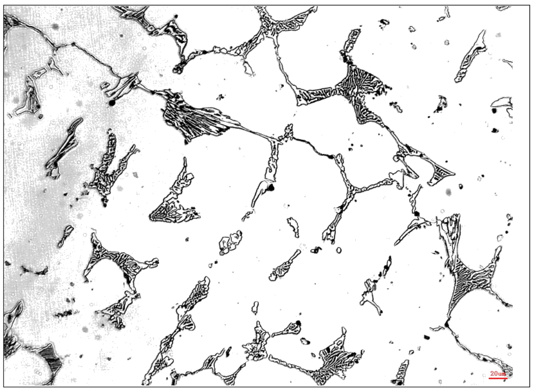

Fig. 3. The microstructure of sample with 0.2 % Ti.

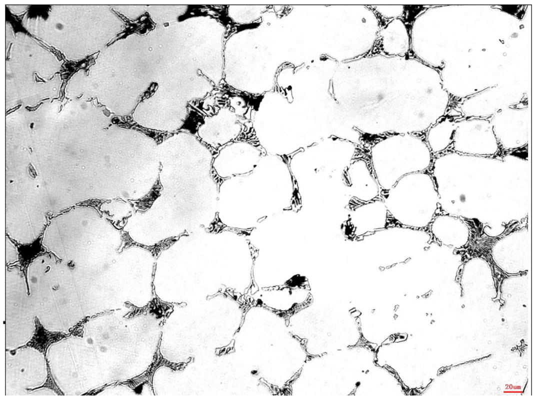

Fig. 4. The microstructure of sample with 0.3 % Ti.

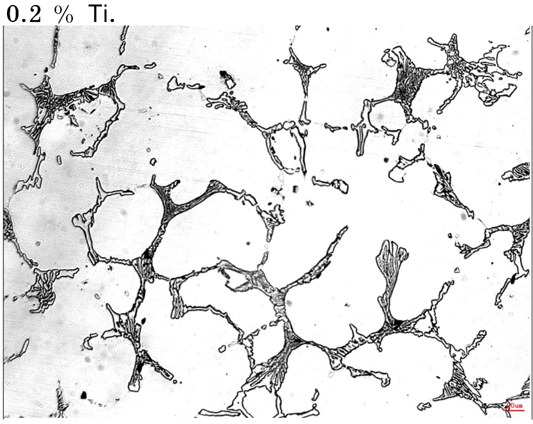

Fig. 5. The microstructure of sample with 0.4 % Ti.

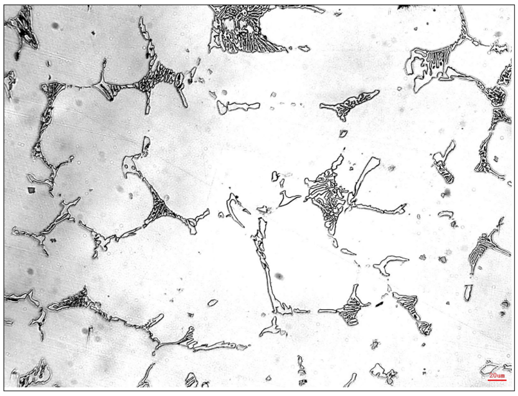

Fig. 6. The microstructure of sample with 0.5 % Ti.

Table 2. The micro-zone component analysis result of sample Z3 (atom %)

| Element | Point A | Point B |
|---|---|---|
| C | 46.75 | 50.87 |
| Ti | 47.55 | 40.74 |
| V | 1.64 | 3.2 |
| Cr | 1.66 | 2.49 |
| Fe | 1.49 | 1.96 |
| Mo | 0.91 | 0.74 |
| Totals | 100 | 100 |

Table 3. The micro-zone component analysis result of sample Z6 (atom %)

| Element | Point A | Point B | Point C | Point D |
|---|---|---|---|---|
| C | 62.52 | 36.8 | 55.15 | 37.19 |
| Ti | 29.69 | 55.33 | 24.91 | 31.04 |
| V | 2.21 | 1.72 | 1.69 | 1.94 |
| Cr | 1.37 | 2.52 | 3.59 | 11.67 |
| Fe | 2.17 | 1.77 | 12.93 | 16.23 |
| Mo | 2.04 | 1.86 | 1.73 | 1.93 |
| Totals | 100 | 100 | 100 | 100 |

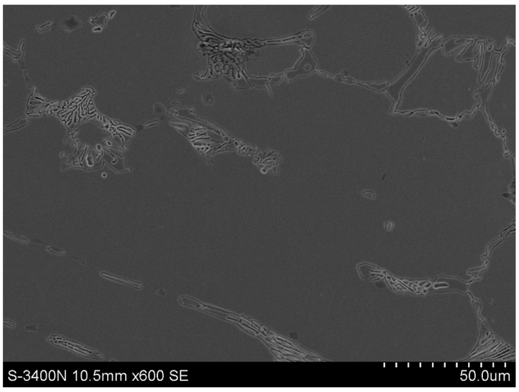


Fig. 7. The SEM micrograph of sample with 0.2 % Ti.

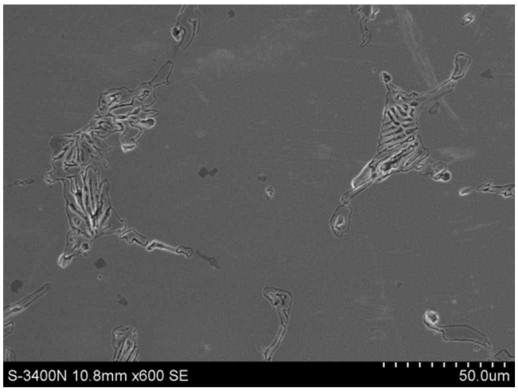


Fig. 8. The SEM micrograph of sample with 0.3 % Ti.

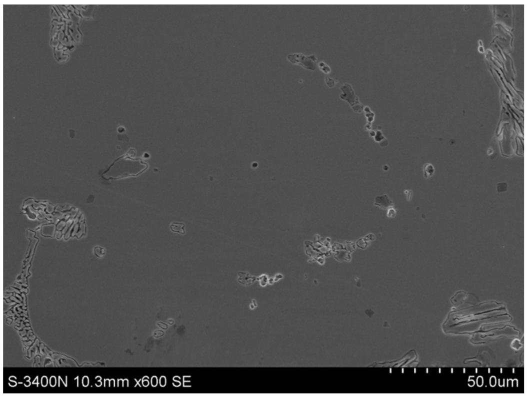


Fig. 9. The SEM micrograph of sample with 0.4 % Ti.

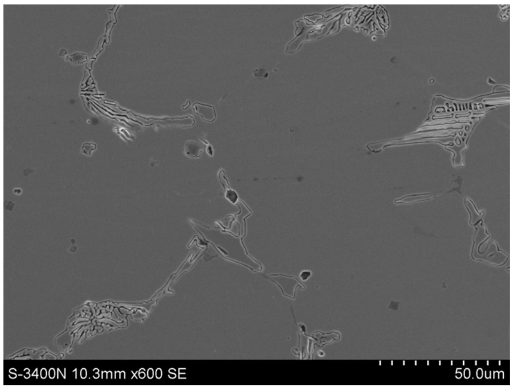


Fig. 10. The SEM micrograph of sample with 0.5 % Ti.

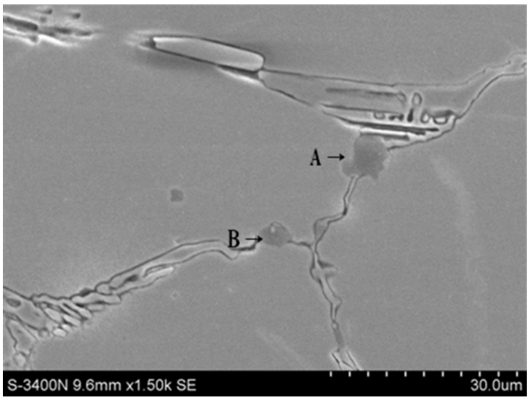


Fig. 11. The SEM micrograph of sample with 0.2 % Ti and the micro-zone component analysis.

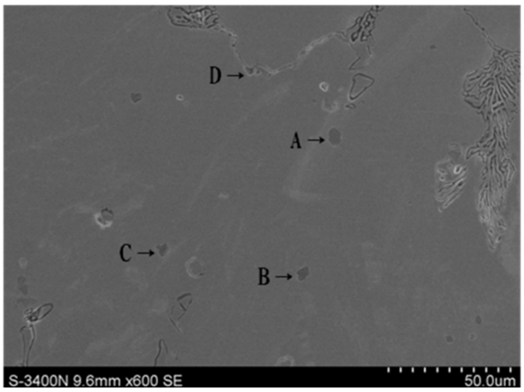


Fig. 12. The SEM micrograph of sample Z3 and the micro-zone component analysis.

13–15 show the effects of the Ti modification on the mechanical properties of the $Cr_{12}MoV$ die steel. It can be observed that the impact toughness has been greatly improved; tensile strength and hardness of the $Cr_{12}MoV$ die steel increase slightly with the increasing of Ti content. When the Ti content is 0.5 wt.%, the impact toughness, tensile strength and hardness of the $Cr_{12}MoV$ die steel is the best. The impact toughness is raised by 1.8 times and reaches to 11.3 $J/cm^2$, the tensile strength increases by 5.88 % and reaches to about 630 MPa, and the hardness increases by 4.68 %.

The nucleation rate can be calculated by the following equation:

$$\mu = \frac{NkT}{h}\exp(-\frac{\Delta G_A}{kT})\exp(-\frac{\alpha\sigma^3}{kT(\Delta G_V)^2}), \quad (1)$$

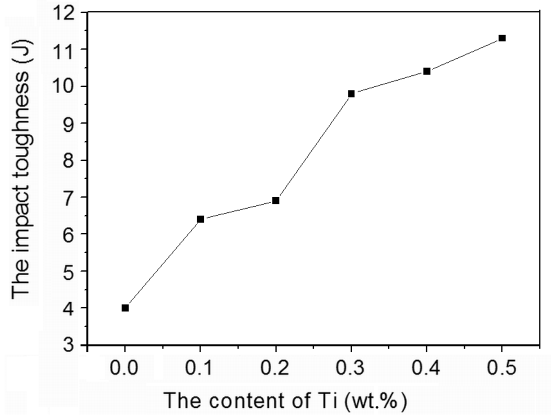


Fig. 13. The effect of Ti content on impact toughness of $Cr_{12}MoV$ stamp steel.

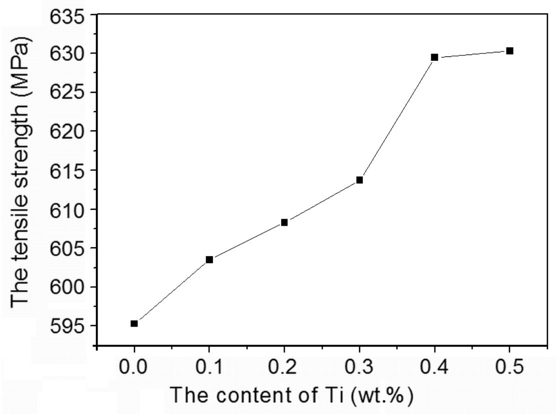


Fig. 14. The effect of Ti content on tensile strength of $Cr_{12}MoV$ stamp steel.

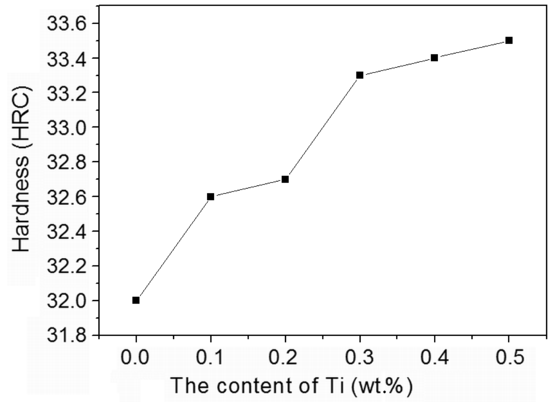


Fig. 15. The effect of Ti content on hardness of $Cr_{12}MoV$ stamp steel.

$$\Delta C_V = \Delta G_V - \frac{V\Delta H}{T_0}\Delta T, \qquad (2)$$

where $\mu$ is the nucleation rate; $N$ is the total number of atoms in per unit liquid volume; $h$ is the Pranck constant; $k$ is the Boltzmann constant; $T$ is the thermodynamic temperature; $\Delta G_A$ is the activation energy of atom crossing the solid-liquid interface; $\alpha$ is the Gibbs free energy difference between liquid and solid per unit volume; $V$ is the crystal nucleus volume; $\Delta H$ is the enthalpy change; $T_0$ is the theoretical solidification temperature; $\Delta T$ is the undercooling degree.

After the Ti modification, the reasons that the mechanical properties of the $Cr_{12}MoV$ die steel have been improved are as follows. Firstly, the contents of oxygen, sulfur and phosphorus in the modified $Cr_{12}MoV$ die steel reduce, which makes the eutectic transformation temperature of the $Cr_{12}MoV$ die steel decrease, and the phase transformation undercooling degree increases. According to the formulas (1) and (2), it can be known that the Gibbs free energy difference decreases with the undercooling degree increase, resulting in the increase of the nucleation rate. Therefore, the microstructure of the $Cr_{12}MoV$ die steel is refined. Secondly, the modifier Ti can react with C in the $Cr_{12}MoV$ steel melt and form a large number of refractory TiC particles. TiC can be formed prior to MC-type carbide in the cooling process of the liquid $Cr_{12}MoV$ die steel. Since both TiC and MC-type carbides have face-centered cubic lattices, and a preferential growing direction of TiC crystal and MC-type carbide crystal is the [100] crystallographic orientation during the crystallization process, and the TiC crystals and MC-type carbide crystals are surrounded by (111) planes when the crystallization completes; as a result, the crystal mismatch between TiC and MC-type carbides is 4.1 % (the lattice parameters of TiC and MC-type carbide are 0.432 nm and 0.415 nm, respectively). Because the crystal mismatch between TiC and Mc-type carbide is very little, so TiC can act as the effective solidification nucleus of MC-type carbide; this causes both primary and eutectic cementite granulated and refined, which obviously improves the morphology and distribution of carbide in the $Cr_{12}MoV$ die steel. Thirdly, TiC and austenite are also face-centered cubic lattices, the lattice parameter of TiC is quite close to that of austenite (the lattice parameter of austenite is 0.357 nm), so TiC acts as the effective solidification nucleus of austenite and causes the refinement of austenite dendrites. In addition, based on the theory of fracture mechanics [8], the hardness depends mainly on the amount of carbides and the hardness of the $Cr_{12}MoV$ die steel matrix, so the hardness of the $Cr_{12}MoV$ die steel has little change.

## *4. Conclusions*

After the Ti modification, the morphology and distribution of eutectic carbide in the $Cr_{12}MoV$ die steel are improved. With the increase of the Ti content, the carbide network is broken, and many little lumpy and granular (Ti, Cr, Mo, V, Fe)C phases occur.

The impact toughness, tensile strength and hardness of the $Cr_{12}MoV$ die steel are improved by the Ti modification. With the increase of the Ti content, the tensile strength and hardness of the $Cr_{12}MoV$ die steel increase to a certain extent, and the impact toughness increases significantly. When the content of Ti is 0.5 wt. %, the impact toughness of the $Cr_{12}MoV$ die steel reaches 11.3 J/cm$^2$, which is 2.8 times that of unmodified $Cr_{12}MoV$ die steel.

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