DIFFERENTIAL THERMAL ANALYSIS AND THE MECHANISMS OF MINOR ADDITIONS IN SUPERALLOYS

Claudia J. Burton

Special Metals
An Allegheny Ludlum Industries Company
New Hartford, New York 13413

ABSTRACT

Differential thermal analysis continues to aid in unraveling the intricacies of superalloy metallurgy. The manner in which different levels of minor additions affect an alloy's behavior is often reflected in a DTA curve. This investigation studies the effects of different levels of carbon, hafnium, and boron upon the thermograms of selected superalloys. It further attempts to show how the interpretation of a DTA curve can be used in the explanation of the mechanism of property changes resulting from addition of these elements.

The effects of carbon level upon both the short and long term properties of superalloys has been the subject of numerous studies. Here, it is shown that DTA can be used to complement the traditional techniques of extraction and x-ray diffraction in defining solid-state carbide reactions.

Varying the hafnium concentration from 0 to 2% in MAR M-200 resulted in marked differences in DTA response, both in the solid-state and during melting. The hafnium level was also observed to influence structure and stress-rupture properties.

The thermograms of a cast alloy doped with four levels of boron suggest that property improvements attributed to boron may be able to be related to the alteration of phase reactions as observed by DTA.

Introduction

Any tool that can assist in defining the phase changes that occur in superalloys is undoubtedly of considerable value to the metallurgist studying these complex systems, some of which consist of up to fourteen alloying elements. The technique of differential thermal analysis provides such a tool by enabling an accurate determination of the temperatures at which superalloy phase changes occur. In a similar fashion, DTA can aid in the examination of the effects of variation of alloy constituents, both major and minor. Certainly, the effects of changes in major elements are easily determined. Elimination of aluminum and titanium from the alloy B-1900 raises the liquidus over 100°F, from 2512°F to 2624°F. The changes associated with minor alloying additions, however, are often more subtle. Correlation of DTA thermograms with increasing amounts of these additions can be of great assistance in providing clues concerning the mechanism by which such additions change properties in superalloy systems.

Experimental

The Technique

Differential thermal analysis, as its name implies, involves heating two bodies, one of which is known to undergo no phase changes, and measuring the temperature differences as the two are heated. If a phase change occurs in the unknown, its temperature will be higher (exothermic) or lower (endothermic) than that of the neutral body. Such temperature differences can be conveniently measured via a differential thermocouple. These are normally recorded as a function of the sample temperature, to determine the temperatures at which phase transformations take place.

The accuracy of the temperatures of phase transformations derived from a DTA thermogram is influenced by many factors. These factors can be divided into two major categories[1]: 1) those associated with the instrument; and 2) those associated with sample characteristics.

To examine the factors in the first category, it must first be assumed that the design of the instrument itself has been optimized; i.e., the furnace geometry is such that both samples are subjected to uniform heating; heating rates can be suitably programmed; the recorder has an appropriate sensitivity and speed of response; the thermocouple type and bead size have been selected to provide the optimum sensitivity. Inaccuracies resulting from imperfections in these factors are essentially uncorrectable once the system has been selected; therefore, more attention will be placed on the variable parameters. First, an appropriate heating rate must be chosen. Experiments conducted to assess the effects of heating rate on the peak resulting from the melting of pure silver indicated that:

1. The temperature "range" between the onset and the completion of melting increases with increasing heating rate. (Theoretically, pure silver should melt at one "point"; however, this would require an infinitely small sample as well as a recorder with an instantaneous response time.)

2. The relationship between heating rate and peak area is both direct and linear.

The combination of these results implies that: 1) the heating rate must be slow enough so that equilibrium is approached; i.e., so that the temperatures observed are as close as possible to the "true" reaction temperature, and 2) the heating rate must be fast enough so that the peaks are observable. It has been found that a rate of 10°C (18°F) per minute provides an adequate compromise to these opposing factors.

Another "controllable" experimental variable is furnace atmosphere; i.e.,

gas composition (reactive, inert, or vacuum), and flow rate. In the analyses to be described in this report, an 80 cc per minute argon flow is passed over the sample and reference. Since the impurities in argon are oxidizing, a helium atmosphere is used if the molten metal is particularly prone to oxidation.

In the category of sample characteristics, the first choice to be made is that of a reference body. The reference should have the following properties: 1) no phase transitions in the temperature range of interest; 2) thermal properties similar to those of superalloys, including heat capacity, and thermal conductivity. Platinum was selected as a reference sample in the analyses conducted to determine solidus-liquidus temperatures and other high temperature reactions. For solid state transitions such as gamma prime solvus determinations, high purity nickel is used as a reference to minimize differences between sample and reference.

It is essential that no temperature gradients in the sample exist during a DTA experiment. In other words, temperature uniformity is required so that phase reactions occur simultaneously within the sample. In the DuPont 990 thermal analysis system, temperature uniformity is attained via the use of small ($\approx$150 mg) samples. However, in superalloy systems, the use of such small samples necessitates running duplicates to minimize effects due to segregation.

To assure that the instrument is properly calibrated, samples of high purity nickel are analyzed through melting. Pure nickel melts at one point, 2650°F. Therefore, the calibration is set up so that 2650°F is the point where the curve departs from baseline. (Actually, a small "range" is observed for the melting of pure nickel, due to a finite sample size, a finite heating rate, and instrument lag.) Using this as a standard technique permits reproducibility of reaction peaks to within ±10°F.

Interpretation

Many phase reactions in superalloys, including melting, occur over a temperature range, and not at a unique point. The onset of any reaction can be said to occur at the point at which the DTA curve departs from baseline. Complications arise in determining the completion of a reaction. Is a phase reaction complete at the point at which the curve returns to baseline (the "recovery" point), or at the minimum or maximum of the reaction peak? In the studies to be described, completion of a reaction; e.g., the liquidus temperature is defined as the minimum, rather than the "recovery" point. This convention is based on the following arguments.

The delay due to instrument lag and finite sample size and heating rate causes a 30°F difference between the minimum of the thermogram and the recovery point when melting pure nickel. Extending this analogy, if the recovery to baseline occurs within 30°F, it is attributed to instrument lag. Therefore, the reaction is complete at the minimum (or maximum). If recovery requires more than 30°F, it is assumed that the reaction is proceeding (the recorder can "keep up"); completion occurs when the curve returns to baseline.

Discussion of Results

The Effect of Carbon and Boron in Udimet 700

Carbon additions have traditionally been added to superalloys to deoxidize VIM baths, to control grain size, and to enhance high temperature creep properties. What effect does carbon have on the DTA curve? Consider Udimet 700. Thermograms representing carbon levels of 0.13% (by weight), 0.07%, and 0.01% are shown in Figure 1. It is observed that carbon influences the DTA curve primarily in the melting range. The solidus increases from 2293°F in

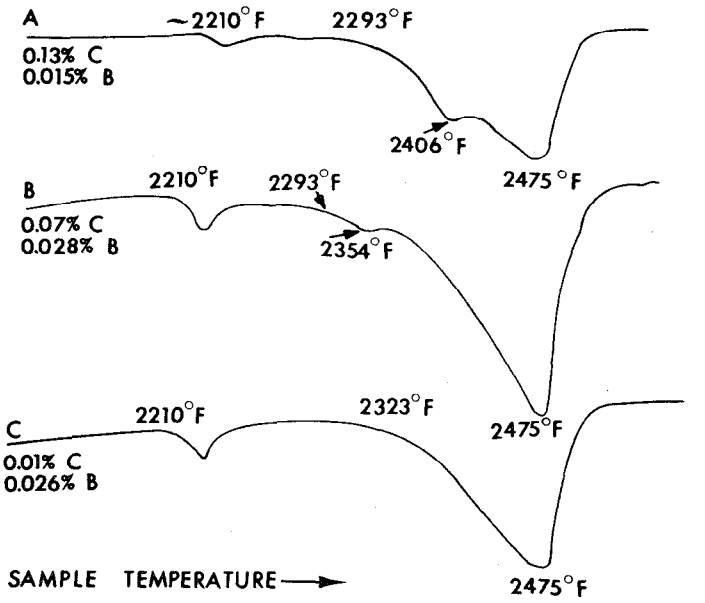


Figure 1: Thermograms of Udimet 700 in the As-Rolled Condition Indicate Differences in Melting Behavior.

0.13% and 0.07% carbon Udimet 700 (Curves A and B) to 2323°F as carbon is decreased to 0.01% (Curve C). The extent to which the melting peak is distorted by the carbon addition is also affected by the amount of carbon; note how perturbation becomes greater in proceeding from 0.07% to 0.13% carbon, also apparently raising the transition temperature from 2354°F to 2406°F.

This "carbon effect" can be assigned to the solutioning of MC carbides. It has previously been demonstrated[2] that MC carbides exist in the "mushy zone" of superalloys; precipitation takes place immediately following formation of the primary dendrites. That the 0.01% carbon version (Curve C) shows no effect is not surprising; this level is well within the solid solution solubility limit for carbon.

The set of curves illustrated in Figure 1 points out another interesting relationship between chemistry and the DTA thermogram. Increasing boron from 0.015% (Curve A) to about 0.03% (Curves B and C) greatly enhances the reaction at 2210°F. Prior investigations[3] have shown via metallographic techniques that this is the melting temperature of a chromium rich ($Mo_{.31}Ti_{.07}Cr_{.49}Ni_{.06}Co_{.07}$) low parameter M_3B_2 boride. This study also states that heating at 2150°F will convert this boride into a higher parameter, molybdenum rich ($Mo_{.48}Ti_{.07}Cr_{.39}Ni_{.03}Co_{.03}$) boride. DTA substantiated this observation; thermal analysis of an as-rolled plus a 2150°F solution treatment did not reveal a reaction at 2210°F.

The Effect of Hafnium in MAR M-200

The merits of hafnium additions to cast superalloys both to enhance transverse ductility and to improve castability are well-known. A recent investi-

Table I: Effect of Hafnium on the Melting Behavior of MAR M-200

Hafnium Level	Solidus (°F)	Liquidus (°F)	Width of Range (°F)
0%	2399	2538	139
0.4%	2379	2527	148
0.9%	2354	2512	158
1.2%	2354	2512	158
1.5%	2354	2512	158
1.6%	2354	2507	153
1.8%	2354	2507	153
2.0%	2354	2507	153

gation studying the effect of variations in hafnium from 0% to 2.0% by weight upon the properties of MAR M-200 have led to some interesting correlations between properties and effects on the DTA curve.

To determine melting characteristics, samples from heats containing each of the hafnium levels were thermally analyzed from 1470°F to 2250°F using a heating rate of 18°F per minute. A trace of the curve obtained from the 0.4% Hf is illustrated in Figure 2. Interpretation of the various phase transformations is included on the chart. Temperatures derived from the on-heating thermograms for the solidus and liquidus of each of the samples are listed in Table I. These data are accurate to within 10°F.

The first observation is that the addition of hafnium depresses both the liquidus and solidus and widens the melting range of MAR M-200. This effect persists up to 0.9% hafnium, above which there is little or no change in melting behavior.

To accurately determine the effect of hafnium upon the gamma prime solvus of MAR M-200, solid-state (2230°F maximum) studies were conducted. Samples are placed in direct contact with the thermocouples to eliminate any effects associated with the alumina crucibles used during melting experiments. To enhance the gamma prime reaction, the samples were heat-treated (2200°F/2hrs/AC+1975°F/4hrs/AC+1600°F/32hrs/AC) to allow aging to bring out the gamma prime. The temperatures in Table II were obtained from the cooling curves, where the transition occurs abruptly, and so is easily read on the thermogram. It is expected that these temperatures are lower than those that would be observed on the heating curves, due to a nucleation barrier on cooling. However, on-heating tests do not enable accurate solvus determinations.

Note that there is a tendency for the gamma prime solvus to increase with increasing hafnium concentration up to about 0.9% hafnium. This increase in

Table II: Effect of Hafnium on the Gamma Prime Solvus of MAR M-200

Hafnium Level	Gamma Prime Solvus (°F)
0%	2174
0.4%	2184
0.9%	2210
1.2%	2188
1.5%	2210
1.6%	2210
1.8%	2210
2.0%	2205

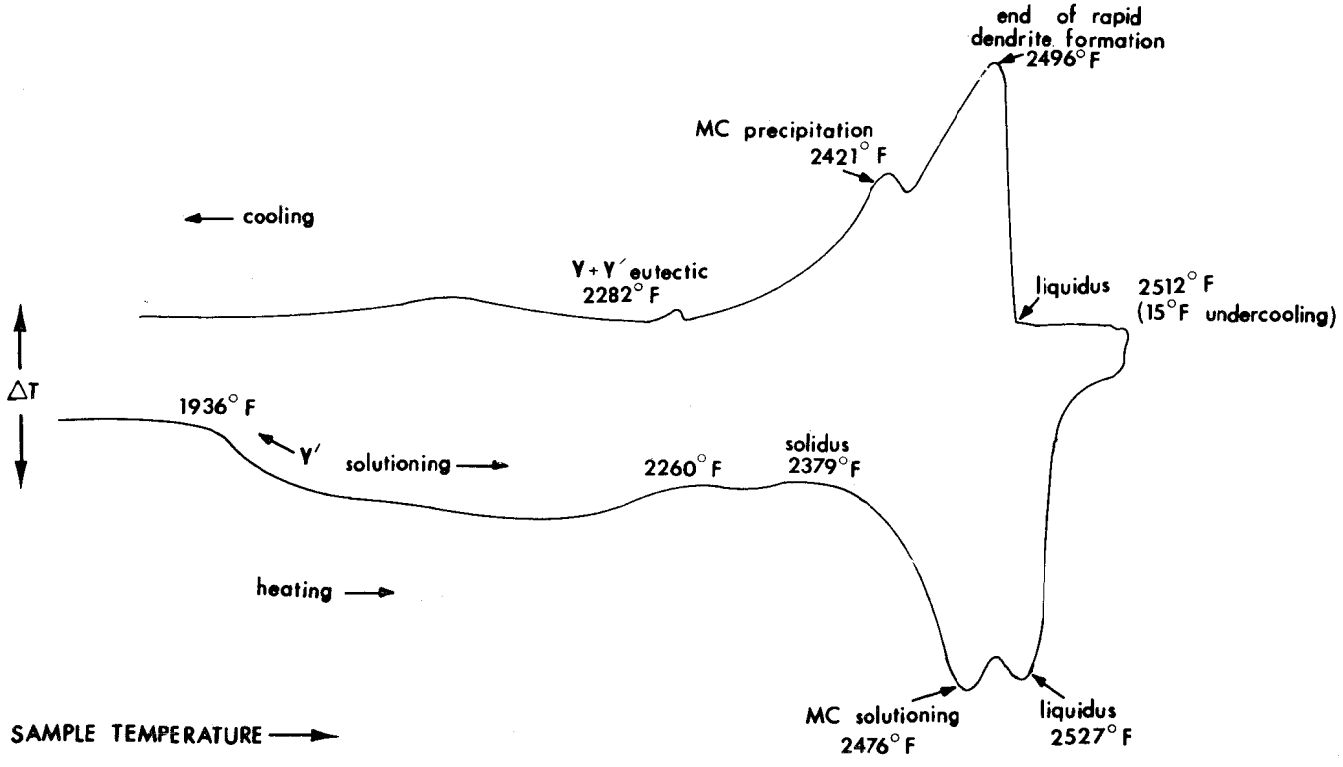


Figure 2: Analysis of MAR M-200 + 0.4% Hf Illustrates the General Features of a DTA Thermogram.

Table III: 1400°F/100 Ksi Transverse Stress Rupture Properties

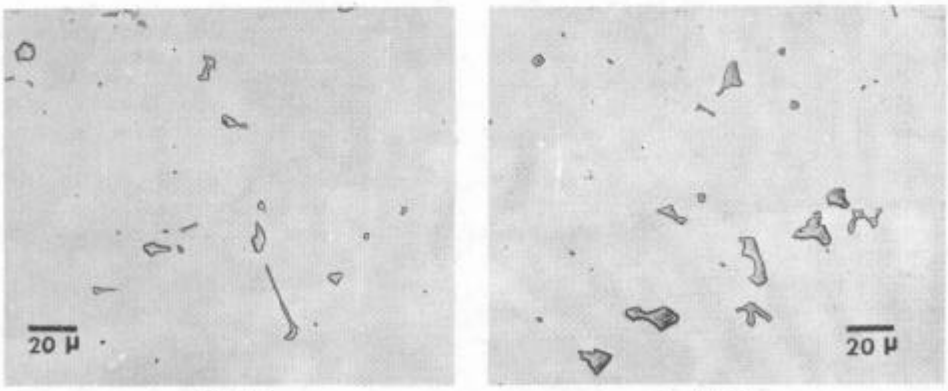
Hafnium Level	Life (Hrs.)	Elong. (%)	R.A. (%)
0%	34.2	2.4	2.5
0.4%	114.3	2.8	3.4
0.9%	176.1	3.1	7.9
1.2%	343.0	5.3	7.3
1.6%	271.5	4.1	9.3
2.0%	227.7	4.1	8.1

solvus temperature can be correlated with the observation[4,5] that hafnium partitions to the gamma prime region rather than to gamma during solidification.

It is interesting to observe that 1400°F/100 ksi stress rupture tests performed on samples machined from a transverse section of a directionally solidified block also appeared to reach a maximum between 0.9% and 1.2% Hf. Results are listed in Table III. A heat treatment of 2200°F/2hrs/AC+1975°F/4hrs/AC+1600°F/32hrs/AC was applied prior to testing. Samples were cut at a distance of approximately 0.5 in. from the chill.

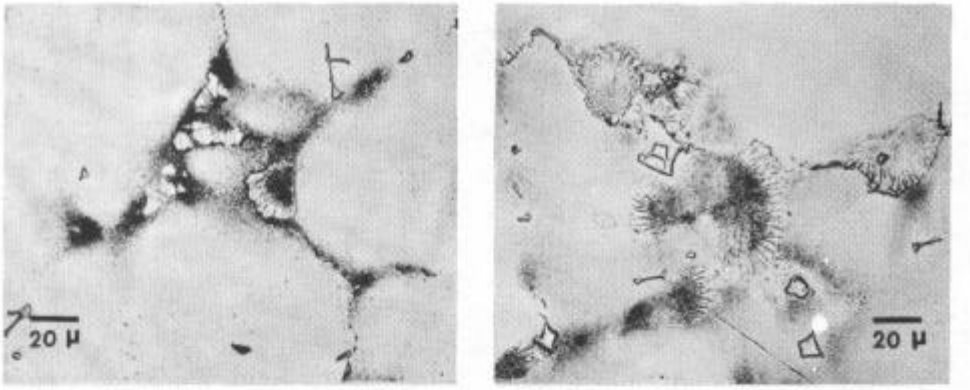
To investigate this improvement in stress rupture properties associated with hafnium, light microscopy was used to examine the structural features of the material. The following observations were made on material in both the as-cast ingot and directionally solidified heat-treated condition:

1. There is a transition in carbide morphology from script to blocky as hafnium is increased. Nearly all carbides are of a blocky morphology in material with 1.2% and greater hafnium. It has been suggested[6] that this alteration of carbide morphology is a mechanism by which hafnium improves properties; i.e., script carbides might enhance crack propagation along grain boundaries, whereas angular carbides surrounded by gamma prime, are not deleterious. It has been proposed[7] that these blocky carbides form preferentially in hafnium-bearing superalloys because the widened melting range allows time for particle coarsening to occur.



0% Hf 1.2% Hf

Figure 3: Carbide Morphology Changes as Hafnium Content in MAR M-200 Is Increased.



0% Hf 1.2% Hf

Figure 4: The Addition of Hafnium Results in an Increase in the Amount of the $\gamma + \gamma'$ Eutectic in MAR M-200.

2. The amount of the gamma + gamma prime eutectic increases with increasing hafnium concentration. It has been reported[4] that this eutectic phase is more creep resistant than the single phase gamma prime which results when excessive amounts of hafnium are added to the alloy.

This effect is also apparent on the DTA curve. The peak (2282°F) associated with the gamma + gamma prime eutectic precipitation (the reaction is only apparent on cooling; the corresponding solutioning on heating takes place too gradually to be observed) is enhanced by the addition of hafnium. In fact, the peak at 2282°F was not observed at all during thermal analysis of the 0% hafnium sample.

The Effect of Boron and Carbon in IN-100

The reported property improvements to cast alloys caused by the simultaneous increase of boron in quantities up to 0.1% and decrease in carbon to levels of 0.02% and lower has stirred considerable interest in the field of superalloy metallurgy[8]. These chemistry modifications, although minor ones on a weight basis, were observed to exert a significant effect on the DTA curves. Certainly, definition of the phase changes observed on the thermograms will assist in determining the mechanism by which property changes occur.

Standard DTA analyses were conducted to determine melting characteristics of IN-100 (Figure 5) along with three versions of the high boron-low carbon modification, called B-1914 (Figure 6). Nominal chemistries are given in Table IV.

Table IV: Chemistry - Weight Percent

	C	B	Cr	Co	Mo	Al	Ti	Zr	V	Ni
IN-100	0.18	0.014	9.5	15.0	3.0	5.5	4.5	0.06	1.0	Bal.
B-1914	<0.02	0.05 0.07 0.10	10.0	10.0	3.0	5.5	5.3	0.04	-	Bal.

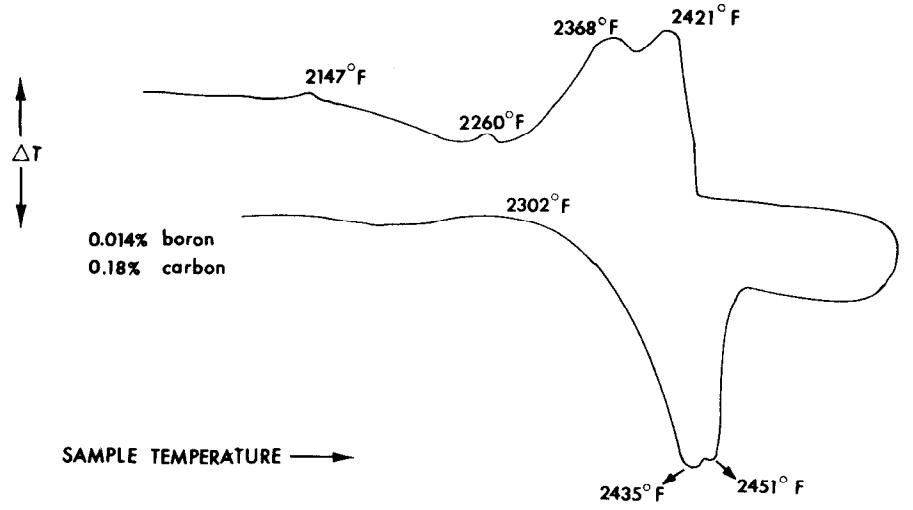


Figure 5: Thermal Analysis of IN-100 Indicates the Presence of a Major Carbide Reaction.

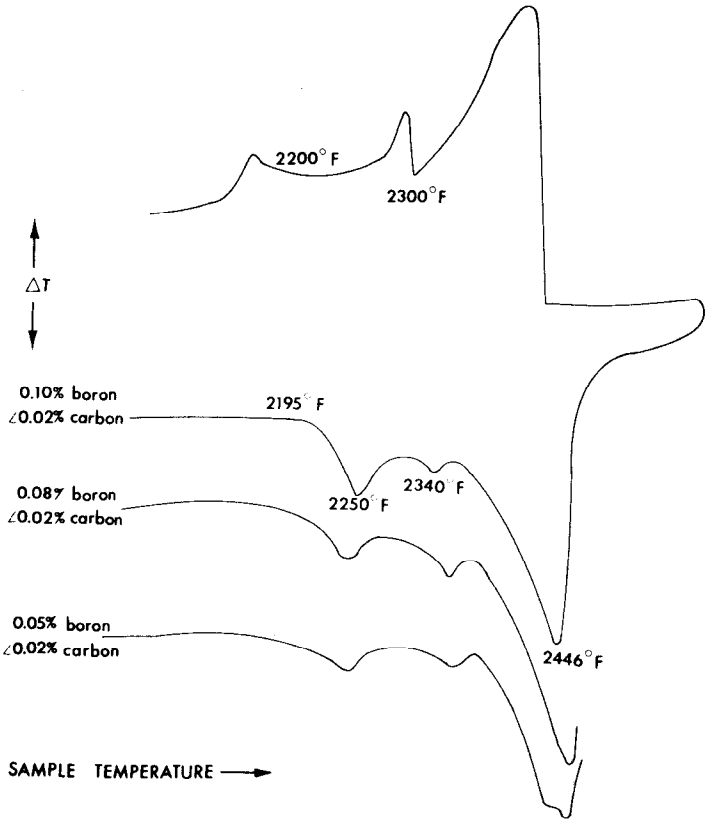
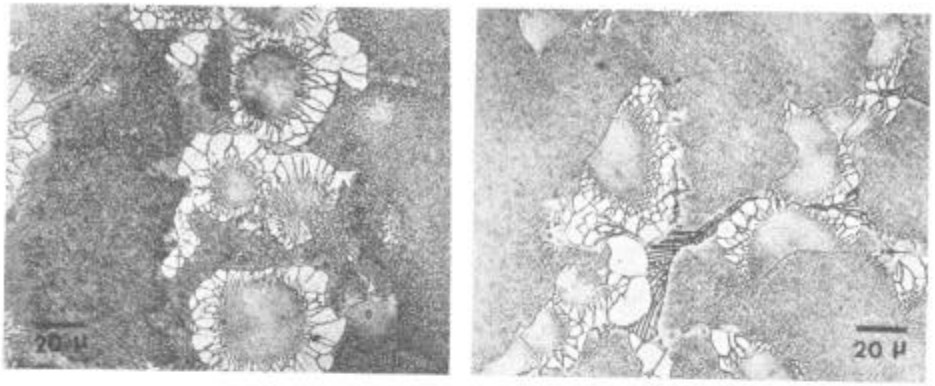


Figure 6: On-Heating Thermograms Show Differences in the Intensities of Incipient Melting Peaks as Boron Level in B-1914 is Changed.



0.05% B 0.07% B

Figure 7: As-Cast Microstructure of B-1914 Consists of Matrix, Primary Borides, a Script, Eutectic Type Phase, and the γ-γ' Eutectic.

Thermal analysis of IN-100 (Fig. 5) illustrates that a carbide solutioning reaction (2435°F) takes place between the solidus (2302°F) and the liquidus (2451°F). In addition, cooling brings out an additional reaction at 2260°F, which can be associated with the gamma + gamma prime eutectic. Subjecting B-1914 to thermal analysis (Fig. 6) shows that two distinct reactions (2250°F and 2340°F) take place between the solidus (2195°F) and the liquidus (2446°F). Note that while the high boron, low carbon modification widens the melting range of IN-100 over 100°F, the liquidus temperature remains essentially the same.

Metallographic examination of as-cast specimens shows that increasing boron increases the amount of the gamma + gamma prime eutectic (Fig. 7). The higher boron modifications show greater amounts of an additional script, eutectic-type phase. Also present in the alloy are small discrete particles, which are most likely primary M_3B_2 particles. Scanning electron microprobe analysis indicated that the script, eutectic-type phase is rich in chromium, titanium, and molybdenum. Further experiments will have to be conducted before the reactions within the melting range can be positively assigned.

Conclusions

These studies have provided ample evidence that the technique of differential thermal analysis can be a useful tool to the superalloy metallurgist. In the studies described in this paper, DTA has assisted in the justification of the following conclusions:

1. The presence of MC carbides in wrought Udimet 700 lowers the apparent solidus 30°F, due to dissolution of carbides in the mushy zone of the alloy.

2. A 2150°F solution treatment eliminates the incipient melting of a low-parameter M_3B_2 boride in Udimet 700.

3. The addition of hafnium depresses the liquidus and solidus and widens the melting range of MAR M-200. This effect persists up to 0.9% hafnium, above which there is little or no change in melting behavior.

4. The gamma prime solvus in MAR M-200 is raised by the addition of hafnium in concentrations up to 0.9% by weight.

5. Differential thermal analysis shows that the addition of boron in quantities up to 0.1% by weight alters the phase relationships in IN-100.

References

1. Wendlandt, W. W., Thermal Methods of Analysis. John Wiley & Sons, New York, 1974. pp. 134-194.

2. Tien, J. K., Columbia University, private communication.

3. Boesch, W. J. and Canada, H. B., Journal of Metals, Vol. 20, No. 4, April 1968. pp 46-50.

4. Doherty, J. E., Kear, B. H., and Giamei, A. F., Journal of Metals, Vol. 23, No. 11, Nov. 1971. pp. 59-62.

5. Kotval, P. S., Venables, J. D., and Calder, R. W., Met. Trans., Vol. 3, Feb. 1972. pp. 453-458.

6. Dahl, J. M., Danesi, W. F., and Dunn, R. G., Met. Trans., Vol. 4, April 1973. pp. 1087-1096.

7. Bhambri, A. K., Kattamis, T. Z., and Morral, J. E., Met. Trans. B., Vol. 6B, Dec. 1975. pp. 523-537.

8. Baldwin, J. F., Maxwell, D. H. and Radavich, J. F., Presentation at the Paris Air Show, Le Bourget, Paris, France. June 5, 1975.