The Study on thermodynamics of martensitic transformation in Laser additive manufacturing alloy steel

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Abstract: Based on the characteristics of metallurgical non-equilibrium solidification behavior during laser additive manufacturing alloy steel, the basic theory of thermodynamics of martensitic transformation precipitating in the process of selective laser melting deposition of alloy steel were introduced, then binary, ternary and multicomponent alloy steel systems thermodynamic evolution process were revealed. Combined with selective laser melting deposited 24CrNiMo alloy steel experiment, laser additive manufacturing 24CrNiMo alloy steel CCT curve and the thermodynamic data-martensite transformation starting temperature were simulated. Simulated by using simulation software and calculated with empirical formula the temperature of martensitic transformation starting point are 366.6℃ and 361.102℃ respectively. It is expected that these studies can provide theoretical reference for laser additive manufacturing brake disc of High-speed rail.

1.Introduction

As one of the revolutionary frontier technologies in the manufacturing field laser additive manufacturing has attracted a great deal of attention and has been developing rapidly worldwide. High speed rail is the strategic leading industry of people's livelihood and its brake disc is key parts of the core equipment guaranteeing the safe and stability of the train operation. Being the traditional method of producing brake discs, casting has some problems such as complex process, long production cycle, short product life. Instead, laser additive manufacturing have distinctive features of one forming for complex structure and short process flow. However, it is a non-equilibrium solidification process with complex organization phase transition behavior. Meanwhile due to cumulative effect of heat from multilayer cladding studying thermodynamics has an important effect on the structure and performance of the final forming alloy.

So far, there is little research on non-equilibrium solidification behavior of alloy steel produced by laser additive manufacturing. As one of the most important phases in alloy steel, martensitic transformation mechanism is the basis for successful manufacture alloy steel with good microstructure and properties. However, process design closely related to the non balance technology is still mainly rely on empirical or semi quantitative theory not to meet the current requirements of alloy steel by laser material manufacturing [1]. It is urgent for people to make new

breakthroughs in solidification theory research.
Thermodynamic development of martensitic precipitating from 24 CrNiMo alloy steel, one material is used to manufacture high speed rail brake disc. This paper analyzed basic theory relative to the mechanism of martensitic phase, simulated the temperature of martensitic transformation starting point (Ms) and CCT curves, and calculated Ms temperature with empirical formula, expected to provide a valuable basic theory for high speed rail brake disc made of laser additive manufacturing.

2. The development of thermodynamics martensitic transformation

Due to rapid heat and cool (cooling rate is above 10^3°C/s) non-equilibrium phase martensite can be observed in laser selective deposited 24CrNiMo alloy steel. Thus, thermodynamic of martensitic transformation are introduced, including thermodynamic model, such as Neural network model, Super member model [3] etc. Hsu T. Y. [2] defined the physical meaning of Gibbs free energy of martensitic transformation, studied martensitic transformation thermodynamics systematically, including binary, ternary alloy steel system. In recent years, some researchers have studied Ms temperature of polynary system iron alloy. Using software to simulate the thermodynamics of martensitic transformation has some reference significance for the experimental study of high-speed brake disc.

2.1 Thermodynamics of martensitic formation in binary alloy steel

While studying the binary alloy steel, Hsu T Y [2] gave the Gibbs free energy formula of martensitic transformation as follows:

$$\Delta G^{\gamma\rightarrow m} = \Delta G^{\gamma\rightarrow\alpha} + \Delta G^{\alpha\rightarrow m} \quad (1)$$

In Eq.(1), $\Delta G^{\gamma\rightarrow\alpha}$ is the energy to extend the nuclear structure of the somatic structure, and $\Delta G^{\alpha\rightarrow m}$ is the energy to made the nuclear structure martensite. Hsu T Y defined the temperature at which the Gibbs free energy of martensitic transformation is zero as the starting point of martensitic transformation. when the value of first part in Eqs.(1) is zero the corresponding temperature is T_0. D-value between the Gibbs free energy between T_0 and M_s temperature is called the martensitic transformation driving force, that is - $\Delta G^{\gamma\rightarrow\alpha}=0$ or $\Delta G^{\alpha\rightarrow m}=0$.
The phase change driving force ($\Delta G^{\gamma\rightarrow\alpha}$) can be calculated by

$$\Delta G^{\gamma\rightarrow\alpha} = (1-Xc)\Delta G_{Fe}^{\gamma\rightarrow\alpha} + (1-Xc)RT\ln\frac{\alpha_{Fe}^{a}}{\alpha_{Fe}^{\gamma}} + XcRT\ln\frac{\gamma_c^a}{\gamma_c^\gamma} \quad (2)$$

In Eq.(2), α_i^j is the activity of i element in the Solid solution j, correspondingly γ is the activity coefficient, X_c is mass percentage of element C.
Using geometric model to calculate the activity value of iron element in ferrite and austenite is feasible. Pure iron Gibbs free energy change can not only be calculated through a variety of models, but also can be calculated by the latest thermodynamic data. In order to calculate $\Delta G^{\alpha\rightarrow m}$ Hsu T Y derived the following formulas:

$$\Delta G^{\alpha\rightarrow m} = \varphi V_m \sigma_{M_S} + \sum \Gamma \quad (3)$$

Combined the third and fourth equations as well as the above data, the following formula can be obtained:

$$\Delta G^{\gamma\rightarrow m} = \Delta G^{\gamma\rightarrow\alpha} + 5[13 + 280X_C + 0.02(800 - M_S)] + 217 \quad (4)$$

2.2 Thermodynamics of martensitic transformation in ternary alloy steel

Considering the Fisher model and the binary system regular solution model, a ternary regular solution model was proposed [2]:

$$\Delta G_{Fe-x-c}^{\gamma\rightarrow\alpha} = (1 - X_c - X_i)\Delta G_{Fe}^{\gamma\rightarrow\alpha} + X_c RT\ln\frac{\gamma_c^a}{\gamma_c^\gamma} + X_i\Delta G_i^{\gamma\rightarrow\alpha} + \Delta\Omega^{\gamma\rightarrow\alpha} \quad (5)$$

Considering Fisher--Hsu method and Zener two parameteric method $\Delta G_{Fe-x-c}^{\gamma\rightarrow\alpha}$ was derived as:

$$\Delta G_{Fe-x-c}^{\gamma\to\alpha} = (1-X_c)\left[\Delta G_{Fe}^{\gamma\to\alpha}(T-100X_i\Delta T_{mag})+141X_i(\Delta T_{mag}-\Delta T_{N,M})\right]\Delta G_{Fe}^{\gamma\to\alpha}$$

$$+(1-X_c)\frac{1}{5}RT\left[3\ln\frac{3-8X_c}{3(1-X_c)}-\ln\frac{1-6X_c}{1-X_c}\right]+X_cRT\ln\frac{\gamma_c^{\alpha}}{\gamma_c^{\gamma}}+\Delta G^* \quad (6)$$

Where $\Delta G^* = -2.13+10^\wedge 5x_c^2+9.13x_cT$ J/mol

It is feasible to estimate the value of $\Delta G^{\alpha\to m}$and then calculate the Ms and martensitic transformation driving force using the same method as binary iron alloys.

2.3 Thermodynamics of martensitic transformation in multicomponent alloys

It is expected to generalized formula of the ternary alloy by using super member model [3] to calculate thermodynamics of martensitic transformation in multicomponent alloys. Fe-ΣX_i is regarded as a super member S in the alloy of Fe-ΣX_i-C(X_i=Si，Mn，Cr，Ni，Mo，Ti ect.). And then it is similar to Fe-C alloy. So multicomponent alloys thermodynamics can be calculated by using the ternary alloy thermodynamics model .

The coresponding a_{Fe}^{γ}, a^{a}_{Fe} and$\Delta G_{Fe}^{\gamma\to\alpha}$ in the binary alloy model can be substituted by a_s^{γ}, a_s^{a} and $\Delta G_S^{\gamma\to\alpha}$ respectively. Their calculations are as follows:

$$\ln\alpha_s^a = \frac{3}{z_\alpha-3}\ln\frac{3-z_\alpha x_\alpha}{3(1-x_\alpha)} \quad (7)$$

$$\ln\alpha_s^a = \frac{3}{z_\alpha-3}\ln\frac{3-z_\alpha x_\alpha}{3(1-x_\alpha)} \quad (8)$$

$$\Delta G_S^{\gamma\to\alpha} = 141\sum x_i(\Delta T_M^i-\Delta T_{NM}^i)+\Delta G_{Fe}^{\gamma\to\alpha}\{T-100\sum x_i\Delta T_M^i\} \quad (9)$$

2.4 Empirical formula of calculating Ms temperature in multicomponent alloy

Using thermodynamic model to calculate directly Ms temperature of SLM deposited 24CrNiMo alloy steel is more complex and the task is heavy due to more alloying elements. To simply calculation and reduce work difficulty Ms temperature can be calculated with empirical formula. More importantly, the value can be reference for selective laser melting deposited 24CrNiMo alloy steel experiment. Then continue studying its thermodynamics model to lay the theoretical foundation for the experiment of the high speed rail brake disc by Laser additive manufacturing technology. Some Empirical formulas [4] of calculating Ms temperature are as follows:

Table1 Empirical formula of calculating Ms temperature

Empirical formula		scope of application
M_s =539-423C-30.4Mn-12.1Cr-17.7Ni-7.5Si-7.5Mo +10Co		High-alloy steel
M_s =499-292C-32.4Mn-22Cr-16.2Ni-10.8Si-10.8Mo+10Co	（10）	low-alloy steel
M_s =767.7-305.4C-30.6Mn-8.9Cr-16.6Ni-14.5Si+2.4Mo+53V +8.58Co+40.4Al+7.4W-11.3Cu+510.4Nb	（11）	Complex component alloy steel

Using equation 12 to calculate Ms temperature of low-alloy steel is proved to be closer to the experimental value, and its error is less than 11.5℃ [5]. According to neural network [4] model it achieved empirical formula 10 , which is suitable for multicomponent alloy steels, but is limited strictly by the content of alloying elements. Albin Stormvinter [6] etc. introduced the relationship between Ms temperature and martensitic transformation driving force at the Ms temperature:

$$\Delta G_m^{*\gamma\to\alpha} = 3857.7-3.3414M_s(K) \quad (12)$$

Ms temperature not only can be calculated by using simple regression empirical formula, but also can be calculated by using the simulation software (Jmatpro). They provide some reference for the experiment of the high speed rail brake disc by laser additive manufacturing technology.

3. Simulation and calculation of martensitic phase in 24CrNiMo alloy steel by laser selective melting

The experimental parameters are as follows. Laser power is 2200W, scanning rate is 8mm/s, defocusing distance is 304. Fig.1(a) and (b) are the metallographic and SEM photographs of the 24CrNiMo alloy sample respectively. It is seen that there exist Martensitic phase in the 24CrNiMo alloy during non-equilibrium cooling process from these two pictures.

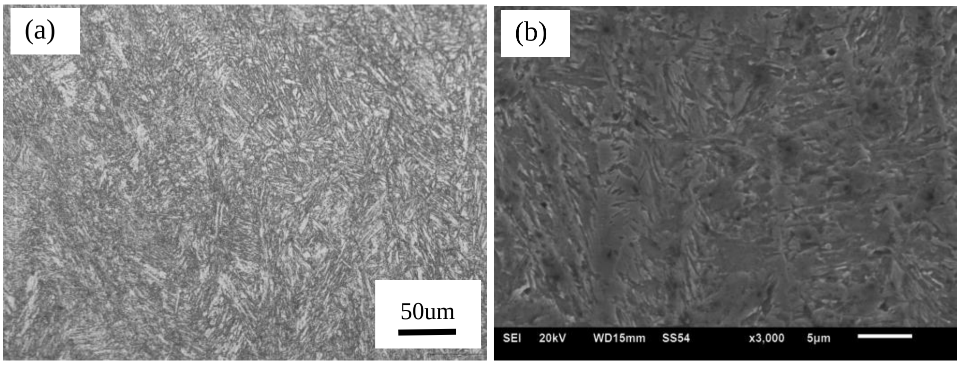

Fig. 1 metallographic and SEM photographs of the 24CrNiMo alloy by laser selective melting

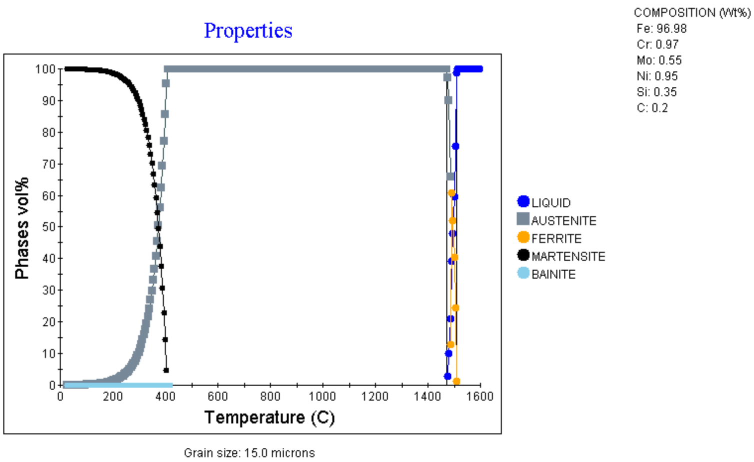

Fig. 2 Relation schema between phase content and temperature of SLM deposited 24CrNiMo alloy steel

Fig. 2 is a non-equilibrium phase diagram of 24CrNiMo alloy steel simulated by Jmatpro software, with a cooling rate of 1000℃/S based on experiment. Fig. 3 is a CCT curve of 24CrNiMo alloy steel simulated by the software. It can be seen from fig. 2 and fig.3 that the martensitic phase of the alloy steel is precipitated in the rapid cooling condition. The Ms temperature of 24CrNiMo alloy can be simulated using the relationship between martensitic transformation and the hardness module in the Jmatpro software. It is 366.6℃. The temperature calculated with the empirical formula （Eq.10）is 361.102 ℃.

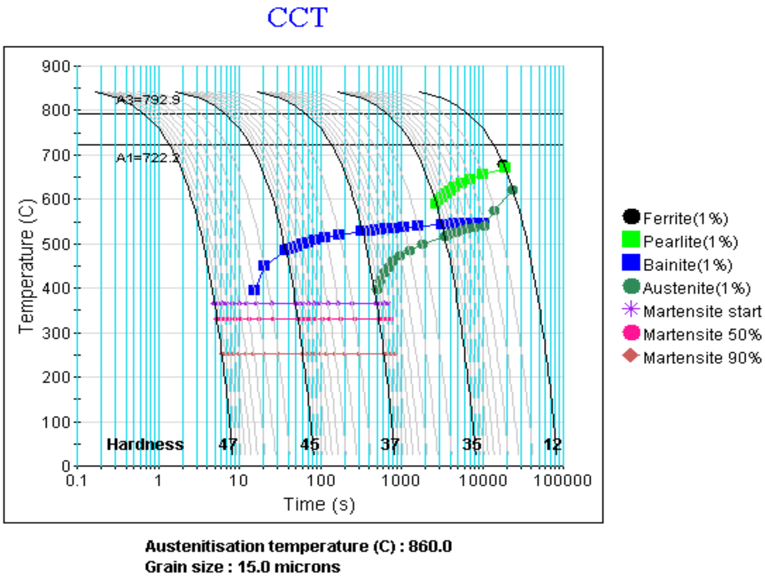

Fig.3 CCT curve of laser selective melting deposited 24CrNiMo alloy steel

4. Conclusions

A simulation of the selective laser melting of 24CrNiMo alloy steel martensite start temperature is 366.6℃, and calculated temperature by using empirical formula is 361.102℃. This value has positive reference value for the high speed rail brake disc experiment. Describing of the thermodynamic has certain guiding significance for selective laser melting of 24CrNiMo alloy steel thermodynamics of martensitic transformation, hoping to generalize the martensitic transformation thermodynamics model in the ternary alloy by super member algorithm. Ensuring it can be applied to the martensitic transformation of 24CrNiMo alloy steel, and then lay the foundation for the manufacture of high speed rail brake disc with laser additive manufacturing.

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References

[1] H.F. Wang, K.Wang, W.W. Kuang , Chinese Science: Technical Science, 45(2015) 358-376.
[2] T. Y. Hsu, Martensitic transformation and martensite， Second ed., Science Press, Bei jing,1999. Reference to a chapter in an edited book: chapter 6.
[3] Y.Wang , K. Zhao ,G.Tang, Heat Treatment of Metals, 38(2013)1-5.
[4] P. Liu, L. He, Y.X. Zhange, Development and Application of Materials, 30(2015) 88-92.
[5] C. Liu, Z. Zhao, D.O. Northwood, Journal of Materials Processing Tech, 113(2001) 556-562.
[6] A. Stormvinter, A. Borgenstam, J. Ågren, Metallurgical and Materials Transactions, 43(2012) 3870-3879.