A NEW WAY TO IMPROVE THE SUPERALLOYS

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Abstract

A metallography coupled with the microprobe method was used to study the solidification process of superalloys. It was found that the final solidification temperatures of the conventional superalloys are generally very low, about 1080-1120°C, the solidification ranges are large enough, reaching 180-240°C, that makes the solidification segregation serious. Strictly controlling the contents of the minor elements P,Zr,B and Si in superalloys can raise the final solidification temperature to 1180-1280°C, and contract the solidification temperature range to 50-120°C, that results in alleviating the solidification segregation obviously. After controlling the contents of the minor elements, a series of new superalloys with low segregation and excellent properties have been developed.

Introduction

From the very beginning, raising service temperature has been the major aim of superalloy development to meet the need of the engine for higher efficiency and thrust. Because the elevated temperature mechanical properties of superalloys mainly depend on their γ' fraction[1,2], how to increase their γ' fraction is the baseline throughout the development history of superalloys. From 1940's to 1960's, in view of composition, the increase of the service temperature of superalloys was mainly obtained by raising the contents of the γ' forming elements such as Al,Ti,Nb and Ta[3]. But this composition-based development has been frustrated since 1970's. For the cast superalloys, further alloying will form the brittle phases such as σ and μ, which impairs the properties. For the wrought superalloys, which forging temperature ranges are already very narrow, further alloying will make the incipient temperature and hence the beginning forging temperature lower, resulting in the lackness of malleability.

Because both brittle phase precipitation and incipient melting take place in the local regions with severe segregation, it is necessary to alleviate the solidification segregation in order to solve this problem. Powder metallurgy technique is one of the efficient methods, but its application is greatly restricted for its limitation. Here, we attempt to solve the problem by finding out the reason of the serious segregation of superalloys.

Experimental Procedure

The solidification segregation of an alloy depends on the relative position of the liquidus and solidus. In general, the larger the temperature interval between the liquidus and solidus, the more the severity of the solidification segregation. In order to overcome the segregation problem, it is necessary to accurately measure the temperature ranges of superalloys first and then figure out the way to contract the ranges.

Because the incipient melting temperature is greatly affected by the solidification condition, the beginning and final solidification temperatures obtained under the same solidification condition were used to decide the temperature interval.

The compositions of the tested alloys are listed in Table I. The experimental technique of the solidification process determination has been discussed elsewhere[4]. The specimens of about 10mmx10mmx10mm were put in graphite boats, heated in a silicon carbide furnace to 1420°C for 5 min, cooled slowly to different temperatures, kept for 10 min, and then, quenched in water. The characteristic temperatures were obtained by metallography.

Micro-zone composition analysis was conducted with a Comebax-Micro microprobe device

Micrographic specimens were etched in an electrolyte of $H_3PO_4(40\%)$ + $H_2SO_4(25\%)$ + H_2O or $HCl(20\%)$ + ethanol(80%).

Table I The Chemical Compositions of the Tested Alloys(wt%)

	K17 (IN100)	K17G	K38 (IN738)	GH33 (Nimonic 80A)	GH37	GH49	GH135	GH761	GH901 (Inco-loy901)	A286
C	0.17	0.22	0.19	0.04	0.075	0.04	0.05	0.05	0.045	0.053
Cr	9.0	9.4	15.5	20.0	15.0	10.0	15.0	13.0	12.1	14.70
Co	14.1	10.1	8.5	--	--	15.0	--	--	--	--
W	--	--	2.6	--	5.9	5.5	2.0	3.0	--	--
Mo	2.9	3.1	1.7	--	3.1	4.8	2.0	1.5	5.8	1.36
Nb	--	--	0.78	--	--	--	--	--	--	--
Ta	--	--	1.7	--	--	--	--	--	--	--
V	0.7	0.7	--	--	0.38	0.40	--	--	--	0.34
Al	5.3	5.2	3.6	0.84	1.8	4.1	2.4	1.5	0.23	0.20
Ti	4.9	4.1	3.2	2.5	2.1	1.7	2.2	3.8	3.3	1.99
B	0.011	0.017	0.014	0.005	0.005	0.016	0.014	0.01	0.015	0.010
Zr	0.06	0.05	0.10	--	--	--	--	--	--	--
Ni	bal	bal	bal	bal	bal	bal	35.0	43.0	43.1	25.70
Fe	0.16	0.15	0.2	0.58	0.76	0.26	bal	bal	bal	bal
P	0.004	0.005	0.005	0.008	0.005	0.004	0.009	0.006	0.005	0.014
S	0.003	0.003	0.003	0.003	0.003	0.003	0.015	0.01	0.01	0.003
Si	0.07	0.06	0.09	0.39	0.21	0.21	0.10	0.15		0.64

Experimental Results and Discussion

The results of the initial and final solidification temperatures obtained by microscopic observation are shown in Table II. For comparison, these temperatures of a number of superalloys, measured by differential thermal analysis(DTA), are also listed in it.The initial solidification temperatures are consistent with each other by these two methods, but the final solidification ones are quite different, especially for the cast nickel-base superalloys and wrought iron-base superalloys, and the differences reach more than 100°C.

From the microscopic observation, it was found that there was a small amount of liquid which solidified very slowly. For example, in K38 alloy, about 90% liquid had rapidly solidified before 1230°C, but the remaining liquid could not complete the solidification process until the temperature was lowered to as low as 1100°C. Figure 1 shows the microstructure of K38 alloy quenched at 1120°C, in which there is still a little liquid.

Because of the extremely slow solidification rate at the late stage of the solidification of the current superalloys, the crystallization latent heat is too small to be detected by the DTA method, and this situation gives rise to the substantial difference between the data of these two methods. It can be concluded from Table II that the temperature range of the solidification of the current superalloys is actually 150-300°C instead of 50-150°C by DTA method.

The composition measurement of this low melting structure was made by electron microprobe in K38 and GH761 alloys. Besides some major alloying elements such as Ti in K38 alloy and Ti, Mo and W in GH761 alloy show obvious segregation, P,Zr,B and Si were highly enriched in both alloys. Table III is the segregation data of P,Zr

Table II The Initial(T_i) and Final(T_f) Solidification Temperatures of Superalloys

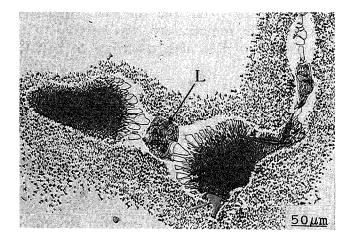|	Microscopic Method			DTA Method		
	Alloy	T_i(°C)	T_f(°C)	Alloy	T_i(°C)	T_f(°C)
Cast Nickel-Base Alloy	K17	1340	1120	IN100	1335	1266
	K17G	1330	1120	ВЖА-12Y	1322	1280
	K38	1320	1100	IN738	1316	1232
				B-1900	1302	1274
				ЖС-6К	1346	1265
Wrought Nickel-Base Alloy	GH33	1370	1220	Nimonic80A	1390	1360
	GH37	1370	1230	Nimonic90	1390	1360
	GH49	1370	1180	Nimonic105	1379	1341
				Waspaloy	1357	1232
				Udimet115	1315	1260
Wrought Iron-base Alloy	GH901	1370	1100	Incoloy901	1399	1232
	GH135	1360	1100	D979	1399	1218
	GH761	1360	1080	IN706	1370	1334
	A286	1410	1100	A286	1426	1371
				IN718	1343	1206

Figure 1 Microstructure of K38 alloy quenched at 1120°C

Table III The Contents of P,Si and Zr in the Final Solidified Region(FSR)*

Alloy	Condition	Composition	P	Si	Zr
K38	1420°C/5min slowly cooled to 1100°C/10 min, WQ	average content in alloy	0.005	0.09	0.1
		content in FSR(wt%)	1.5/3	3/5	10
		segregation ratio	600	30-50	100
GH761	1420°C/5min slowly cooled to 1080°C/10 min, WQ	average content in alloy	0.005	0.11	--
		content in FSR(wt%)	4/7	8/11	
		segregation ratio	1000	100	

*B segregation data are not given because of the difficulty of correct measurement.

and Si. It can be seen that the segregation ratio of P is the largest, up to 1000, that of Zr and Si is also quite high.

A high pure K38 alloy with <0.0005P, <0.05Si, no B and Zr was melted, and the solidification process measurement indicated that its final solidification temperature was raised to 1280°C. The metallographic observation of the as-cast microstructures revealed that a lot of ($\gamma+\gamma'$) eutectic existed in the conventional K38 alloy was eliminated after purification[4]. In superalloys, ($\gamma+\gamma'$) eutectic is resulted from the non-equilibrium solidification, and its amount indirectly indicates the segregation degree. The above fact means that the high pure K38 has an obviously low segregation.

According to the above mentioned results,it is clear that P,Zr,B and Si are responsible for the serious segregation of the current superalloys. In order to understand the influence of individual elements on the segregation, a systematical test was performed in the high pure K38 alloy by changing the contents of P,Zr,B and Si respectively, the results are shown in Table IV. It can be seen that the incipient melting temperature and ($\gamma+\gamma'$) fraction of K38 alloy rapidly change with these minor elements, but when their contents are too high, the incipient melting temperature basically keeps unchanged because of the formation of other types of eutectic. Among them, P is most harmful to the solidification segregation, followed by B, and Si the smallest.

The combined effect of these minor elements on the segregation of K38 alloy is shown in Table V. It can been seen that their combined effect is larger than their individual effect.

In spite of the extreme detriment of its severe segregation on the malleability of pure Ni and simple Ni-base alloys[5,6,7], S shows no obvious segregation in K38 and

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Table IV Effect of P,Zr,B and Si on the Incipient melting Temperature(T_i') and the Amount of ($\gamma+\gamma'$) Eutectic in K38 Alloy

P(wt%)	<0.0005	0.0014	0.0019	0.0049	0.015	0.051	0.064	0.097
T_i'(°C)	1280	1260	1230	1200	1120	1100	1075	1075
($\gamma+\gamma'$)(wt%)	0	0	0	0.8	1.5	1.7	2.4	4.2
Zr(wt%)	0	0.01	0.096	1.28				
T_i'(°C)	1280	1260	1160	1160				
($\gamma+\gamma'$)(wt%)	0	0.7	0.9	2.3				
B(wt%)	0	0.0014	0.009	0.1				
T_i'(°C)	1280	1260	1220	1190				
($\gamma+\gamma'$)(wt%)	0	0.4	1.0	8.9				
Si(wt%)	0.05	0.12	1.0					
T_i'(°C)	1280	1260	1200					
($\gamma+\gamma'$)(wt%)	0	0.3	5.0					

Table V The Combined Effect of P,Zr,B and Si on the Segregation of K38 Alloy

P(wt%)	Zr(wt%)	B(wt%)	Si(wt%)	T_i'(°C)	($\gamma+\gamma'$) Eutectic(wt%)
<0.0005	--	--	0.05	1280	0
<0.0005	0.025	0.003	0.05	1200	1.2
<0.0005	0.093	0.011	0.05	1160	2.4
0.005	0.1	0.01	0.07	1140	3.0
0.055	0.097	0.009	0.07	1110	3.8
1.1	0.098	0.011	0.08	1110	12.0

GH761 alloys. This can be contributed to the high Ti content in these two alloys, resulting in the formation of Ti_2SC phase with relatively high melting point which prevents the extravagant enrichment of S[8].

The above results show that the contents of P,Zr,B and Si seem to be low in the commercial superalloys, but they still profoundly aggravate their solidification segregation. Therefore, there is a new way available to improve the properties of the current superalloys by greatly decreasing or properly controlling these trace elements and hence a series of low segregation alloys have been developed.

Cast Nickel-Base Superalloys with Low Segregation

Higher contents of P,Zr,B and Si in the current cast nickel-base superalloys obviously

enlarge their solidification temperature ranges, promote the dendritic segregation of major alloying elements and the formation of a lot of ($\gamma+\gamma'$) eutectic. ($\gamma+\gamma'$) eutectic is poor in Cr,Mo and Co, and their formation in large quantity will bring about serious eutectic segregation and make these TCP phase forming elements enrich in the front of ($\gamma+\gamma'$) eutectic with the result of poor structure stability due to the easy precipitation of σ, μ and etc.[9]. Therefore, the ($\gamma+\gamma'$) eutectic can be greatly decreased in quantity or even completely eliminated by lowering the contents of P,Zr,B and Si without changing other elements.

In consideration of alleviating segregation, the contents of P,Zr,B and Si should be decreased as low as possible, but it is not so in consideration of mechanical properties. P and Si are detrimental to mechanical properties [10], so it is beneficial to decrease them by the most. B and Zr were considered necessary as grain boundary strengthening elements[10-13]. A lot of research on the high pure superalloys shows that B is still necessary for mechanical properties, but its content can be lowered, while Zr appears no good effect and should be removed from the alloys.

After considering the necessity of lowering segregation as well as the technique available to control these minor elements, the following composition can be accepted for the cast nickel-base superalloys: P<0.0005, Si<0.05, B the lower limit of the specification and no Zr. By this so-called low segregation technique, the segregation of the current cast superalloys can be greatly decreased and their alloying levels are permitted to increase without damaging the structure stability. Based on IN100, IN792 and IN738 alloys which are the advanced cast blade superalloys respectively for aeroplane, marine and industrial engines, a series new alloys with improved mechanical properties or hot corrosion resistance have been developed by raising the contents of Al,Ti,Ta or Cr[4,14]. These alloys were proved without harmful phase precipitation after prolonged exposure.

Among these new alloys, the high temperature strength of M17F alloy can match with that of PWA1422 alloy, M38G and M40 alloys have obvious advantage over IN792 and IN738 alloys, the best blade materials for marine and industrial engines, and M36 alloy keeps at the same level of mechanical properties but has much better hot corrosion property compared with IN738 alloy, making it suitable for the blade material of those engines which use low grade oil as their fuel. Now, one set of M17F blades have been produced and are waiting for engine trial, while M38G blades have already passed 250h engine trial.

DS Superalloys with Low Segregation

Early directionally solidified(DS) superalloys could not be used for their poor transverse properties at intermediate temperature and sensitivity to longitudinal cracking. It is because there is a small amount of the structure in these alloys where remains unsolidified until very low temperature, namely, there is a wide temperature range in which the columnar grains have already contacted one another at some positions but other regions are still liquid, resulting in the poor cohesion at the grain boundaries and the easy cracking under thermal stress. In addition, the structure with low melting point is highly rich in various harmful impurities and hence greatly deteriorates the transverse properties.

The addition of Hf in DS superalloys can efficiently overcome these two drawbacks. The mechanism of the beneficial effect is that Hf obviously increases the quantity of the low melting point liquid and prevents the bridging between the columnar grains before eutectic reaction during solidification. Because of the flexibility of liquid, cracking is difficult to take place. Moreover, the synchronous solidification of a lot of remaining liquid at eutectic reaction temperature dilutes the impurity elements , eases their damage and consequently improves the transverse property. But the addition of Hf greatly increases the material cost and the rejuvenation of scrap is difficult. Moreover, Hf-containing DS alloys still can not get rid of longitudinal cracking.

It is well proved that due to much narrower solidification temperature ranges, low segregation DS superalloys are much easier to adopt DS technology. In addition, their properties at intermediate temperature are higher than those of their cast counterparts without the addition of Hf. For example, IN738 was considered not suitable to adopt DS technology due to little improvement of its properties. The test on IN738 alloy, as shown in Table VI, indicates that the mechanical properties of the conventional IN738 alloy are indeed not improved by the DS technology, but those of the low segregation ones are improved same as other successful DS superalloys. Although the addition of Zr is not detrimental to the longitudinal properties, but it obviously lowers the transverse properties.

Table VI the Stress Rupture Properties of Several IN738 Alloys

Alloy		760°C/595MPa		815°C/421MPa	
		Life(h)	EL(%)	Life(h)	EL(%)
Conventional DS738	L*	117.5	21.0	158.3	22.5
	T*	44	3.2	64	2.0
Low Segregation DS738 with 0.01Zr	L	482.2	13.9	408	12.8
	T	92.8	3.0	183	2.8
Low Segregation DS738 without Zr	L	346.1	17.4	406.5	14.4
	T	148	3.7	281.7	4.2
Conventional Cast IN738		64	9.7	112	7.7

*L--Longitudinal, T--Transverse.

DZ38G is a directionally solidified M38G alloy with 50°C higher service temperature than IN738 alloy[4,14], several hundreds of blades made by this alloy have been produced without the appearance of any cracking and passed 250h engine trial.

Wrought Superalloys with Low Segregation

In the production of the wrought superalloys, the starting forging temperature is

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generally lower than 1150°C[15] depending on the incipient melting temperature. The larger the ingot size, the lower the temperature due to the decrease of incipient melting temperature resulted from the aggravation of solidification segregation. Low forging temperature will give rise to high resistance to deformation and damages the technological properties. Therefore, alleviating the solidification segregation and raising the starting forging temperature are important in the production of large forgings.

In A286, Incoloy901 and GH761 alloys, their beginning forging temperatures are generally 1120°C. These temperatures can be raised to 1220°C by lowering their P content to <0.001, Si to <0.05 and B to 0.001-0.003wt%. Adequate tests show that such low B content is still large enough for the mechanical properties. It is estimated that the 100°C increase of beginning forging temperature can lower the resistance to deformation by two thirds and hence greatly favors the forging process.

Maybe there are some worries that high forging temperature would result in coarse grain size. In fact, the grain size of forgings is related to not only the forging temperature but also the degree of deformation in every cycle and reduction. High temperature can accelerate the grain growth, but it can also reduce the resistance to deformation which allows to practise higher deformation degree, resulting in more and homogeneous recrystallization nucleation and hence fine grain. It was verified by the result on A286 alloy, in which an ingot with 220mm diameter was forged into a bar with 110mm diameter in one cycle at 1220°C, and the grain size of this bar is homogeneous ASTM6-7.

In Inconel718 alloy, the incipient melting temperature is elevated not so much as in A286, Incoloy901 and GH761 alloys by the low segregation technique because of the existence of a lot of (γ+Laves) eutectic, but its segregation and Laves phase fraction are obviously decreased. Therefore, the ingot size of low segregation Inconel718 alloy can be enlarged. Now in China, several turbine discs have been produced from the low segregation ingots in 16.7 inch diameter. An ingot in 20 inch diameter, never successfully produced before in China, has been melted and forged into disc and rings.

Conclusions

1. P,Zr,B and Si are largely responsible for the serious solidification segregation of the current superalloys, they imposes their effect by greatly lowering the final solidification temperature.

2. A series of new superalloys with low segregation have been developed by reasonably decreasing or controlling these minor elements.

3. Low segregation cast superalloys have greatly improved mechanical properties or hot corrosion resistance compared with the same type of superalloys used now because they are allowed to be further alloying without damaging the structure stability.

4. Using low segregation technique, DS superalloys can get rid of the drawbacks of poor transverse properties and large sensitivity to longitudinal cracking without the addition of Hf.

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5. Higher starting forging temperature gives rise to the improved technological properties of the low segregation wrought superalloys and lighter segregation makes it possible to enlarge the ingot size.

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