The Development and Long-Time Structural Stability of a Low Segregation Hf Free Superalloy - DZ125L

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Abstract

Solidification studies of cast superalloys carried out at the Institute of Metals Research showed that the trace elements P, Si, B, and Zr had a profound effect on the resultant as-cast structure. These trace elements lowered the liquidus and incipient melting temperatures as well as enhanced solidification segregation.

The control of the P, Si, B, and Zr levels, called low segregation technology, can raise the incipient melting temperature as to provide a higher service temperature of 20-25°C and reduce the segregation to enhance long-time stability at 900°C.

A new Hf free DS alloy has been developed by the low segregation technology called DZ125L. It shows rupture strengths two to three times longer than the corresponding conventional alloys either at high or medium temperatures in both longitudinal or transverse directions. These properties are attributed to less shrinkage porosity due to a smaller liquidus-solidus gap and lower segregation.

Introduction

At the present time and in the future, superalloys will still be the "workhorse" of materials for jet engines and industrial gas turbine engines. Current studies are underway to raise the service temperature of existing alloys by melt practice, design, or new coatings. However, the melting point limits the temperature of application of superalloys and the addition of large amounts of refractory elements for high temperature strength lowers the melting point and increases segregation which affects the stability of the alloy during service.

Solidification studies of superalloys have been carried out since the sixties at the Institute of Metal Research. It was found that some trace elements, notably P, Si, B, and Zr, affected the segregation of these elements resulting in lower incipient melting points. A number of new superalloys have been developed based on the principle of trace element control (1-3). A most recent application of low segregation technology has been in the field of directionally solidified alloys.

DS superalloy blades were developed in the early sixties to take advantage of no grain boundaries perpendicular to the direction of applied stress, which resulted in higher creep and rupture strengths. However, because of the high refractory element content, the DS blades showed erratic third stage creep, low ductility, and exhibited transverse cracks along the grain boundaries. This detrimental behavior was solved by the addition of 1-2% Hf (4,5).

Hf is a rare and expensive element and reacts strongly with oxygen to form HfO either during the melt or remelt cycles. A number of studies have been carried out on the effects of Hf on the microstructure and mechanical properties of a number of superalloys (6,7). The objective of this paper is to describe the results of applying the low segregation technology to the development of a Hf free DS superalloy.

Alloy Development

To study the effects of trace elements P and Si on the solidification and mechanical properties of a Ni base alloy with high refractory content, a series of alloys were made with varying amounts of P and Si and stress-rupture tested at 760°C and 804 MPa. The results of the tests are given in Table 1.

Based on these results, a low segregation alloy called DZ125L was developed similar in composition to René 125 except the Hf and Zr were removed and the B, P, and Si contents were reduced to very low levels as shown in Table 2.

The nominal composition of René 125 is shown in Table 2. Although René 125 was put in a DS form in order to compare it to a Hf free composition, DZ125L, René 125 is a Ni base superalloy developed by GE and is used in equiaxed turbine blades. The development and application of René 125 has been described by P. Aldred (8).

The René 125 and DZ125L compositions were directionally solidified in a conventional DS furnace. Samples of DS René 125 and DZ125L alloys were stress-ruptured tested in the longitudinal and transverse directions. The results are given in Table 3.

The results show a much longer life in stress-rupture for the DZ 125L alloy. To understand and explain the reasons for the longer stress rupture life of the DZ 125L alloy compared to that of the DS René 125 alloy, a solidification study was carried out on both alloys as well as a long time structural stability program.

Solidification Behavior of DZ125L and DS René 125

In the solidification study, a 10 mm cube of each alloy was melted in a graphite boat and heated to 1420°C in a SiC tube furnace and held for 5 minutes to ensure a total molten condition. It was then cooled down slowly to a preset temperature, held for 10 minutes and water quenched. The percent of liquid and (γ+γ') eutectic structure of the solidified material was determined under an optical microscope. Table 4 shows the results of this study.

The data in Table 4 shows that DS René 125 begins solidification below 1350°C and (γ+γ') precipitates below 1230°C. The alloy is finally solidified at 1100°C. For the DZ125L alloy, the liquidus is 1370°C, the (γ+γ') eutectic precipitates from 1250°C, and the solidus is at 1230°C from which γ' precipitates. The difference in the solidus temperatures of the two alloys can range up to 130°C.

The (γ+γ') eutectic formation range for the DZ125L is about 30°C while in the DS René 125 alloy the eutectic keeps forming until 1100°C. The amount of eutectic measured is 14.5% for the DS René 125 alloy to only 5% for the DZ125L alloy.

An electron probe study of the final liquid to freeze in the DS René 125 alloy, Table 5 shows the greatest enrichment takes place in the P content followed by Zr, B, and Si. These elements can form low melting point eutectics such as Ni-P and Ni-Zr. Samples that were quenched from 1350°C and 1230°C show the degree of MC formation at 1350°C is more advanced in the DZ125L alloy, Figure 1a, while a large amount of segregation is still present in the DS René 125 alloy at 1230°C, Figure 1b.

The nature of the segregation is quite different in the DS René 125 at 1290°C as compared to the DZ125L alloy as shown in Figure 2. The segregation area shown for the DS René 125 contains small discrete borides and Hf enrichment while the segregation areas in the DZ125L tend to show high Ti liquid giving rise to an MC structure.

Structure Analysis

As-Cast Condition

The as-cast microstructure of the DZ125L alloy consists of two MC phases. The main MC phase is a script form with lessor amounts of a discrete carbide. The MC carbide in the DS Rene 125 is a discrete shaped carbide.

Table 1. Effect of P on the stress rupture life (hr).

P(wt%)	0.0005	0.0022	0.0034	0.0052
760°C/804MPa	336	218	187	126

Effect of Si on the Stress Rupture Life (hr).

Si(wt%)	0.03	0.1	0.2
980°C/235MPa	117	111	59

Table 2. Composition of the Experimental Alloys (wt%)

Alloy	C	Cr	W	Al	Ti	Mo	Co	Ta	Hf	B	Zr	P	Si	Ni
A*	0.11	9	7	4.8	2.5	2	10	3.8	1.8	0.015	0.1	0.005	0.1	Bal
B*	0.11	9	7	4.8	2.5	2	10	3.8	--	0.008	0.05	0.0005	0.05	Bal

Table 3. Stress Rupture Life of DS René 125 and DZ125L Alloys (hr).

Alloy	Rupture Strength (hours)		
	980°C/235MPa(L)**	760°C/804MPa(L)**	760°C/725MPa(T)***
A*	25-50	72-104	28-39
B*	98-135	218-354	62-97

A*= conventional DS Rene'125   B*= low segregation DS Rene'125 without Hf.
L**= longitudinal   T***= transversal

Table 4. Solidification of Two Alloys.

Temperature °C	DS Rene' 125		DZ125L	
	L(%)	(γ+γ')(%)	L(%)	(γ+γ')(%)
1370	100		100	
1350	100		70	
1330	60		35	
1310	40		25	
1290	20		10	
1270	19		6	
1250	18		3	2
1230	17	1	Trace	5
1215	10	7		
1200	8	10		
1180	6	11		
1160	5	12		
1140	3	13		
1120	2	14		
1100	Trace	14.5		

Table 5. Enrichment in the Final Residual Liquid in DS Rene' 125 Alloy.

Element	P	B	Zr	Hf	Si
Alloy(wt%)	0.0029	0.019	0.10	1.15	0.21
In final residual liq.(wt%)	0.8/1.3	0.6/1.2	3.8/5.7	15/21	1.4/3.3
Enrichment rate	275/48	31/63	38/57	13/18	6/15

Table 6. Content of M in MC

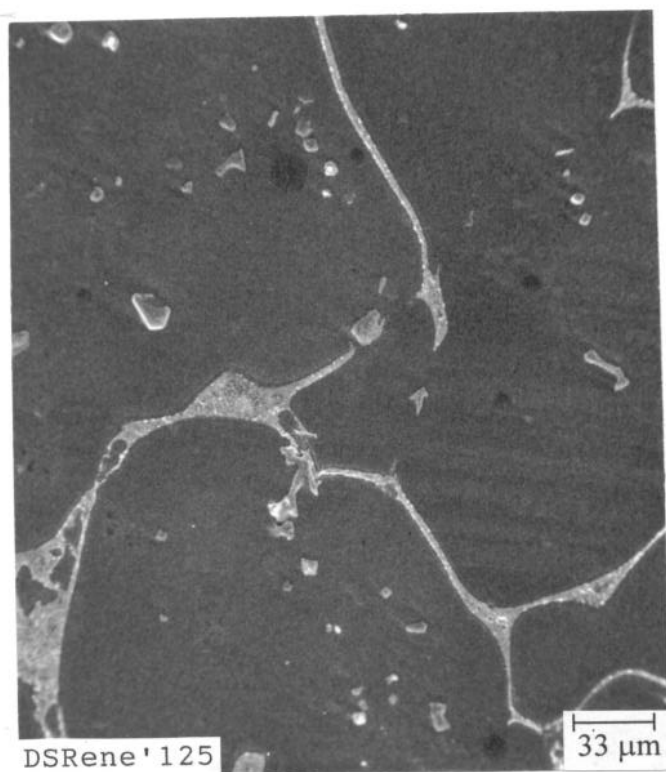| Element		Ti	Ta	Hf	W	Mo	Cr	Ni	Co
DZ125L	wt%	19.9	56.7	-	15.9	2.6	1.0	3.4	0.6
	at%	44.6	33.7	-	9.3	3.0	2.1	6.3	1.0
DS	wt%	17.0	62.5	2.1	11.7	1.7	0.7	4.1	0.5
	at%	40.1	39.2	1.3	7.2	2.0	1.4	7.0	1.0
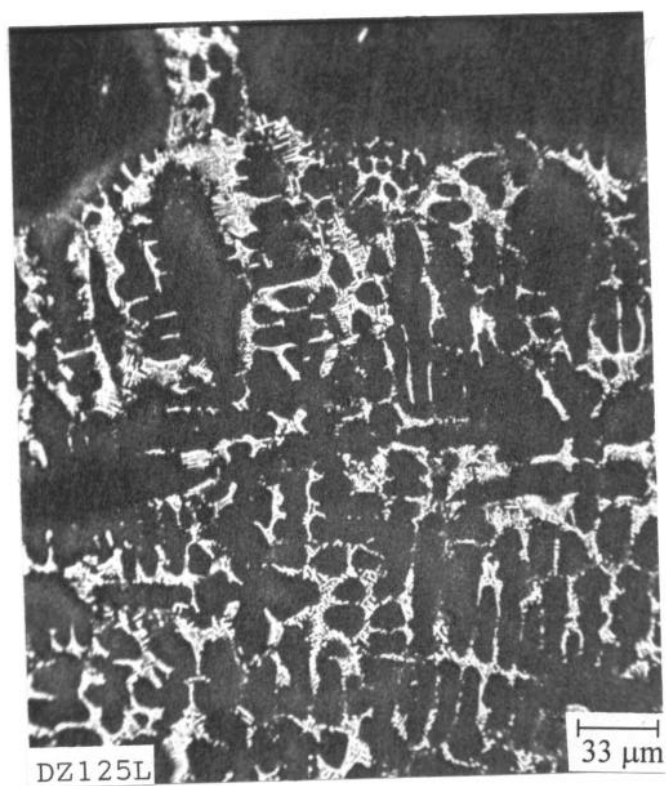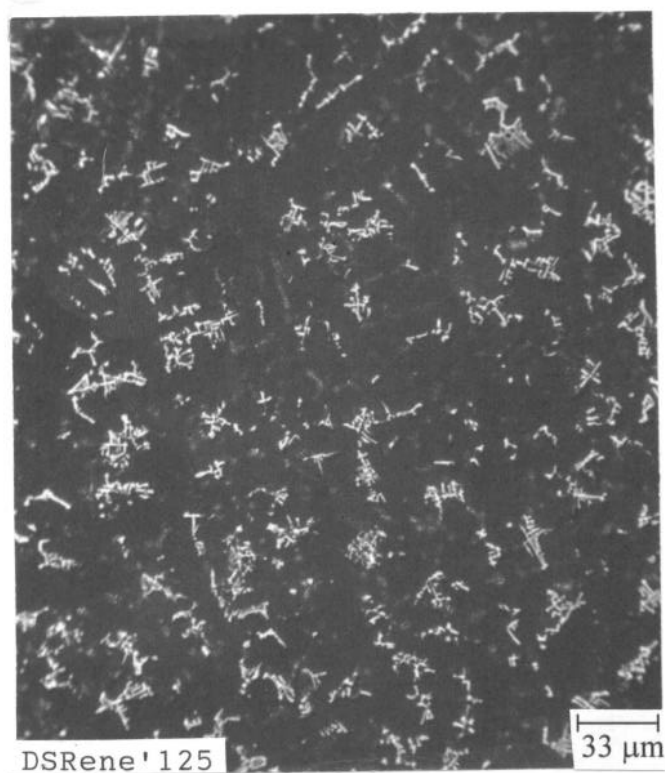
Figure 1a: MC precipitation at1350ºC
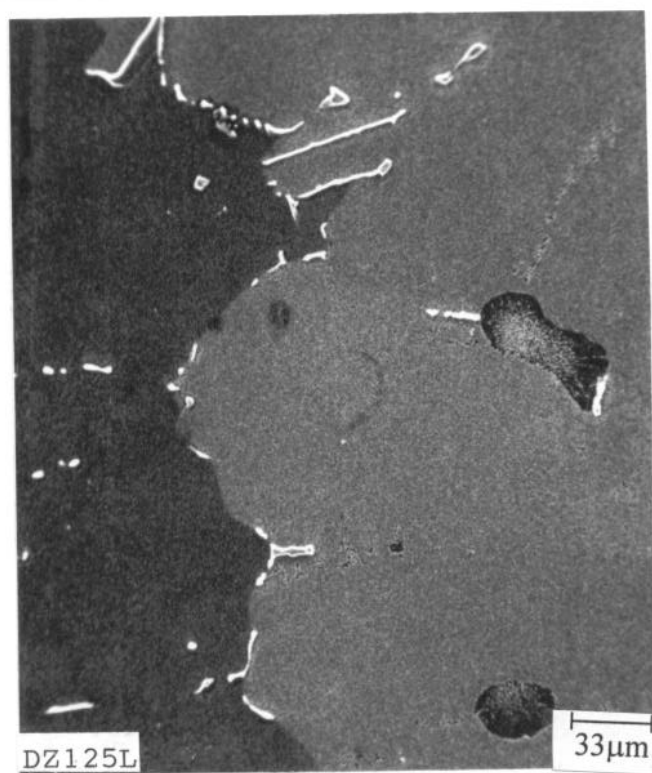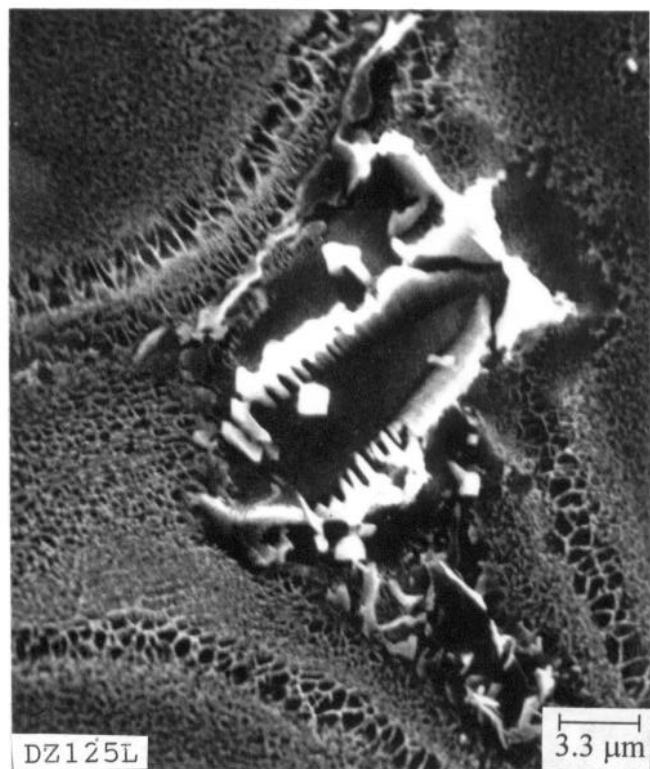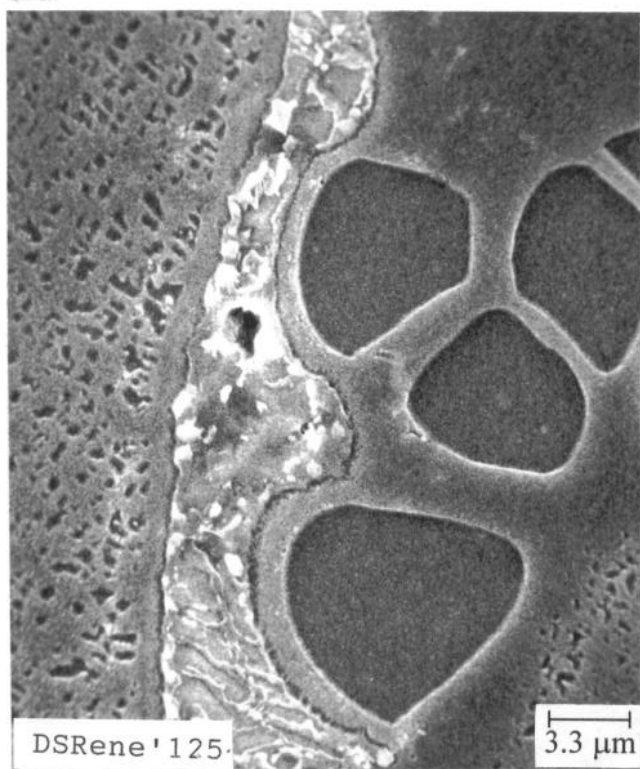

Figure 1b: Segregation structure at 1230ºC
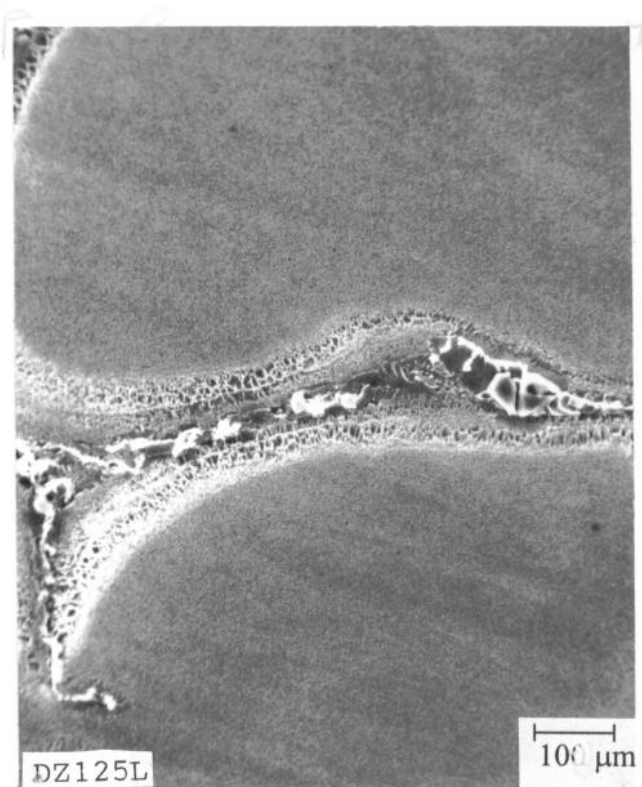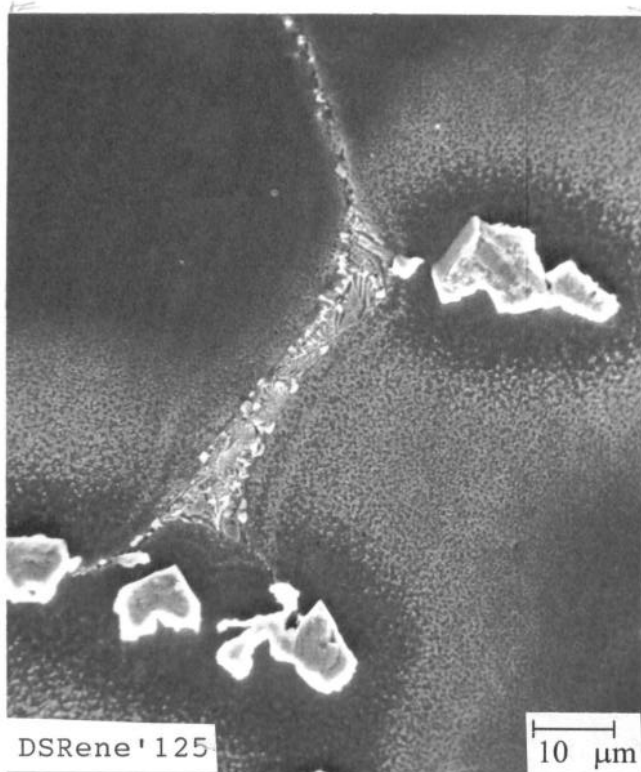
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Figure 2: Segregation areas at 1290°C and 1140°C

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Both alloys contain eutectic or primary γ' islands but the amount of these island on M23s is much greater in the DS René 125 alloy, Figure 3. There appears to be one γ' size in the DS René 125 alloy while two sizes of γ' appear in the DZ 125L in a dendrite pattern.

The amount of γ' forming elements are the same in both alloys but the presence of a large amount of primary γ' islands in the DS René 125 alloy would indicate higher segregation and less possible γ' for strengthening in the DS René 125 alloy. The periphery of the primary γ' islands are known areas where borides and Hf rich carbides form upon high temperature heat treatments.

The chemical analyses of the carbides in both alloys are given in Table 6. High Ti and Ta are present in the carbides in both alloys with minor amounts of Cr, Ni, and Co. However, the carbides in DS René 125 also contain Hf and lessor amounts of W+Mo than those in the Hf free DZ125L. Additional micro probe studies show the discrete carbides in the DZ125L alloy are richer in Ti than the script carbides which would indicate a greater tendency to decompose during heat treatments and/or long-time exposures.

Heat Treatment

Both alloys were given the same heat treatment before testing and long-time stability tests at 900°C. The heat treatment consisted of 1220°C/2 hours-A.C. + 1080°C/4 hours A.C. + 900°C/16 hours A.C.

The resultant structures are shown in Figure 4a. The DS René 125 alloy shows some small precipitation near primary γ' islands due to the 1220°C temperature, $M_{23}C_6$ at the grain boundaries and a uniform γ' phase. Near the primary γ' islands there are areas of finer γ' present. The main γ' precipitation is due to the γ' solutioning at 1220°C and re-precipitation of γ' at 1080°C.

The γ' has not totally solutioned at 1220°C in the DZ125L alloy. The γ' precipitated at the 1080°C temperature is more carboidal in shape than the unsolutioned γ'.

The grain boundaries also show some $M_{23}C_6$ precipitates.

900°C Stability

After 1000 hours exposure at 900°C, the DS René 125 shows more fine precipitates near regions of primary γ'. Some carbides show evidence of decomposition and additional $M_{23}C_6$ is seen at the grain boundaries, Figure 4b. An occasional needle or plate is present in random areas.

In the case of the DZ 125L, the discrete carbides show decomposition resulting in a rosette like formation of $M_{23}C_6$. More $M_{23}C_6$ is present at the grain boundaries and no plate structure is seen.

After 2000 hours exposure at 900°C, there is more discrete $M_{23}C_6$ precipitation in the grain boundaries of each alloy. The γ' phases do not appear to have changed due to the additional 1000 hour exposure as shown in Figure 5a. The most notable change appears to be as large additional formation of the plate phase in the DS Rene 125 and only a few small areas showing plates in DZ 125 L as shown in Figure 5b.

A micro-probe analysis of the plate phase gives in wt.% 39.1W, 15.3Mo, 13.4Cr, 16.9Ni, 11.7Co, 1.3Al, 1Ti and 1.4Ta. The composition suggests the Mu phase which by extraction and x-ray analysis confirms the phase to be Mu.

Phase Identification

The inert carbide and other phases present after 2000 hours at 900°C were extracted in a 10% HCl-methanol solution and analyzed by x-ray diffraction.

The x-ray chart for the DZ125L shows only $M_{23}C_6$ and an MC whose lattice parameter is 4.36Å. The presence of only one $M_{23}C_6$ phase indicates that the grain boundary carbide is $M_{23}C_6$ and the rosette structure due to the discrete breakdown is also $M_{23}C_6$.

The x-ray pattern of the DS René 125 is more complex. Two MC phases are present with lattice parameters of 4.37Å and 4.52Å, a $M_{23}C_6$ phase, and a Mu phase.
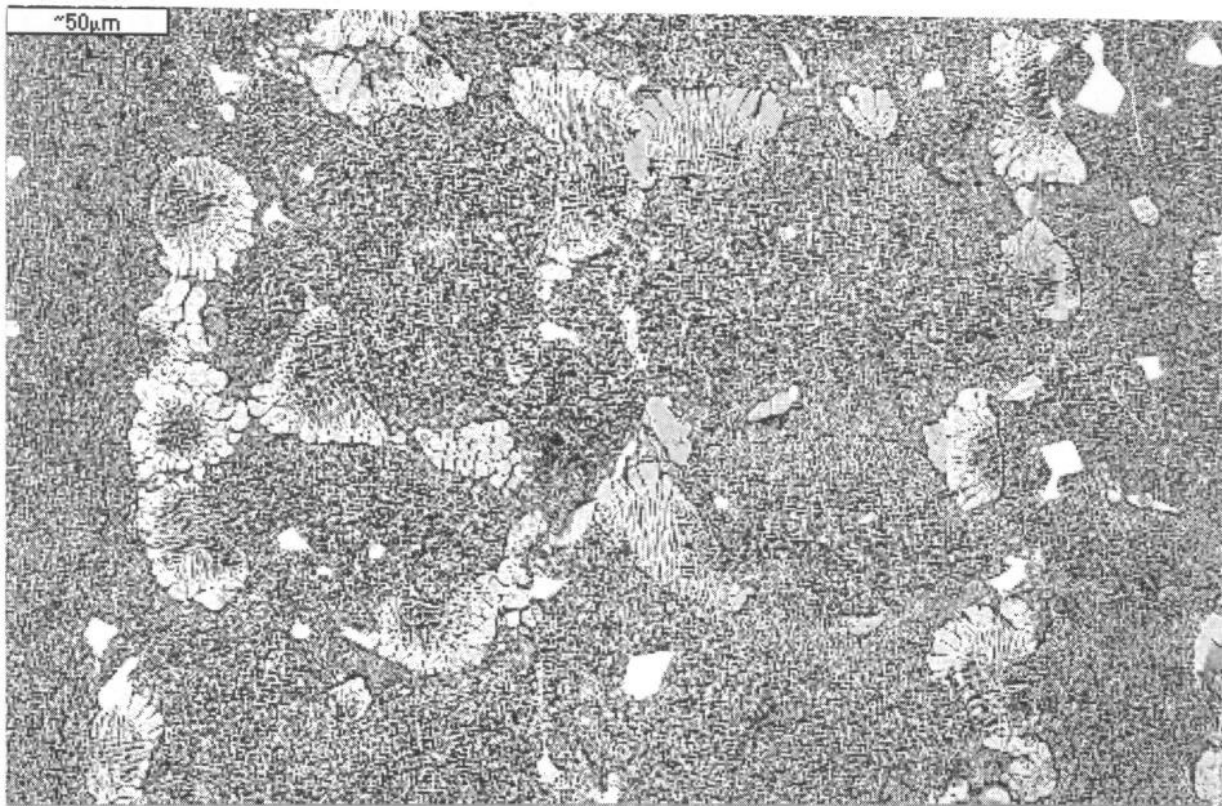
DS René 125   (γ+γ′) · Eutectics   14%
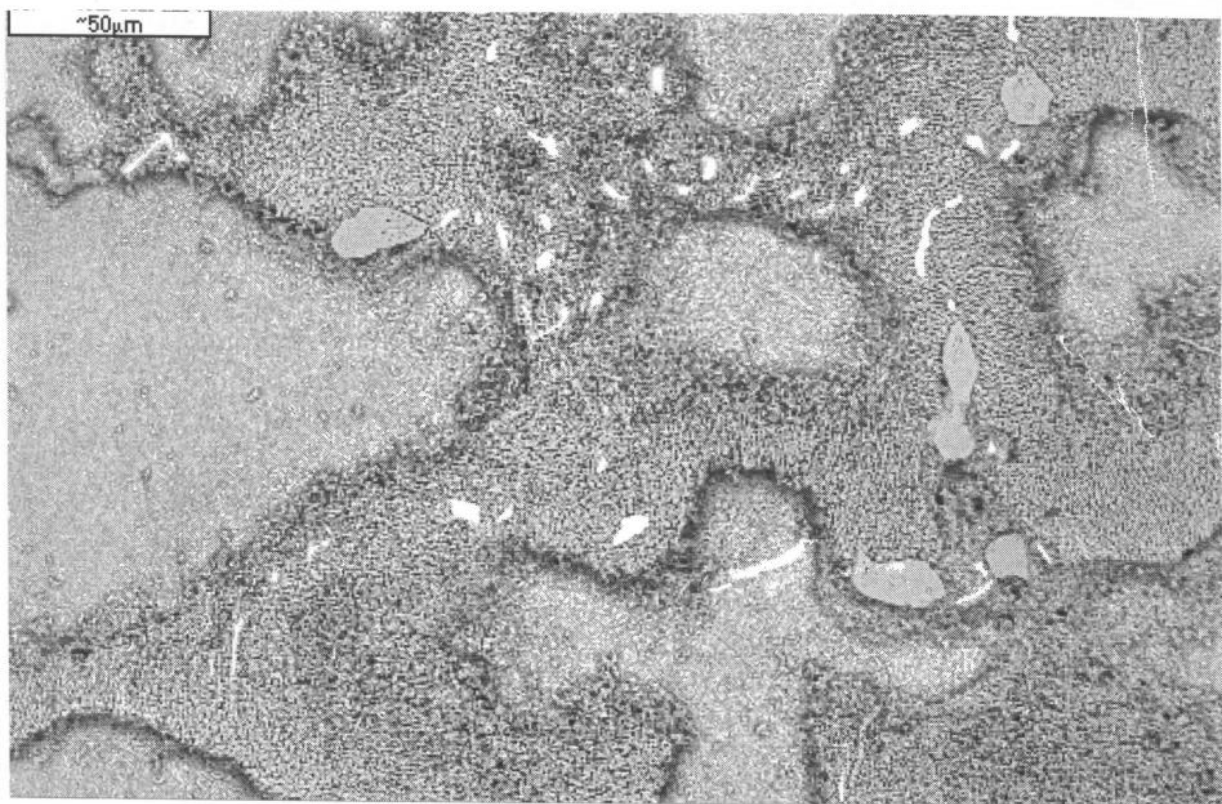
DZ 125L   (γ+γ′) Eutectics   5%

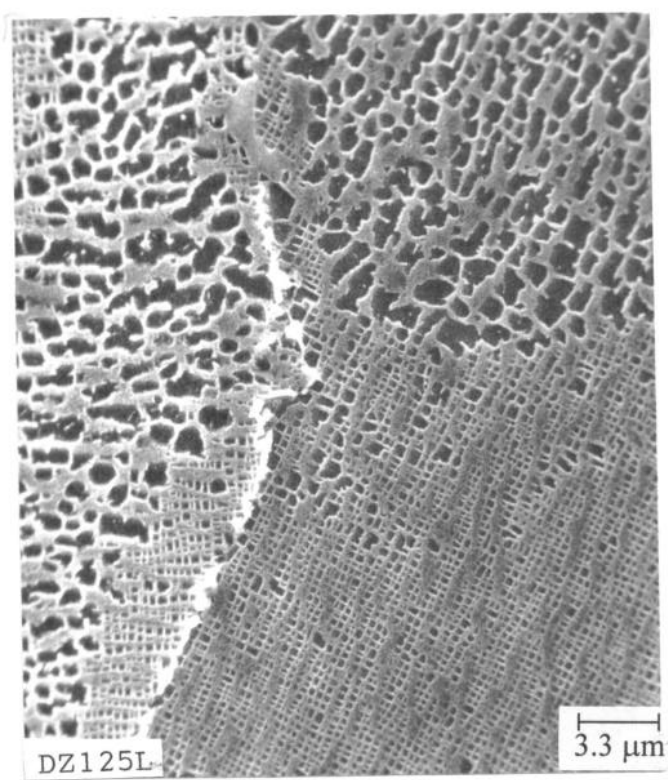Figure 3: A-cast (γ+γ′) eutectic structure
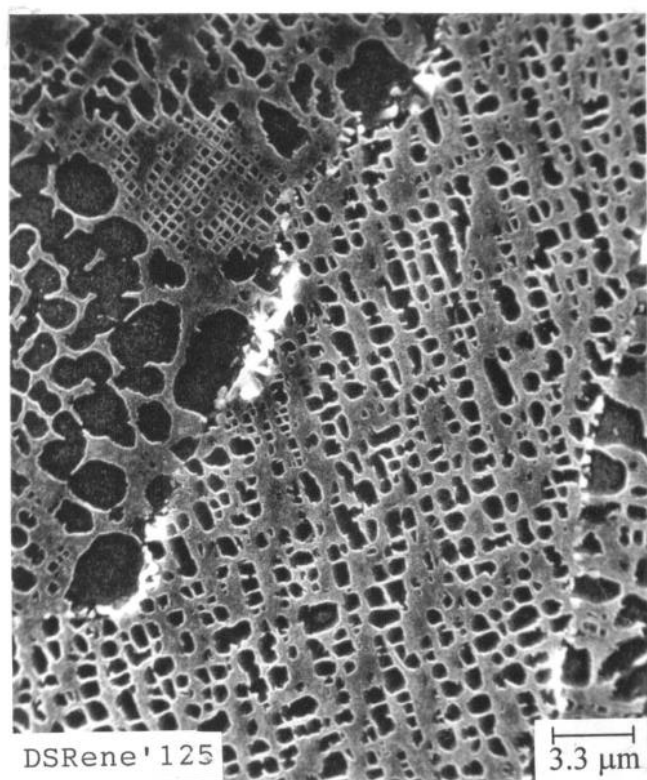
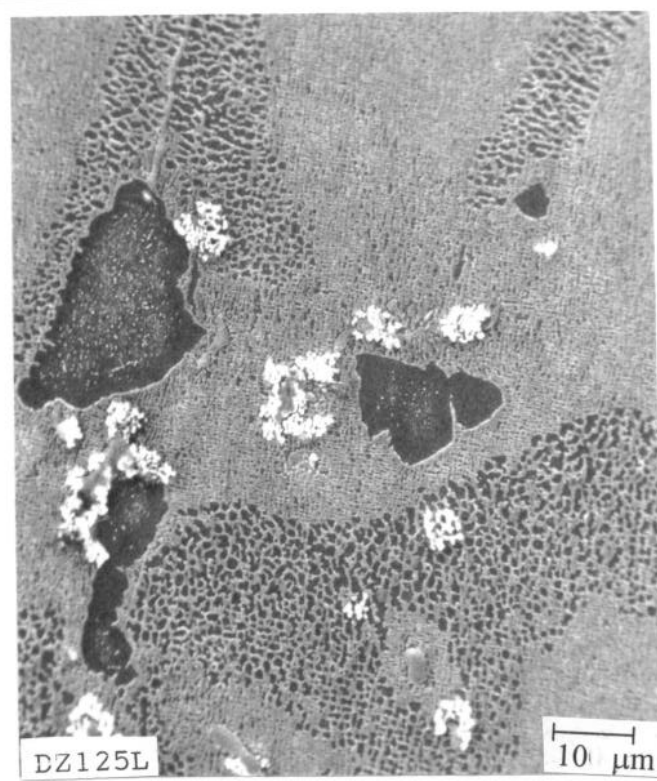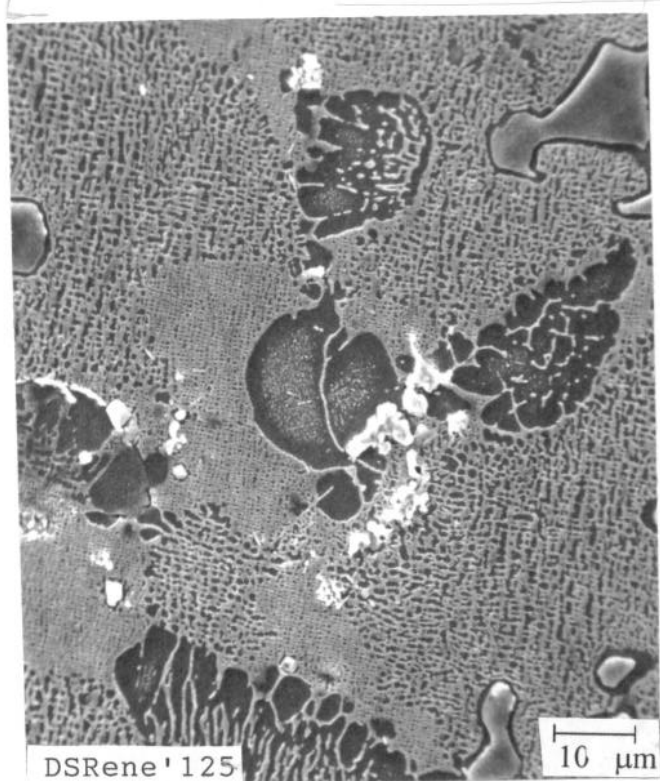Figure 4a: As heat treated structures

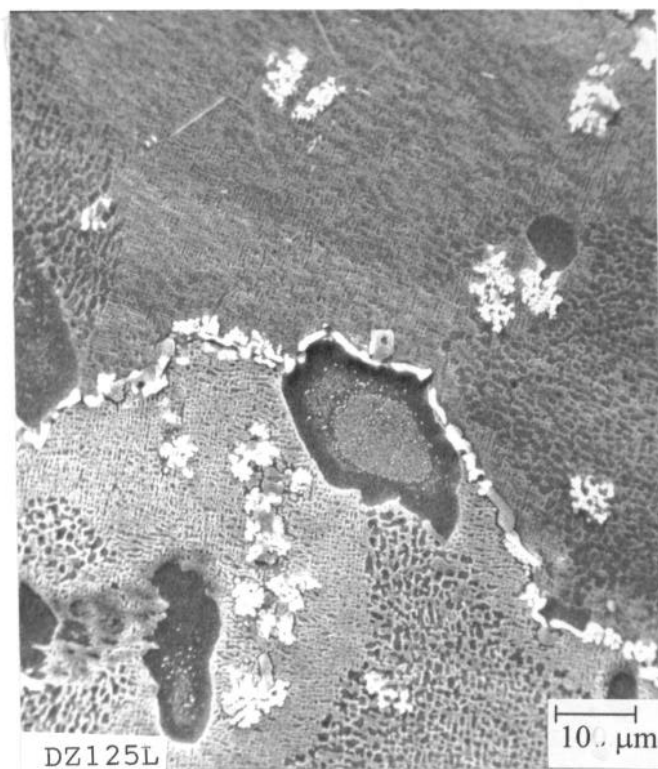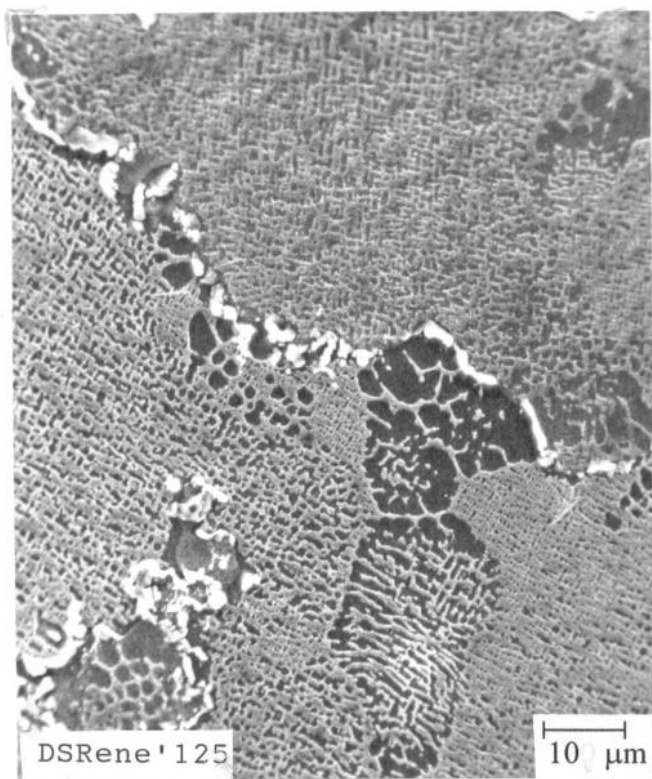Figure 4b: Microstructures after 1000 hrs at 900°C

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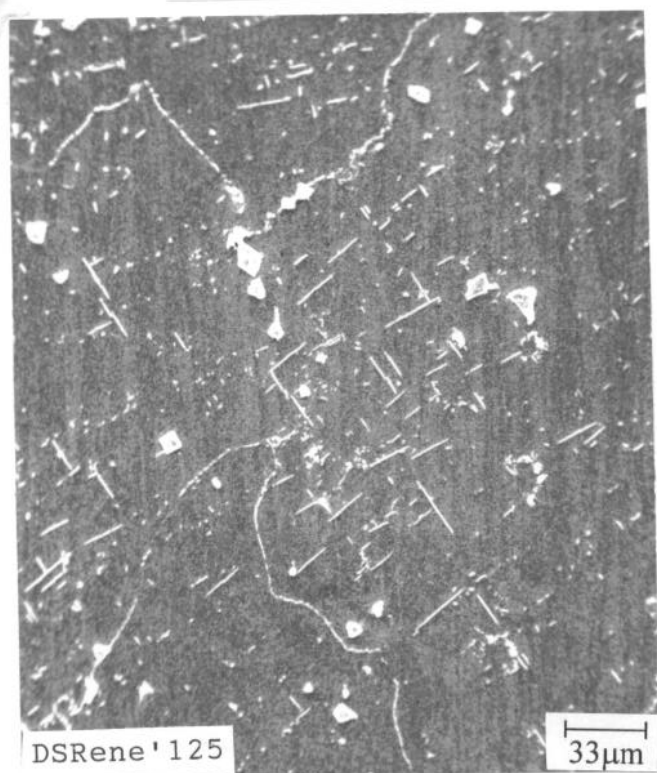Figure 5a:Microstructures after 2000 hrs at 900°C

Figure 5b: Mu phase precipitation after 2000 hrs at 900°C

Conclusions

A low segregation alloy DZ125L similar in base composition to DS René 125 was developed in China. It contains low P, Si, B and no Hf or Zr. Solidification studies show DZ125L to have a much narrower solidification gap compared to DS René 125 and has much fewer primary γ' islands (5% vs. 14%). As the Al+Ti in primary γ' islands does not contribute to strengthening, it is felt the higher stress-rupture properties of DZ125L compared to DS Reneé 125 is attributed to more Al+Ti available because of the fewer primary γ' islands.

As cast DS René 125 contains segregation areas on the periphery of many γ' islands. These areas are rich in Mo and Hf and they form borides and Hf rich carbides during high temperature processing or heat treatments. In contrast, the areas of segregation found along some primary γ' islands in the DZ125L alloy are richer in Ti and revert to TiC during processing.

High segregation areas in alloys with high γ' and refractory elements form plate structures when the solubility of the matrix is exceeded by more alloying or long-time exposures. DS René 125 develops appreciable Mu plates after 2000 hours at 900°C while only a small amount of isolated Mu phase is found in DZ125L alloy in the same exposure time. Because the solidification gap in DZ125L is small, the degree of porosity is minimized and columnar growth during solidification is improved. Porosity enhances the tendency for longitudinal cracking and lowers the transverse properties at intermediate temperatures.

References

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