Advanced Materials '93, VI / Frontiers in
Materials Science and Engineering, edited by S. Sōmiya et al.
Trans. Mat. Res. Soc. Jpn., Volume 19B
1994 Elsevier Science B.V.

Superalloys with Low Segregation by Trace Elements Control

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Superalloy is a kind of critical materials for modern aeronautics,ship building and industrial gas turbine, especially for modern jet engines,the proportion of superalloys could be about one half of the total weight. Some of the critical parts, such as disks and turbine blades are working at very complicated and corrosive conditions in terms of stress and environments.Therefore,the materials scientists and engineers have made big efforts on the development of superalloys since the early 1940's in order to get higher efficiency,higher safety and longer life of the engine. Fig. 1 shows the progress of superalloys.

It is shown that the highest temperature can be used from 700° to 950℃ for blades, and the yielding strength from 600 to 1000 MPa for disks from 1940 up to now.

The improvement of properties of alloys was mainly by increase and adjustment of alloying elements until

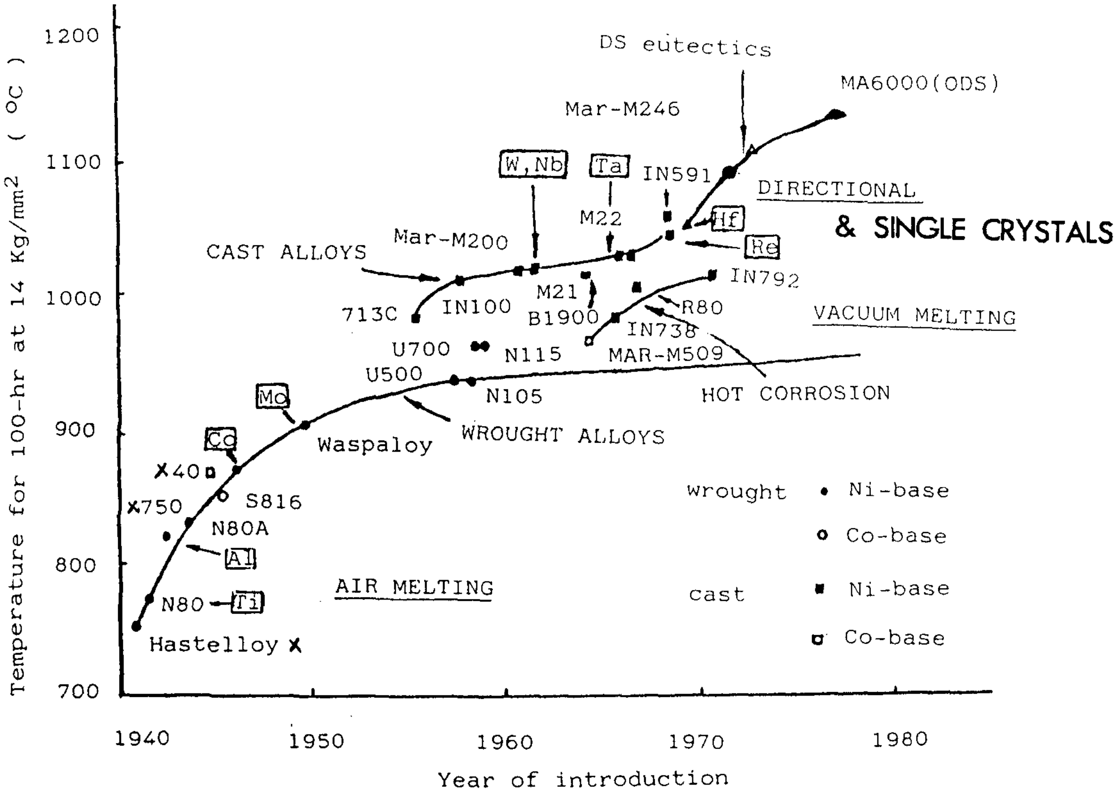

Figure 1 Progress of superalloys

the early sixties. However, brittle phases, such as topologically close-packed phases(TCP) σ, Laves, μ etc may precipitate out with excessive additions of alloying elements.Therefore, development of different kinds of processing was followed up, that is,from air melted to vacuum melted wrought alloys;from wrought to precision cast; then directionally solidified and single crystals, powder metallurgy, oxide dispersion strengthing alloys(ODS) etc. Of course,the most effective measure is air-cooling, this may cause hundreds of degrees increase of the operation temperature. Nevertheless,the improvement of the performance of the engine by development of new materials such as intermetallic compounds, engineering ceramics and composite materials,as well as the improvement of the existing superalloys are still very important. One of the main drawbacks of the present alloys is segregation. It is especially serious for those with high alloy contents. Hence study of solidification is critical in order to get the segregation improved.The consequence of segregation of alloying elements or impurities may at least have two effects: one is lowering of melting point and thus limiting the service temperature; the other is TCP prone due to segregation of some elements. Therefore, different measures have adopted to solve the problem, such as powder metallurgy,plane front solidification, rapid solidification,mechanical alloying etc.,but one of the most important ways is the study of process of solidification in order to understand the behavior of all the elements during solidification, and find the way of improvement.

Process of solidification of superalloys

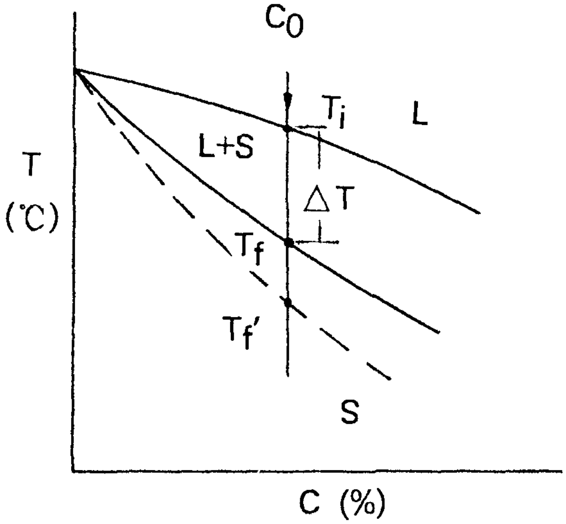

Fig. 2 Schematic diagram showing solidification of superalloys

T temperature
C concentration of solute elements
T_i starting temperature of solidification
T_f final solidification temperature as indicated in equibrium phase diagram
T_f' actual temperature of solidification
ΔT solidification gap (T_i-T_f)

For convenience of explanation, the phase diagram of solidification of superalloys of complex composition is expressed by a simplified binary, as schematically shown in Fig. 2.

It is well known that the way of lowering segregation by plane-front solidification is expressed as follows:

$$G/R \geqslant \Delta T/D$$

G, temperature gradient in the vicinity of solid-liquid interface;
R, rate of motion of solid-liquid interface;
ΔT, solidification gap between

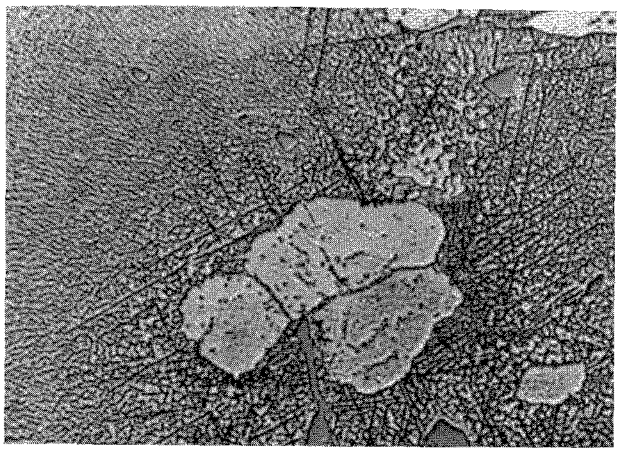

Fig. 3 σ phase formed in IN100 around eutectics

solidus & liquidus as shown in Fig.2;

D, diffusion constant in the liquid phase adjacent to the interface.

Table 1 shows some of the typical superalloys just for reference.

Table 1 Compositions of some typical superalloys

Alloy		Composition (wt%)														
		C	Cr	Co	W	Mo	V	Nb	Ta	Hf	Al	Ti	B	Zr	Ni	Fe
Cast Ni-base	IN100	0.16	9.0	10.0	--	3.0	1.0	--	--	--	5.3	4.8	0.015	0.06	base	--
	IN738	0.18	16.0	8.5	2.6	1.7	--	0.7	1.7	--	3.5	3.2	0.01	--	base	--
DC	Mar-M200	0.14	9.0	10.0	12.0	--	--	1.0	--	1.8	5.0	2.0	0.02	0.08	base	--
	Rene' 125	0.11	9.0	10.0	7.0	2	--	--	3.8	1.8	4.8	2.5	0.015	0.1	base	--
Wrought Fe-Ni-Cr base	IN718	0.08	19.2	--	--	3.0	--	5.1	18.5	52.5	0.5	0.9	--	--	52.5	18.5
	InCo901	0.10	12.5	--	--	6.0	--	--	36.2	42.5	--	2.7	--	--	42.5	36.5
	A286	0.04	15.0	--	--	1.25	--	--	55.2	26.0	0.2	2.0	0.005	--	26.0	55.2
	GH761	0.05	13.0	--	3.0	1.7	--	--	33.2	44.0	1.6	3.4	0.01	--	44.0	33.2
Cast Co-base	X-40	0.50	22.0	5.5	7.5	--	--	--	1.5	--	--	--	--	--	--	1.5

It is evident that the larger the D or G value, the smaller the △T or R, the easier the realization of plane front solidification. D is fixed by the alloy system and cannot be changed too much, and R cannot be too low by considering the practical production rate. It is more practical to narrow down △T or increase the temperature gradient G. G can be increased by improving the directional solidification process or adoption of enhanced cooling rate to create a large gradient, however, this is limited by thermal conductivity of solidified superalloy concerned and some other factors.

△T is different with different alloy system, for super pure semiconductor materials, △T is only a few degrees, and for superalloys of eutectic composition, △T is no more than 20℃ in general. For superalloys with complex composition, △T is usually very large, and it is very difficult to get plane front solidification, therefore, lowering of △T is critical. However, precise measurement of △T is very difficult, differential thermal analysis (DTA) is generally used for this purpose, but the sensitivity is not good enough, although the apparatus of DTA has been very much improved. Prof. Zhu and his associates of Institute of Metal Research, Academia Sinica, Shenyang, acquired an extraordinarily accurate results by using ordinary metallographic method. One can get quantitative results of different phases if a quantitative metallograph is used. This is especially useful for the analysis of superalloys with a multiphase structure. The process of the analysis is as following:

Put the specimen of 15 mm cube in a graphite boat, heated in a silicon carbide tube furnace, then followed by a sequence as:

$$1400℃\ (5\text{min.}) \xrightarrow{\text{(furnace cool)}} \text{the preset temperature}(10\ \text{min.}) \xrightarrow{\text{(quench in water or saline)}} \text{room temperature}$$

The composition of the specimen is practically unchanged except the carbon content is increased by 0.02-0.03%.

Table 2 shows △T of some of the superalloys together with their

Table 2 △T measured by microscopic method and differential thermal analysis (DTA) method (℃)

Superalloys	microscopic			DTA			T_i'
	T_i	T_f	△T	T_i	T_f	△T	
Cast Ni-base							
IN 100	1340	1120	220	1335	1266	69	1150
IN 738	1320	1100	220	1316	1232	84	1140
Wrought Ni-base							
Nimonic 80A	1370	1220	150	1390	1360	30	
Wrought Fe-Ni-Cr-base							
Incoloy 901	1370	1100	270	1399	1232	67	
A286	1410	1100	300	1426	1371	55	

Table 3 The contents of P, Si and Zr in the final solidified regions (FSR)

Alloy	Treatment	Composition	P	Si	Zr
IN 738	1420℃ (5min) →1100℃ (10min) →WQ	average content in alloy (%)	0.005	0.09	0.1
		content in FSR (%)	1.5/3	3/5	10
		segregation ratio (k)	300/600	30/50	100
GH 761	1420℃ (5min) →1080℃ (10min) →WQ	average content in alloy (%)	0.005	0.11	-
		content in FSR (%)	4/7	8/11	-
		segregation ratio (k)	800/1400	7/100	

B segregation ratio data are not given due to difficulty of measurement

incipient melting points (T_i') which are temperatures starting to melting from solid state.They are a few tens degrees higher than that of the actual final solidification temperature T_f', depending on the rate of cooling or heating, as indicated in Fig. 2.

It is shown that (ΔT) by microscopic observation could be a few hundreds degrees larger than that by differential thermal analysis which is very significant for the process of solidification and heat treatment for superalloys.

The sequence of phase formation during solidification can also be observed by this technique.By means of electron probe, elements in different phases can be determined.It is shown that the σ forming elements, Cr,Mo and Co are enriched in the residual liquids to a great extent, that is, σ-prone for the residual liquids. These residual liquids are usually in the vicinity of eutectics where is the most probable place to form σ phase, as shown in Figure 3.

Discovery of low segregation superalloys

Data from Table 2 illustrate that T_f determined by DTA is not the real temperature of final solidification, but there still exists about 2% of liquid which cannot be detectable by conventional thermal analysis. These last trace of liquid pools will persist to more than 100 ℃ lower until the whole mass solidified.What is the reason that the residual drops of liquid phase can last such a long period? Zhu and his associates analyzed with microprobe very carefully. They found that the last drops were concentrated with trace elements, such as P, Si, Zr, B. Table 3 shows the segregation of the trace elements during solidification of two alloys, one is a nickel-base cast alloy (IN738) and the other is an iron-nickel-chromium base alloy(GH761).

In order to confirm the new findings, an IN738 superalloy with high purity, that is $P < 0.0005\%$, $Si < 0.05\%$ without additions of B and Zr was melted in a vacuum furnace. The solidification process measurements indicated that the final solution temperature (T_f) was raised to 1280℃ as compared with that of 1100℃ for conventional alloy as given in Table 1. That is, ΔT is narrowed down to 1320℃-1280℃=40℃. Thus the dendritic growth and

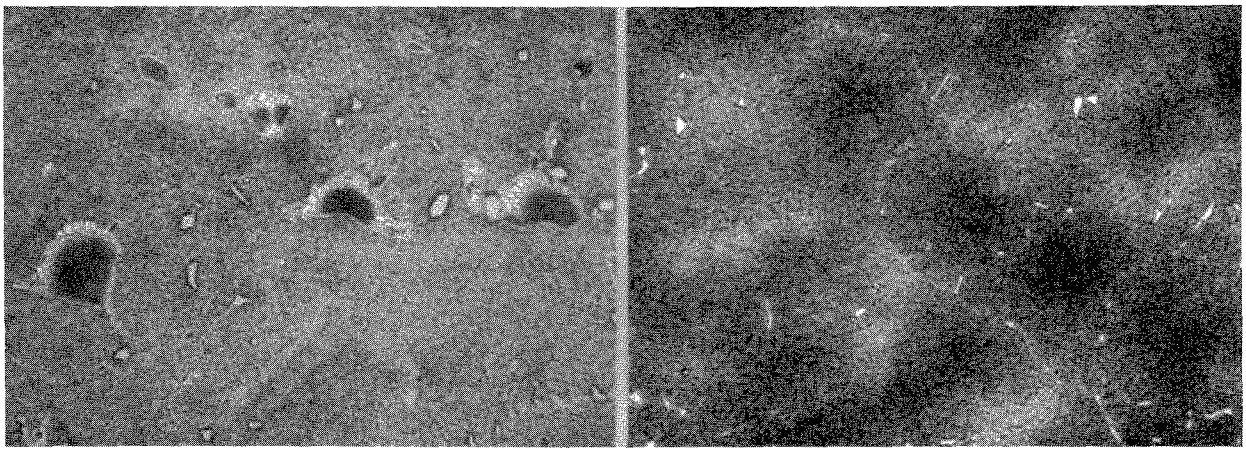

Fig. 4 Microstructure of IN738 (a) conventional, (b) low segregation

serious segregation will be pronouncedly reduced; the amount of $\gamma+\gamma'$ eutectics is consequently eliminated, as shown in Figure 4.

It is clear that P, Zr, B and Si are responsible for the serious segregation of superalloys. In order to clarify the effect of individual element on segregation, a systematic investigation has been performed. It is concluded that P is the most serious element and followed by B and Si,Zr is the least harmful one.

Similarly for Fe-Ni-Cr base Incoloy 901,combined effect of these trace elements on segregation of IN738 has also been investigated. It is concluded that the effect is even more serious for the trace elements being coexisted than that of individuals.

Prospects of low segregation superalloys

Through several years of investigation on low segregation superalloys,it has indicated that this technology has a very bright future.

(1) Development of cast nickel-base low segregation superalloys

It has been shown that higher contents of P, Zr, B and Si in cast Ni-base superalloys will greatly extend the range of solidification temperature (△T) and consequently the structure stability is poor due to precipitation of TCP phases and more eutectics.

However, in consideration of strength at elevated temperatures, certain trade-off has to be considered, such as the grain boundary strengthening elements, B and Zr have to be carefully re-examined. According to the experimental results, B is still necessary, but the content should be kept at lower level, while Zr could completely be removed from the alloy. In order to get the best results, the following contents of trace elements (%) are suggested for cast nickel-base superalloys

P <0.0005
Si <0.05
B at the lower limit of the specification
Zr not necessary to be added

By the low segregation technology, the working temperature could be increased by 20-25℃ through addition of more strengthening alloy elements without damaging the structure

Table 4 The stress rupture properties of IN738 alloy

Alloy		760℃ / 595 MPa		815℃ / 421 MPa	
		Life(h)	Elong(%)	Life(h)	Elong(%)
Conventional	L	117.5	21.0	158.3	22.5
DS IN738	T	44	3.2	64	2.0
Low Segregation	L	482.2	13.9	408	12.8
DS IN738+0.01Zr	T	92.8	3.0	183	2.8
Low Segregation	L	346.1	17.4	406.5	14.4
DS IN738, No Zr	T	148	3.7	281.7	4.2
Conventional Cast IN738		64	9.7	112	7.7

stability. For superalloys used for marine or industrial gas turbine, more Cr can be added and the hot corrosion property is thus improved accordingly.

(2) Directionally solidified (DS) superalloy with low segregation

DS superalloy was invented in sixties, but it had not been commercialized until seventies due to its poor transverse properties and sensitive to longitudenal cracking at intermediate temperatures,the properties could be improved by addition of Hf. However, the cost is increased and recycling of scraps is difficult. If low segregation technology is applied, the transverse strength of the DS alloy will be very much improved, as shown in Table 4.

It is noticed that the stress rupture strength of the low segregation DS IN738 is much higher than that of conventional DS IN738 both in longitudinal and transverse direction. Furthermore, it has been considered that IN738 is not suitable to adopt DS technology due to little improvement of its mechanical properties. However,it has been proved that the low segregation alloy can be improved as much as other DS superalloys. The reason is that the solidification temperature range of the low segregation alloy is narrowed down, and easier to fit the DS technology.

In order to clarify the effects of low segregation and the function of hafnium (Hf) during solidification of superalloys, the solidification of Rene'125 was investigated.Table 5 is the composition of the experimental alloys, the first is normal Rene'125, the second is same as the first but with no addition of Hf, and the last one is same as the second but with low segregation.

If the process of solidification is examined by the metallographic method as described above,it is shown that the temperature range of solidification of the 3 alloys is different, the solidification gap of the low segregation alloy is only a little more than 100℃, while that of the other two is about doubled,thus leads to more segregation of impurities and high porosity. It is more interesting

Table 5 Experimental alloys (wt%)

Alloy	C	Cr	W	Al	Ti	Mo	Co	Ta	Hf	B	Zr	P	Si
A Rene′125	0.11	9	7	4.8	2.5	2	10	3.8	1.8	0.015	0.1	0.005	0.1
B Rene′125 Without Hf	0.11	9	7	4.8	2.5	2	10	3.8	--	0.015	0.1	0.005	0.1
C Low Segregation Rene′125 Without Hf	0.11	9	7	4.8	2.5	2	10	3.8	--	--	--	0.0005	0.05

that the segregation and the amount of $(\gamma+\gamma')$ eutectic in alloy with the addition of Hf are even more serious than those without addition of Hf, while the transverse mechanical properties at intermediate temperatures of the former are superior, Fig.5 gives the answer. It can be noticed that the residual liquids of the alloy without Hf as shown in (a) are scattered as isolated islands in the solidified mass, while that of Hf added alloy are continuous, hence the filling property is good and consequently porosity after solidification is much lower, that means the transverse mechanical property is improved.

(3) Wrought superalloys with low segregation

In the production of a wrought superalloy, the starting forging

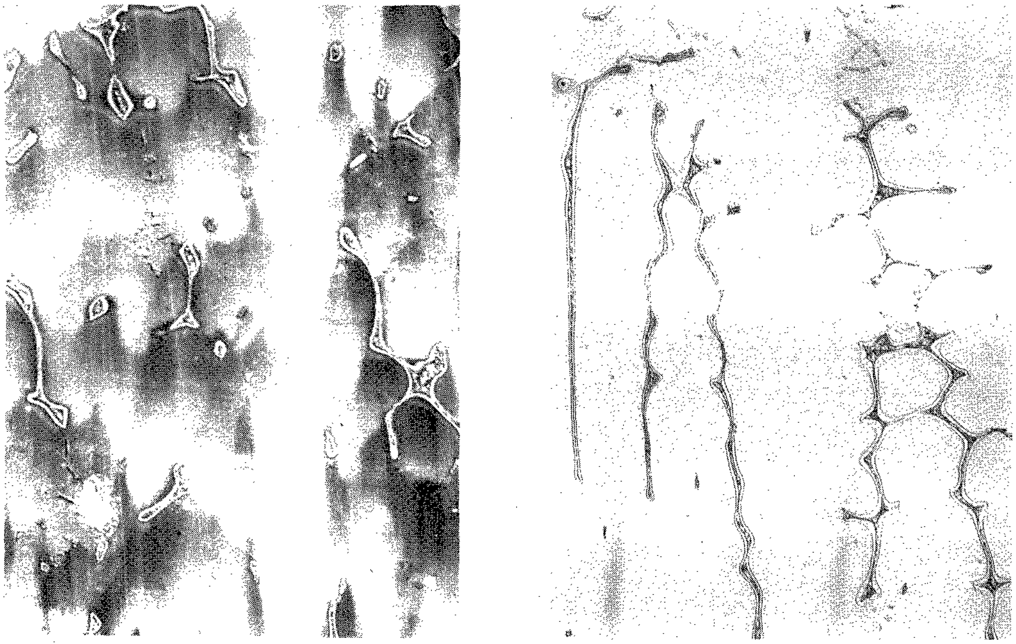

Fig. 5 The distribution of residual liquid during solidification of René 125, (a) without Hf, (b) Hf added

temperature is usually limited by the incipient melting temperature. As stated above, the final solidification temperatures could be more than one hundred degrees higher for the low segregation superalloys, and it would be true the incipient melting point. Therefore, the initial forging temperature can be about 100℃ higher than that of the conventional alloys. For instance, A286, Incoloy 901 and GH761 are Fe-Ni-Cr base disc alloys, their starting forging temperature is usually at 1120℃, they will be smashed if the forging temperature is too high. The temperature can be raised to 1220℃ without damage by lowering the trace element contents, such as $P \leqslant 0.001$, $Si<0.05$ and B from 0.001 to 0.003%. It is estimated that the resistance of deformation can be lowered by two thirds, by 100℃ increase of starting forging temperature. This process cannot only save energy due to low resistance of forging, but also can use smaller forging press or hammer to produce larger products. Another advantage is that good filling property for die forging due to high plasticity of the alloy at higher temperatures. The grain size of the final product can also be better controlled due to less chance to be performed at the critical deformation range which will cause excessive grain growth.

Some alloys with a composition containing large amounts of segregation prone elements, such as Nb, W, they are not suitable to produce very large ingot, such as Incoloy718, if low segregation technology is adopted, larger ingot could be produced. Consequences of this are high yield, high quality and low costs.

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