Study on the modification of Cr₁₂MoV die steel

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In this paper, $Cr_{12}MoV$ die steel was modified using Ti. Microstructural analysis and mechanical properties of samples with different Ti content were performed. The results show that after the Ti modification, the microstructure of $Cr_{12}MoV$ die steel shows obvious change. 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: Cr₁₂MoV steel, Ti modification, microstructure, mechanical properties.

В работе сталь $Cr_{12}MoV$ модифицирована с использованием Ті. Проведен микроструктурный анализ и исследованы механические свойства образцов с различным содержанием Ті. Результаты показывают, что после модификации Ті микроструктура штампованной стали $Cr_{12}MoV$ изменяется. Карбидная сетка разрушается, образуется много мелких кусковых и зернистых фаз. Прочность на растяжение и твердость стали $Cr_{12}MoV$ немного увеличиваются, но ударная вязкость значительно улучшается. Когда содержание Ті составляет 0,5 мас.%, ударная вязкость в 2,8 раза превышает ударную вязкость немодифицированной штампованной стали $Cr_{12}MoV$.

Дослідження модифікації інструментальної штампованої сталі Cr_{12} MoV. Fu Sijing, Jiang Binghua, Wang Jing, Cheng Hong

У роботі сталь $Cr_{12}MoV$ було модифіковано з використанням Ті. Проведено мікроструктурний аналіз і досліджено механічні властивості зразків з різним вмістом Ті. Результати показують, що після модифікації Ті мікроструктура штампованої сталі $Cr_{12}MoV$ змінюється. Карбідна сітка руйнується, утворюється багато дрібних кускових і зернистих фаз. Міцність на розтягнення і твердість сталі $Cr_{12}MoV$ трохи збільшуються, але ударна в'язкість значно поліпшується. Коли вміст Ті становить 0,5 мас.%, ударна в'язкість у 2,8 рази перевищує ударну в'язкість немодифікованої штампованої сталі $Cr_{12}MoV$.

1. Introduction

Due to the advantages of good hardenability, high hardness, good wear resistance and small heat treatment deformation, $Cr_{12}MoV$ die steel is often used to manufacture cold working dies with heavy load, large batch production and complex shape [1-3]. However, as the $Cr_{12}MoV$ steel is a high carbon and high chrome one, the coarse ledeburite eutectic segregation will be formed inevitably especially in high dimension steel ingots and at low cooling rate, which causes the $Cr_{12}MoV$ steel to be prone to brittleness in use. Therefore, great attention of different researchers was at-

Functional materials, 27, 1, 2020



Fig. 1. Microstructure of sample Z1.



Fig. 3. Microstructure of sample Z3.

tracted to improve the toughness of $Cr_{12}MoV$ die steel and extend the dies service life. The results show that the toughness of $Cr_{12}MoV$ 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 $Cr_{12}MoV$ die steel confronts some difficulties: on one hand, the irregular and network eutectic carbides in $Cr_{12}MoV$ die steel are distributed along 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 $Cr_{12}MoV$ die steel. Therefore, the forging temperature range is relatively narrow. In addition, the modification treatment is used to improve the morphology and distribution of carbides in high carbon and high alloy





Fig. 4. Microstructure of sample Z4.

steel. For example, Wei Daibin et al. [7] analyzed the effect of Al–Zn modification on the microstructure and mechanical properties of cast Cr12 die steel. Fu Hanguang et al. [8, 9] studied the microstructure and properties of high speed steel modified by RE–Mg–Ti. However, there are a few reports on the modification of $Cr_{12}MoV$ die steel.

2. Experimental

The compositions of different samples of $Cr_{12}MoV$ die steel are given in Table 1. Cr₁₂MoV die steel scrap, steel scrap, pig iron, ferrochromium, ferromolybedenum, ferrovanadium and ferrotitanium as raw materials, were melted to produce different samples of $Cr_{12}MoV$ die steel by using a medium frequency vacuum induction furnace at the vacuum degree of 20 Pa. The microstructure of different samples of Cr₁₂MoV die steel was analyzed by using OLYMPUS metallurgical microscope and SS3400N scanning electronic microscope (SEM) equipped with an energy dispersive spectrum (EDS) analyzer. The impact toughness, the tensile strength and hardness of different $Cr_{12}MoV$ samples were tested by a

Functional materials, 27, 1, 2020



Fig. 5. Microstructure of sample Z5.



Fig. 7. SEM micrograph of sample Z3.

JB30A pendulum impact testing machine, a CMT-6104 electronic universal testing machine and a 200 HRS-150 Rockwell hardness meter, respectively.

3. Results and discussion

As-cast microstructure of samples Z1-Z6is shown in Figs. 1-6; the microstructure consists of the 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. Because $Cr_{12}MoV$ is a high carbon and high alloy



Fig. 6. Microstructure of sample Z6.



Fig. 8. SEM micrograph of sample Z4.

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 Figs. 7-10. Compared to the corresponding $Cr_{12}MoV$ die steel sample without modification (sample Z1), the microstructure of the $Cr_{12}MoV$ die steel sample modified with Ti shows obvious difference. The carbide network is broken, and many little lumpy and granular phases are produced as well. The content of the lumpy and granular phases becomes more and more in the $Cr_{12}MoV$ die steel sample with the increasing of Ti content. Fig. 11 and Fig. 12 show

Sample	Element and content (wt.%)									
No.	С	Cr	Мо	V	Si	Mn	S	Р	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

Table 1. Compositions of different $Cr_{12}MoV$ die steel samples

Functional materials, 27, 1, 2020



Fig. 9. SEM micrograph of sample Z5.



Fig. 11. SEM micrograph of sample Z3 and the micro-zone element analysis.

the SEM micrographs and the micro-zone element analysis of the samples Z3 and Z6, respectively. The Table 2 and Table 3 give the results of the micro-zone element analysis of the little lumpy and granular phases. It can be concluded that the phases marked A and B in Fig. 11 are carbide (Ti, Cr, Mo, V, Fe)C compounds, and the phases marked A, B, C and D in Fig. 12 are also the carbide compounds (Ti, Cr, Mo, V, Fe)C.

Figs. 13–15 show the effects of the Ti modification on the mechanical properties of $Cr_{12}MoV$ die steel. It can be observed that the impact toughness is greatly improved; tensile strength and hardness of $Cr_{12}MoV$ die steel increase slightly with the increasing of Ti content. When Ti content is 0.5 wt.%, the impact toughness, tensile strength and hardness of $Cr_{12}MoV$ die steel are the best. The impact toughness raises 1.8 times and reaches to 11.3 J/cm², the tensile strength increases by 5.88 % and reaches about 630 MPa, and the hardness increases by 4.68 %.

The nucleation rate can be calculated by the following equations:



Fig. 10. SEM micrograph of sample Z6.



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

Table 2. Micro-zone element analysis of sample Z3 (atomic %)

Element	Point A	Point B
С	46.75	50.87
Ti	47.55	40.74
V	1.64	3.2
Cr	1.66	2.49
Fe	1.49	1.96
Мо	0.91	0.74
Totals	100	100

Table 3. The micro-zone element analysis of sample Z6 (atomic %)

Element	Point A	Point B	Point C	Point D
С	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
Мо	2.04	1.86	1.73	1.93
Totals	100	100	100	100

Functional materials, 27, 1, 2020



Fig. 13. Effect of Ti content on impact toughness of $Cr_{12}MoV$ die steel.



Fig. 15. Effect of Ti content on hardness of $Cr_{12}MoV$ die steel.

$$\mu = \frac{NkT}{h} \exp\left(-\frac{\Delta G_A}{kT}\right) \exp\left(-\frac{\alpha\sigma^3}{kT(\Delta G_V)^2}\right).$$
 (1)
$$\Delta G_V = -\frac{V\Delta H}{T_0} \Delta T,$$
 (2)

where μ is the nucleation rate; N is the total number of atoms in per unit liquid volume; h is the Planck constant; k is the Boltzmann constant; T is the thermodynamic temperature; ΔG_A is the activation energy of atom crossing the solid-liquid interface; α is the Gibbs free energy difference between liquid and solid per unit volume; V is the crystal nucleus volume; ΔH is the enthalpy change; T_0 is the theoretical solidification temperature; ΔT is the undercooling degree.

The reasons that the mechanical properties of $Cr_{12}MoV$ die steel have been improved after Ti modification are as follows. Firstly, the content of oxygen, sulfur and

Functional materials, 27, 1, 2020



Fig. 14. Effect of Ti content on tensile strength of $Cr_{12}MoV$ die steel.

phosphorus in the modified $Cr_{12}MoV$ die steel reduces; as a result, the eutectic transform temperature of $Cr_{12}MoV$ die steel decreases, and the phase transformation undercooling degree increases. According to Eqs. (1) and (2), the Gibbs free energy difference decreases with the undercooling degree increase, resulting in the increase of the nucleation rate. Therefore, the microstructure of $Cr_{12}MoV$ die steel is refined. Secondly, the Ti modificator can react with C in the $\mbox{Cr}_{12}\mbox{MoV}$ steel melt and form a large number of refractory TiC particles. TiC can form prior to MC-type carbide in the cooling process of the liquid $Cr_{12}MoV$ die steel. Both TiC and MC-type carbides have face-centered cubic lattices, and the preferential direction growth of TiC and MC-type carbide crystals is [100] crystallographic orientation during the crystallization process, therefore, the TiC and MCtype carbide crystals are surrounded by (111) plane 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). The crystal mismatch between TiC and MC-type carbides is very little, so, TiC can act as an effective solidification nucleus of MC-type carbides; this causes both primary and eutectic cementite granulating and refining, which obviously improves the morphology and distribution of the carbides in $Cr_{12}MoV$ die steel. Thirdly, TiC and austenite have 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 an 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 $Cr_{12}MoV$ die steel has little change.

4. Conclusions

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

The impact toughness, tensile strength and hardness of $Cr_{12}MoV$ die steel are improved by the Ti modification. With the increase of Ti content, the tensile strength and hardness of $Cr_{12}MoV$ 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 $Cr_{12}MoV$ die steel reaches 11.3 J/cm², which is 2.8 times that of unmodified $Cr_{12}MoV$ die steel.

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