Rev. Adv. Mater. Sci. 33 (2013) 305-310

CALCULATION AND EXPERIMENTS ON THE SOLIDIFICATION BEHAVIOR OF SINGLE CRYSTAL SUPERALLOY CONTAINING Ru

Lirong Liu[1], Tao Jin[2], Jingjing Liang[2], Xiaofeng Sun[2] and Zhuangqi Hu[2]

[1]Materials Science and Engineering School, Shenyang University of Technology, Shenyang, 110023, China
[2]Department of Superalloy, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, China

Received: October 17, 2011

Abstract. In this paper, the calculation and experiments on solidification behavior were investigated in single crystal superalloys with different content of Ru. The solidification paths and phase composition were calculated by Scheil model in Thermo-Calc software.
The results calculated by Scheil model show that liquid, gamma, gamma prime, NiAl and P phase would occur sequentially during solidification, while the equilibrium phases calculated by Thermo-Calc software include liquid, gamma, gamma prime, mu, P-phase in single crystal superalloys with different content of Ru. The testing results show that the single crystal superalloys with different content of Ru were solidified with dendritic structure. Except for γ/γ' eutectics, some NiAl based β phase enriched in Ru element with blocky morphology formed in the interdendrtic region. With the increase of Ru, the amount of NiAl based β phase will be enlarged. During long term thermal exposure for 500 h, mu-phase with needle-like shape was found in these alloys. It was found that the transformation temperatures measured by DSC has the same tendency to the results calculated by Scheil model in Thermo-Calc software.

1. INTRODUCTION

HOT-section materials developments have made substantial contributions to the performance of both aircraft engines and land-based gas turbines. For example, advances in directional solidification technology for Ni-based superalloy blades have provided single-crystal components with higher temperature resistance. As a result of developments in both alloy chemistry and casting technology, the temperature capabilities of high-pressure turbine blades have increased by more than 125 °C in the past approximately 30 years.

Recently, a fourth generation of single crystal superalloys with Ru as a new alloying addition has been under development [1-3]. Ru additions to Ni-base superalloys have also been reported to increase microstructural stability during high temperature exposures and lower the propensity for the formation of topologically closepacked phases, thus improving the stress rupture life [1]. Thus, the creep properties of some experimental Ni-base single-crystal superalloys have been reported to improve significantly with Ru additions [2,4]. However, Ru element is a precious metal elementwhich is similar to rhenium. Considering the costs, to date, the investigation on Ru-containing Ni-base superalloys has been conducted over a relatively narrow range of composition.

Simulation has become an important tool in materials science. Calculations replace time consuming experiments and help to develop and process more and more complex materials. By now there is a variety of models for the simulation of microstructure, starting from the CALPHAD approach to the phase field method. Increasing

Corresponding author: : Lirong Liu, e-mail: lrliu866@sohu.com

accuracy is usually paid for by increasing complexity of the models and more computational time. However, here we calculated solidification behavior under equilibrium conditions and according to the Scheil model [5,6]. This model assumes perfect mixing in the liquid and no solute back diffusion in the solid. No kinetic data are needed and calculations are fast. Therefore the Scheil model is frequently used to estimate the solidification sequence and the fraction solid as a function of temperature [7]. Both equilibrium and Scheil calculations were performed using the software Thermo-Calc. Results are compared to experimental data. The single crystal superalloys were produced by directional solidification furnace with high gradient. The solidification characteristics of alloys with different Ru were studied.

2. EXPERIMENTAL

The experimental single crystal superalloys used in this investigation are three alloys containing different content of Ru (0, 1.5, 3 wt.%), whose main alloying elements are Cr, Al, W, Re, Co, Ta, Mo, and Ru. Three alloys are defined as 0Ru alloy, 1.5Ru alloy, and 3Ru alloy. The Scheil module and Ni database of the Thermo-Calc software was used to predict the nonequilibrium solidification process. Solidification and cooling were simulated in a temperature interval from liquidus temperature down to 900 °C. This temperature range covers the solidification and also the phase transformations in the solid state of superalloy. The solidification paths and phase composition at different temperature were calculated by Scheil model in Thermo-Calc software. The Scheil module is an implementation of the Scheil¨C gullive which assumes that diffusion occurs in model infinitely fast within the liquid phase and that there is no diffusion in the solid phases that form. The single crystal bars with the dimension of Ø16*160 mm were produced in <001> direction by screw selection method with the mould drawing rate of 6 mm/min in a directional solidification vacuum induction furnace. EBSD technique was used to determine the longitudinal crystal orientation of each bar. The single crystal bars with the longitudinal crystal orientation within 10 degree of the <001> direction were used in this study. The effects of alloy chemistry on solidus and liquidus temperatures as well as other high temperature phase transformations were investigated by differential scanning calorimetry (DSC) instrument. The microstructures of as cast and after heat treatment are examined on S3400N scanning electron microscope (SEM) equipped with energy dispersive spectrometers (EDS).

3. RESULTS AND DISCUSSIONS

The equilibrium and nonequilibrium solidification behaviors predicted for the three alloys through the Scheil simulation performed in this study are shown in Fig. 1. The results calculated by Scheil model show that liquid phase, gamma phase, gamma prime phase, NiAl phase and P phase would occur sequentially during solidification, while the equilibrium phases calculated by Thermo-Calc software include liquid phase, gamma phase, gamma prime phase, mu-phase in the three alloys with different content of Ru. From the comparison, it can be concluded that the NiAl phase is the non-equilibrium phase in the single crystal superalloy.

The initial formation temperatures for each of the predicted phases can be estimated as a corollary to the graphical information presented in Fig. 1. The initial formation temperatures of each phase under equilibrium and nonequilibrium condition are given in Table 1. It can be concluded that with the increase of Ru content, the solidus (T_s) , liquidus (T_l) and the precipitation temperature of γ' phase decrease appreciably, the solidification range increase. The values of T_s and T_l calculated by scheil module are close to that of equilibrium condition, while there exist large difference in the γ' precipitation temperature for the two conditions. The Scheil module assumes that diffusion occurs in model infinitely fast within the liquid phase and there is no

Table 1. Transformation temperatures for three alloys predicted from Thermo-Calc software.

	condition	T_l/ °C	T_s/ °C	γ' precipitation /°C	ΔT/°C
0Ru alloy	Scheil module	1387	1329	1308	
	equilibrium	1386	1328	1284	58
1.5Ru alloy	Scheil module	1384	1322	1302	
	equilibrium	1381	1319	1277	62
3Ru alloy	Scheil module	1380	1313	1296	
	equilibrium	1379	1313	1272	66

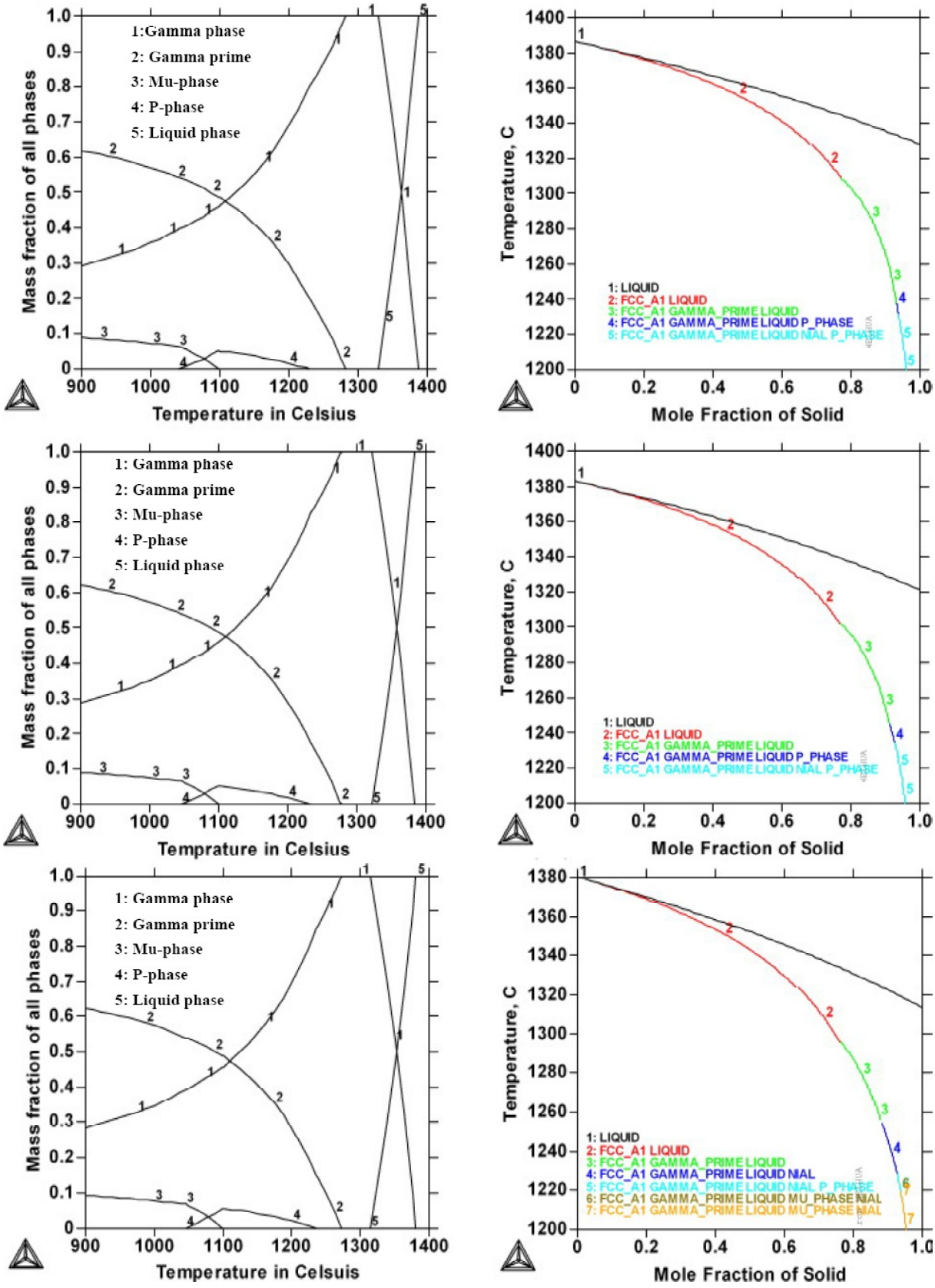

Fig. 1. Solidification path of alloys predicted by Thermo-Calc and Scheil model. (a)(c)(e) equilibrium phases and weight fractions at each temperature ; (b)(d)(f) solidification path calculated by Scheil model; (a)(b) 0Ru alloy;(c) (d) 1.5Ru alloy; (e)(f) 3Ru alloy.

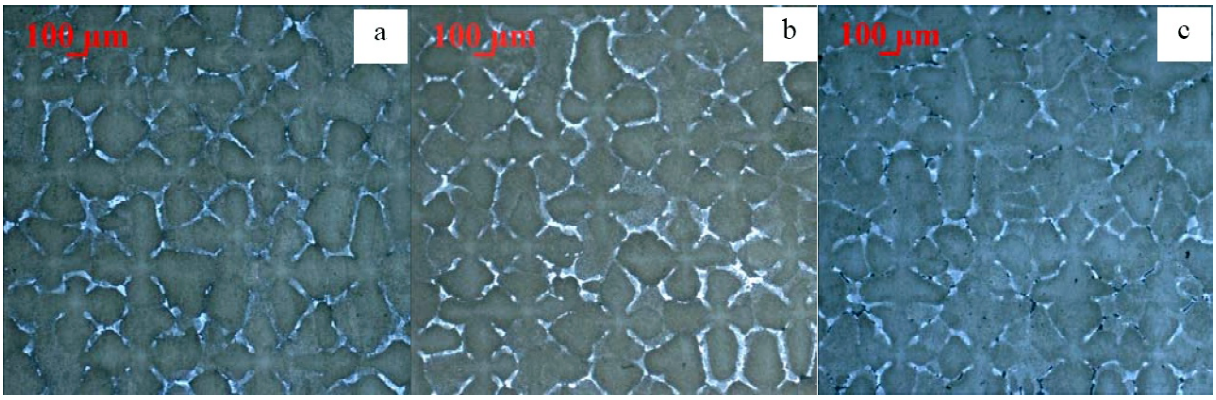

Fig. 2. Microstructures as-cast state of alloys with different content of Ru (a) 0Ru alloy; (b) 1.5Ru alloy; (c) 3Ru alloy.

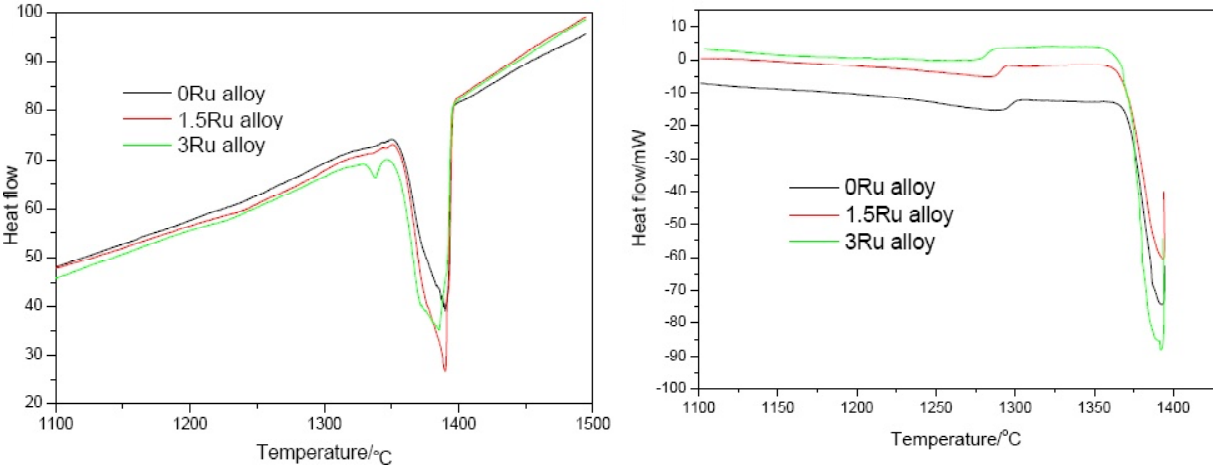

Fig. 3. DSC heating curves of three alloys with different content of Ru: (a) Samples as-cast state; (b) Samples after heat treatment.

diffusion in the solid phases that form. Under this nonequilibrium solidification, γ'/γ eutectic will occur. In the Scheil module, the γ'/γ eutectic formation temperature was considered as that of γ' precipitation. This is why there exists large difference in the γ' precipitation temperature for the two conditions. The fourth stage in the three Scheil model diagrams represents the formation of NiAl phase. From the length of the segment represented NiAl phase, it can be seen that with the increase of Ru, the volume fraction of NiAl phase increase.

The testing results show that three alloys are all dendrtic structure by withdrawaling rate of 6mm/min, as shown in Fig. 2. The microstructure of the alloys consists of dendrite core, dendrite arm, and interdendritic region, where there exist some γ/γ' eutectics in three alloys. In 3Ru alloy, except for γ/γ' eutectics, there are some black blocky NiAl-based β phase in interdendritic region as shown in Fig. 2c, which have been mentioned in reference [8]. The testing results is basically consistent with the calculated results, i.e., with the increase of Ru, the volume fraction of NiAl phase increase. Under the solidification condition of withdrawl rate at 6mm/min, the segregation tendency is inferior to that of Scheil module, therefore, the nonequlibrium NiAl-based b phase was not found in 0Ru alloy and 1.5Ru alloy. Because the NiAl phase is non-equlibrium phase, in 3Ru alloy, after solution heat treatment under the condition of 1315 °C /8 h+1325 °C /16 h, the NiAl phase was disappeared, which were solutioned into γ matrix and subsequently precipitated from γ matrix as γ' phase.

In order to investigate the solidification sequence and transformation temperatures in three alloys, DSC analysis were used by the heating rate of 5 °C /min. Fig. 3 shows the DSC heating curves of three alloys with different content of Ru. It shows that there are three endothermic peaks in the heating curves in each alloy. The first peak corresponds to the endothermic reaction of γ' phase solution. Because of alloying elements segregation in dendrite structure, the composition of γ' phase in dendrite core and interdendritic region is not identical, the

Table 2. Transformation temperatures for three alloys obtained from DSC heating curves.

No.	γ' solves	Incipient melting temperature $T_{i.m.}$/°C	Solidus (T_s/°C)	Liqudus (T_f/°C)	Freezing range
0Ru alloy	1293	1342	1352	1390	48
1.5Ru alloy	1286	1335	1350	1390	55
3Ru alloy	1278	1328	1348	1392	58

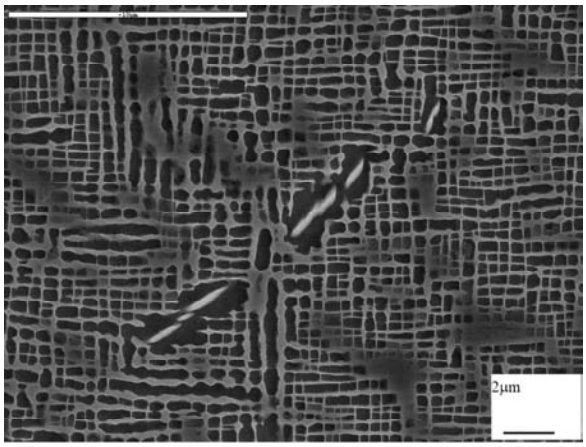

Fig. 4. Morphology of TCP phase after long-term thermal exposure for 20 h at 1100 °C in 0Ru alloy.

precipitation or solution of γ' phase would be in a large temperature range. Moreover, the precipitation of γ' phase from γ phase belongs to coherent precipitation, the transformation need absorb less heat. Therefore, the endothermic peak of γ' phase are gently and unapparent. In order to study the effect of Ru on the solution temperature of γ' phase, the full heat treated sample was analyzed by DSC, as shown in Fig. 2b. In the DSC curves there are two endothermic peaks: one is for the dissolution of γ' phase, whose peak value temperature was listed in Table 2; the other one is for the melting of g phase. From the position of peaks, we concluded that with the increase of Ru content, the solution temperature of γ' phase decreases.

In single crystal superalloy, the γ/γ' eutectic was the last part to solidify during solidification, therefore, the incipient melting temperature was defined as the melting temperature of γ/γ' eutectic, which correspond to the second peak in the heating curves. The solidus and liquidus temperature in this study was defined as the temperature where the onset and maximum of the main peak was located in. The main peak is the exothermic peak for melting of γ phase. Therefore, from the heating curves of DSC, the γ' phase solves, incipient melting temperature, solidus and liquids were obtained and listed in Table 2. From Table 2, it can be concluded that the addition of Ru has no significant effect on the solidus and liquids temperature, while with the increase of Ru content, the γ' phase solves and incipient melting temperature decreases. Moreover, Ru increases the freezing range. The testing results from DSC have the same tendency with the calculated results from Thermo-Calc software.

Three alloys with different content of Ru were thermal exposed at 1100 °C for different time. The results show that in 0Ru alloy a small quantity of needle like phase were found after long term exposure for 20 h at 1100 °C as shown in Fig. 4. Because three alloys contain a large amount of refractory elements, it is prone to form the TCP phase during long term thermal exposure and creep tests,

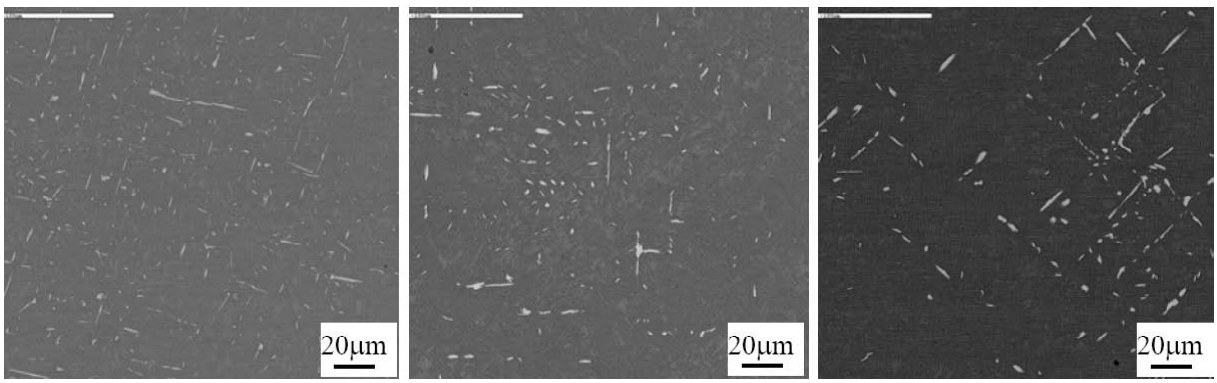

Fig. 5. The distribution of TCP phase after long term aging at 1100 °C for 1000 h in three alloys: (a) 0Ru alloy; (b) 1.5Ru alloy; (c) 3Ru alloy.

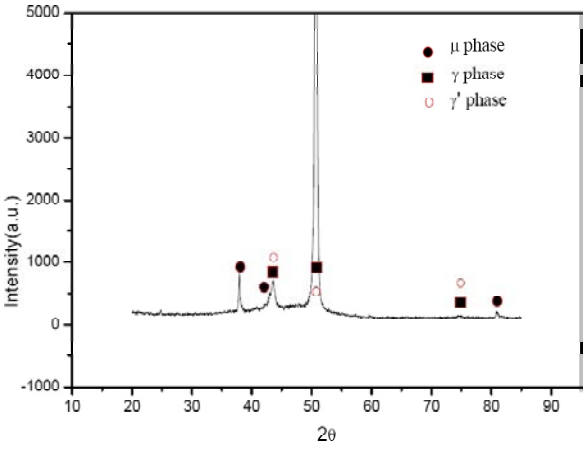

Fig. 6. X ray diffraction pattern of 1.5Ru alloy after long term aging at 1100 °C for 500 h.

which is detrimental to the mechanical property. However, in 1.5Ru alloy and 3Ru alloy the needle-like phase was found until long term thermal exposure for 200 h and 500 h. With the prolonging of time during thermal exposure, the amount of TCP phase increase in three alloys. The results indicate that the addition of Ru can inhibit the formation of TCP phase. Fig. 5 shows the distribution of TCP phase in three alloys after 1000 h at 1100 °C.

Fig. 6 shows the X-ray diffraction pattern of 1.5Ru alloy after long term thermal exposure for 500 h at 1100 C, which shows that the TCP phase is mu phase (μ phase), which is a common TCP phase in superalloys.

From the above results, we know that in three alloys the equilibrium phases include liquid phase, gamma phase, gamma prime phase and mu-phase, which is the same as the results calculated by Thermo-Calc software except for P-phase. From Fig. 1, P-phase occurred in the temperature range of 1050 °C ~1240 °C, therefore P–phase can not be found at room temperature.

4.CONCLUSION

The results calculated by Scheil model show that liquid, gamma phase, gamma prime, NiAl and P phase would occur sequentially during solidificationwhile the equilibrium phases calculated by Thermo-Calc software include liquid phase gamma phase, gamma prime, mu-phase, P-phase in single crystal superalloys with different content of Ru. The testing results show that the single crystal superalloys with different content of Ru were solidified with dendritic morphology. Except for γ/γ' eutectics, some NiAl based β phase enriched in Ru element with blocky morphology formed in the interdendrtic region. With the increase of Ru, the amount of NiAl based β phase will be enlarged. During long term thermal exposure for 500 h, mu-phase with needle-like shape was found in these alloys, which is rich in rhenium and tungsten element. It was found that the transformation temperatures measured by DSC has the same tendency to the results calculated by Scheil model in Thermo-Calc software. The Scheil module and Ni database of the Thermo-Calc software can predict the nonequilibrium solidification process of the superalloy preferably.

ACKNOWLEDGEMENT

Supported by the National Natural Science Foundation of China under grant no. 50901046.

REFERENCES

[1] K.S. O'Hara, W.S. Walston, E.W. Ross and R. Darolis, *U. S. Patent, No. 5.482,789,1996.*
[2] P. Caron, In: *Superalloys 2000*, ed. by T.M. Pollock, R.D. Kissinger, R.R. Bowman, K.A. Green, M. Mclean, S. Olson and J.J. Schirra (TMS, Miner. Metals & Mater. Society, 2000), p. 737.
[3] H. Murakami, Y. Koizumi and H. Harada, In: *Superalloys 2000*, ed. by T.M. Pollock, R.D. Kissinger, R.R. Bowman, K.A. Green, M. Mclean, S. Olson and J.J. Schirra (TMS, Miner. Metals & Mater. Society, 2000), p. 747.
[4]J.X. Zhang, T. Murakumo and Y. Koizumi // *Metall. Mater. Trans. A* **33** 20023741.
[5] G.H.Gulliver // *J. Inst. Met*. **9** (1913) 120.
[6] E. Scheil // *Z. Metallkunde* **34** (1942) 70.
[7] B.A. Boutwell, R.G.Thompson and N.Saunders, In: *Superalloys718, 625, 706 and Various Derivatives* (he Minerals, Metals and Materials Society, 1997), p. 99.
[8] T. Jin, L.R. Liu and J.L. Liu // *Submitted to Journal of Materials Science*.