# DETERMINATION OF THE SOLIDIFICATION BEHAVIOUR OF SOME SELECTED SUPERALLOYS

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#### Summary

Equilibrium solidification ranges and melt equilibria of the alloys 625, 718, 825 hMo, X, X-750 and 80 A have been determined. After isothermal holding and quenching of alloy samples the partition coefficients of the alloy components Ni, Cr, Mo, Fe, Cb and Ti as a function of temperature have been evaluated by means of microprobe measurements. There is no identical segregation behaviour of the individual alloy components in the above mentioned alloys. The partition coefficients nevertheless can be described by a linear function of temperature. The segregation behaviour of Cr and Cb in alloy 718 during quasi-isothermal solidification is in accordance with a mathematical model which was developed previously for binary alloys.

The influence of increasing solidification rates on dendrite arm spacing as well as on microsegregation has been studied by directional solidification experiments. The primary dendrite arm spacing is related to the cooling rate by a power function. However, a pronounced reduction of segregation can only be achieved at the cost of significant extension of the dendrite arm spacing.

#### Introduction

The development and application of new casting technologies in the manufacturing of semi-finished products of nickel base alloys demands a more precise knowledge of the solidification behaviour of these complex multi-component systems. The usually appplied multi-stage hot forming of ingots allows working towards an optimum microstructure by means of forming and annealing operations. With the aim of cost reduction, continuous casting has already been introduced to the manufacturing of nickel base alloys which includes the advantage of steady state solidification. However, with new near net shape casting technologies the potential to influence the microstructure by extensive forming and annealing operations will be reduced considerably.

Superalloys 1988 Edited by S. Reichman, D.N. Duhl, G. Maurer, S. Antolovich and C. Lund The Metallurgical Society, 1988 Because of this development a better knowledge of the proceedings during solidification gains more importance. At an early stage already, mathematical models had been developed to describe the solidification behaviour of binary alloys. These models differentiated between microand macrosegregation. Basic research in this field was done by Scheuer (1), Scheil (2), Brody and Flemings (3), Clyne and Kurz (4), as well as by Oeters and coworkers (5). For the description of segregation in multicomponent systems, as they are to be found in superalloys, no mathematical models have been published so far. Therefore, the process parameters governing the solidification have to be verified experimentally.

Table 1 shows the alloys which have been studied with regard to their solidification behaviour. The solid solution hardening nickel base alloys 825 hMo, X and 625 have been examined. Alloys 718, X-750 as well as 80 A have been included as examples of age-hardenable materials. In addition to the principal alloy components Ni, Cr, Mo and Fe the segregation behaviour of Cb and Ti was examined.

Table 1: Chemical composition of the experimental alloys, wt%

Alloy	<u>Ni</u>	<u>Cr</u>	Mo	<u>Fe</u>	<u>Cb</u>	<u>Ti</u>	<u>Al</u>	<u>other</u>
825 hMo X 625 718 X-750 80 A	bal. bal. bal.	21.0 21.8 18.2 15.7	9.0 8.9 3.2		- 3.4 5.4 1.0	0.19 0.93 2.6	- 0.18 0.64	2.3 Cu 0.56 W,1.0 Co

# Examination of the equilibrium solidification behaviour

Equilibrium solidification is usually described by means of a phase diagram which refers to extremely slow cooling. In case of binary systems thermal analysis is preferred because knowledge of both the individual basic components and the liquidus and solidus temperatures allows the design of a phase diagram and provides a measure for the segregation to be expected, characterized by the width of the liquidus-solidus temperature interval. In multi-components system this procedure cannot be applied. Therefore, the method of isothermal holding in the heterogeneous area between the liquidus and solidus temperatures was introduced to determine the equilibrium solidification behaviour. Subsequent to the adjustment of the equilibrium at a previously defined temperature, the sample is quenched in water.

During quenching, the residual melt, which is in the state of equilibrium with the precipitated solid crystal, solidifies with the shape of extremely fine dendrites. By means of microprobe analysis both phases were subsequently analyzed with respect to their composition. Several experiments within the equilibrium solidification interval allow an exact determination of the partition coefficients of the individual alloy components as a function of temperature and composition.

<u>Figure 1</u> shows a typical microstructure as it is to be found in this experimental procedure. Coarse primary crystals are surrounded by a dendritic solidified residual melt. The analysis of the concentration profiles across the coarse primary crystals verified that the equilibrium was reached completely in the solid crystal.

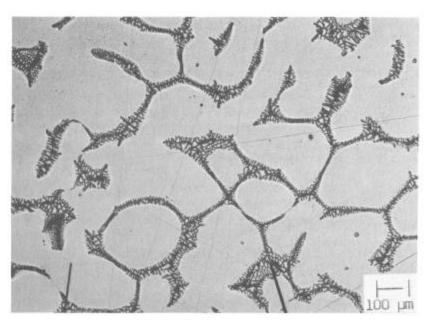


Figure 1:

Microstructure of alloy 718 after isothermal holding at 1310°C and water quenching

S : primary crystal

L : residual melt

The microprobe analysis showed, that during solidification, the primary crystals become enriched with nickel and iron in all alloys under consideration. The same applies for chromium. There are, however, exceptions. As demonstrated in  $\underline{\text{Fig. 2}}$  it is only in alloy X that chromium segregates preferentially into the residual melt and the chromium concentration in the residual melt does not vary during solidification of alloy 80 A. In all alloy compositions examined so far, molybdenum, titanium and particularly columbium are enriched to a high degree in the residual melt. Columbium segregation is shown in  $\underline{\text{Fig. 3}}$ .

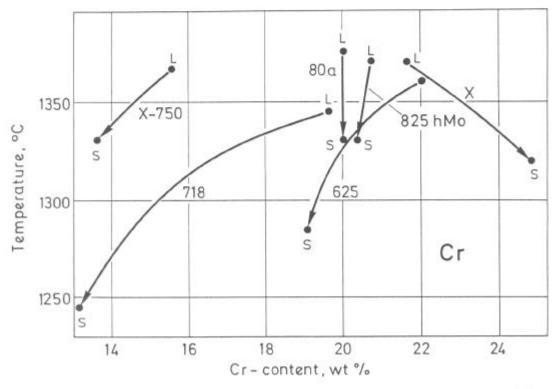


Figure 2: Chromium equilibrium concentration in the residual melt of various nickel base alloys as a function of temperature

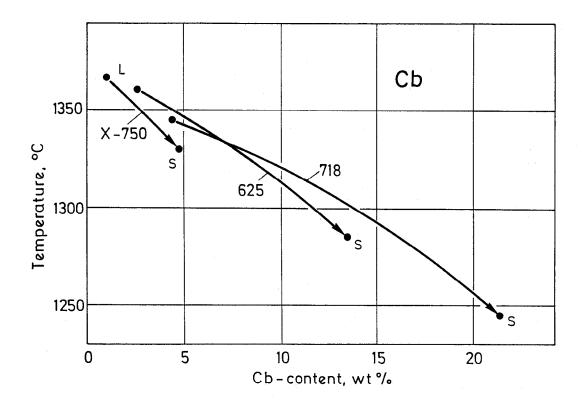


Figure 3: Columbium equilibrium concentration in the residual melt of various nickel base alloys as a function of temperature

The microprobe measurements revealed that the degree of segregation as defined by the equilibrium partition coefficient  $K_0 = C_0/C_1$  is not the same within the whole solidification interval, but can be described as a linear function of temperature of the form:

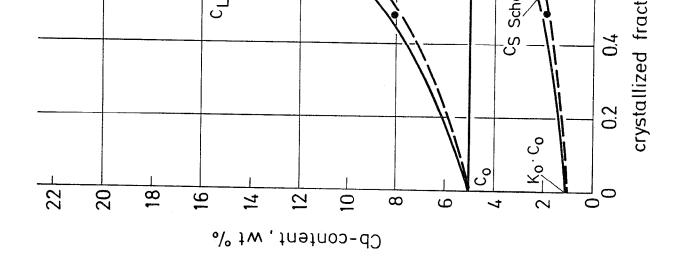
$$K_0 = a + bT$$

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Out of all the alloys examined so far, columbium is remarkable for its extreme segregation behaviour. An enrichment of up to 21.5 % Cb has been observed in alloy 718. Since in case of the 3 alloys examined the partition coefficient is at about the same low level the width of the liquidus-solidus solidification interval L-S strongly determines the amount of segregation (Fig. 3).

	ب- ٥	ار د د	N. K.	ح و د د	చి ~	<sub>8</sub>	, <del>X</del> 0
alloy 825	1370	1330	1370 1330 2.08-7.50 10 <sup>-3</sup> t 10.29-6.75 10 <sup>-3</sup> t	10.29-6.75 10 <sup>-3</sup> 1	n.d.	-5,47+4,50 10 <sup>-3</sup> T	ט•ט
alloy X	1370	1320	1370 1320 9.04-5.80 10 <sup>-3</sup> T	1	2.87-1.20 10 <sup>-3</sup> t 0.36-0.40 10 <sup>-3</sup> t 0.64+0.8 10 <sup>-3</sup> t	0.64+0.8 10-31	n.c
alloy 625	1360	1285	1360 1285 4.13-2.27 10 <sup>-3</sup> T	7.45-4.67 10 <sup>-3</sup> 1	7.45-4.67 10 <sup>-3</sup> t 3.54-1.87 10 <sup>-3</sup> t 0.18+0.53 10 <sup>-3</sup> t	0.18+0.53 10 <sup>-3</sup> t	-1.29+1
alloy 718	1345	1245	1345 1245 1.72-0.50 10 <sup>-3</sup> T	5.50-3.2 10 <sup>-3</sup> t	5.64-3.40 10 <sup>-3</sup> 1	***************************************	0.2
alloy X-750	1367	1367 1330	2.85-1.35 10 <sup>-3</sup> T	2.85-1.35 10 <sup>-3</sup> t 10.39-6.76 10 <sup>-3</sup> t 4.38-2.43 10 <sup>-3</sup> t	4.38-2.43 10 <sup>-3</sup> T	n.d.	-6.68+9
alloy 80 A	1375	1330	1375 1330 3.14-1.56 10 <sup>-3</sup> T	n.d.	2.22-0.89 10 <sup>-3</sup> T	n.d.	חים

\* independent of temperature



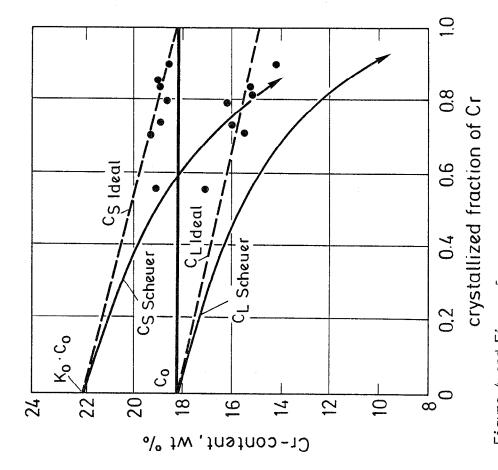


Figure 4 and Figure 5: Variation of chromium and columbium concentrations in the crystal and in the residual melt of alloy 718 with progressing solidification (calculation according to E. Scheuer and the ideal solidification model).

## Mathematical description of the solidification processes

Under real solidification conditions the residual melt will be segregated stronger than under ideal solidification conditions, since a complete equalization of the chemical composition by diffusion according to the equilibrium in the solid crystal and the residual melt cannot be obtained. As mentioned above, mathematical models for the solidification processes of binary alloys have already been developed and shall now be applied to the complex multi-component systems. This is, however, done on the basic assumption that the individual alloy components do not influence each other with respect to segregation behaviour.

Assuming a complete mixing of composition in the liquid and no equalization by diffusion at all in the crystal, the course of the change of chemical composition in the residual melt can be determined according to E. Scheuer (1) as a function of the crystallized fraction fs:

$$C_L = C_0 (1 - fs)^{-(K_0 - 1)}$$
  
 $C_s = K_0 C_0 (1 - fs)^{-(K_0 - 1)}$ 

In case of ideal solidification conditions with a complete balance of composition by diffusion in both the solid and the residual melt the element concentration will always change according to the following equations:

$$C_{L} = \frac{C_{o}}{1 - fs + K_{o}fs}$$

$$C_{s} = \frac{C_{o} \cdot K_{o}}{1 - fs + K_{o}fs}$$

Since on this assumption the element concentrations do not depend on the solidification rate, the results obtained by means of isothermal holding experiments are expected to follow this rule.

Figures 4 and 5 show, as an example, the element concentrations of Cr and Cb in alloy 718 as a function of the crystallized fractions for both assumptions. As to be expected, the experimental data correspond well with the model for ideal solidification. Under real solidification conditions the element concentration in the residual melt will be found somewhere between both lines, since some equalization by diffusion can take place in the crystal as soon as a concentration gradient is built up at the solidification front.

# The influence of the cooling rate on the microstructure and segregation

In order to analyze the microstructure obtained at different cooling rates, samples of alloys 625, 718 and X were cooled down in a temperature controlled tube furnace. The temperature gradient at the solidification front was about 20 K/min. The cooling rates ranged from 24°C/min to 1°C/min. A solidified microstructure is given in Figure 6 for alloy 625. The transverse microsection clearly shows the primary dendrite arm spacing which had been determined as a function of the cooling rate. As shown in Fig. 7 and to be expected, the primary dendrite arm spacing is becoming smaller with increasing cooling rates.

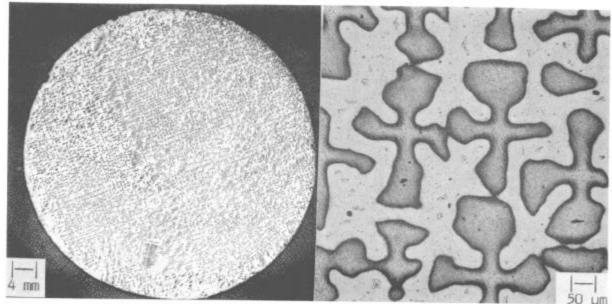


Figure 6: Transverse microsection of an alloy 625 sample, which had been directionally solidified. Cooling velocity was 12°C/min.

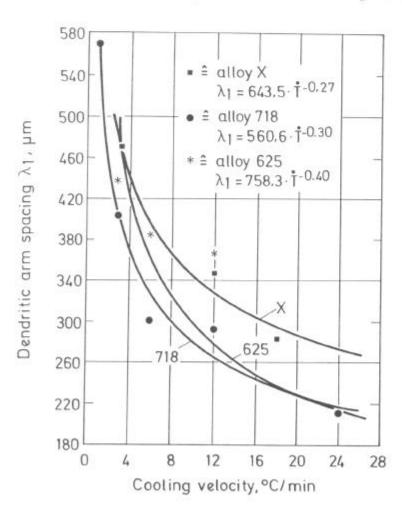


Figure 7: Comparison of the dendrite arm spacing of different nickel base alloys as a function of the cooling velocity

The influence of the cooling rate T on the primary dendrite arm spacing  $\mathbf{\lambda}_1$  can be described by the emperical equation indicated in Fig. 7.

In order to assess the amount of microsegregation as a function of the cooling rate, concentration profiles across the dendrite arms have been determined by microprobe analysis. Some of the results having been obtained on alloy 625 are shown in Table 3.

Table 3: Segregation behaviour of alloy 625 at controlled rates of cooling

dT °C min	a <sub>l</sub> μm		Ni	Cr	Fe	Мо	СЬ
		C <sub>s</sub>	65.0	23.0	2.37	8.0	1.6
12	367	c <sub>L</sub>	59.0	20.0	1.62	11.0	6.5
		$K_E = \frac{C_S}{C_L}$	1.10	1.15	1.50	0.73	0.25
2 = 2 = 2 = 2 = 2 = 2 = 2 = 2 = 2 = 2 =	THE	c <sub>s</sub>	66.0	22.9	n.d.	7.7	2.0
3	436	c <sup>r</sup>	61.0	20.4	n.d.	10.3	6.3
		$K_E = \frac{C_S}{C_L}$	1.08	1.12	n.d.	0.75	0.32

The influence of the cooling rate can be seen from the fact that the slowly cooled sample has effective partition coeffi-\_ cients which are closer to the ideal value 1. However. reduced segregation can only be achieved at — the cost of signifi cant extension of the diffusion distance. here characterized \_by the dendrite arm spacing (Fig.7).

Further microprobe analyses allowed to assess how different diffusion annealing treatments result in a reduction of segregation. Table 4 summarizes the results of a 20 and 50 hrs homogenization annealing at  $1200^{\circ}\text{C}$  ( $2192^{\circ}\text{F}$ ) in correlation to the dendrite arm spacing.

Thus, under identical annealing conditions, an extension of the diffusion distance of 19 % results in a remarkably less reduced segregation profile. If the concentration profile has to be equalized to a similar extent, the extension of the diffusion distance of 19 % demands an increase in the diffusion annealing time of about 150 %, provided the temperature is the same.

Table 4: Influence of diffusion annealing treatments on the reduction of segregation in controlled cooled

alloy	625 samples						
L <sub>l</sub> µm	diffusion annealing treatment		Ni	Cr	Fe	Мо	Cb
		C <sub>s</sub>	63.1	22.2	2.17	8.6	2.8
		c <sub>L</sub>	61.6	20.8	1.83	9.6	3.6
567	20 h, 1200°C	$K_{E} = \frac{C_{s}}{C_{L}}$	1.02	1.07	1.19	0.9	0.78
		reduction of segr.	80 %	53 %	62 %	63 %	68 %
		C <sub>s</sub>	64.6	22.9	<del>-</del>	8.5	ÿ <b>.</b> 1
		c <sub>L</sub>	61.3	20.6	_	10.4	4.5
	20 h, 1200°C	$K_E = \frac{C_s}{C_L}$	1.05	1.11	-	0.82	0.69
36 ·		reduction of segr.	38 %	8 %	-	28 %	59 %
. JO		C <sub>s</sub>	63.5	22.5	_	7.8	3.0
	50 h, 1200°C	c <sub>L</sub>	62.5	21.8	_	9.2	3.5
		$K_E = \frac{C_s}{C_L}$	1.02	1.03	-	0.85	0.86
		reduction of segr.	<b>75 %</b>	75 %	_	40 %	81 %

### Conclusions

- 1. During quasi-isothermal solidification of the nickel base alloys 625, 718, 825 hMo, X, X-750 and 80 A the alloy elements Mo, Ti and Cb will be enriched in the residual melt. Ni and Fe are segregating into the primarily solidifying crystals. Depending on the type of alloy Cr will be enriched either in the residual melt or on the primary crystals.
- 2. During quasi-isothermal solidification the degree of segregation as defined by the equilibrium partition coefficient  $K_0 = C_0/C_1$  is, in most cases, not constant within the solidification range but varies with temperature according to the equation  $K_0 = a + bT$ .
- 3. Within the scope of the alloys examined, liquidus temperatures T<sub>L</sub> varied between 1345 and 1375°C (2451 to 2507°F) only, whereas solidus temperatures T<sub>S</sub> showed a much broader range from 1245°C to 1330°C (2273 to 2426°F).
- 4. In all of the alloys examined so far, columbium is distinguished by its extreme segregation behaviour. The final degree of columbium segregation is largely depending on the solidification interval  $\Delta T$ , i.e. increasing from alloy X-750 ( $\Delta T = 37^{\circ}$ C) over alloy 625 ( $\Delta T = 75^{\circ}$ C) to alloy 718 ( $\Delta T = 100^{\circ}$ C).
- 5. The segregation of Cr and Cb during quasi-isothermal solidification of alloy 718 is in accordance with the ideal model for binary alloys. Also E. Scheuer's model for extreme non-equilibrium solidification (no equalization of composition at all in the primarily solidifying crystals) may be applicable to superalloys and the segregation occuring under real conditions will probably lie between both models.
- 6. The primary dendrite arm spacing is related to the cooling rate by a power function  $\lambda_1 = cT^{-d}$ , the parameters c and d depending on the type of alloy. With decreasing cooling rate the partition coefficients are approaching the ideal value 1. However, a pronounced reduction of segregation can only be achieved at the cost of significant extension of the dendrite arm spacing, i.e. the diffusion distance in subsequent homogenization treatments.
- 7. The reduction of segregation in diffusion annealing is mainly influenced by the width of dendrite arm spacing. Therefore, it is most important to create a narrowly spaced and uniform dendrite pattern during solidification whereas the amount of microsegregation is less important.

#### Acknowledgement

This work was promoted by the German Federal Ministry for Research and Technology (03 ZG 201 6). The responsibility for this report is with the authors.

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